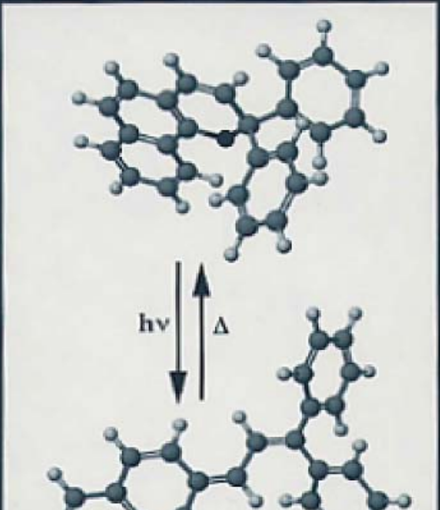
Topics in Applied Chemistry

Organic Photochromic and Thermochromic Compounds

Volume 1

Main Photochromic Families



Edited by

John C. Crano and Robert J. Gugliemetti

Organic Photochromic and Thermochromic Compounds

Volume 1: Main Photochromic Families

TOPICS IN APPLIED CHEMISTRY

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Organic Photochromic and Thermochromic Compounds

Volume 1: Main Photochromic Families

Edited by

John C. Crano

Late of PPG Industries, Inc.
Monroeville, Pennsylvania

and

Robert J. Guglielmetti

University of Aix-Marseille II
Marseille, France

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In Memoriam

DR. JOHN C. CRANO

On January 10, 1998 Dr. John C. Crano, 62, one of the co-editors of this book, and his wife Dorothy were killed instantly in an automobile accident in Florida. In this tragic death the world of photochromism has lost the person chiefly responsible for the success of the largest commercial application of organic photochromics.

Dr. Crano received a B.S. degree in Chemistry in 1957 from Notre Dame and M.S. and Ph.D. degrees from Case Western Reserve University in 1959 and 1962, respectively. He joined PPG Industries in 1961, and had spent his entire career with that firm, at first in various roles in the Chemical Research & Development area. In 1974 PPG began research upon means to impart photochromic properties to ophthalmic lenses made from plastics, in particular from poly(allyl diglycol carbonate), CR-39®. Plastic lenses command over 85% of the total ophthalmic market in the US, principally because a lightweight plastic product is more comfortable to wear and permits more attractive fashion designs.

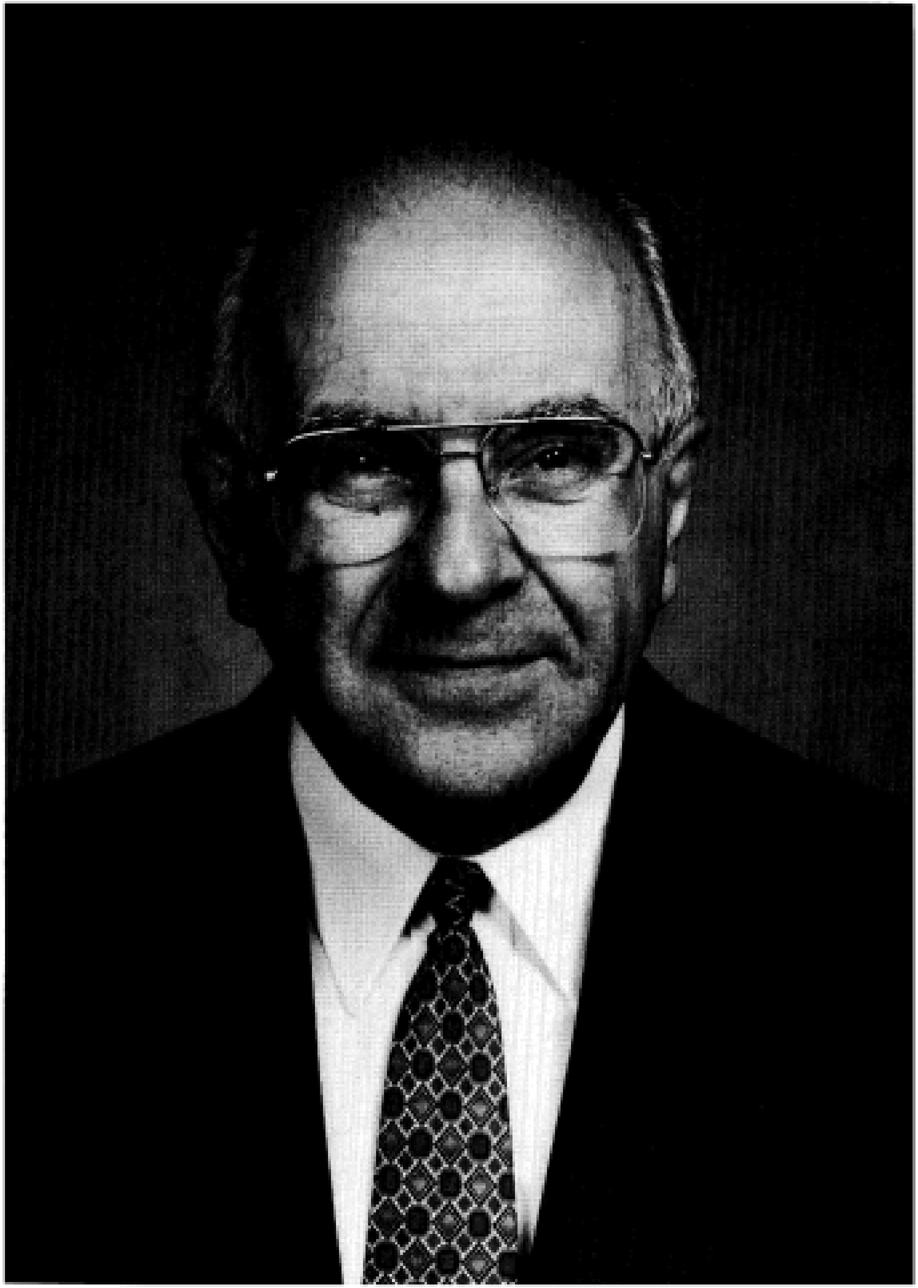
Comparative testing of all classes of photochromics, including inorganic compounds, indolinospirobenzopyrans and naphthoxazines, occupied the first few years. In the early 1980’s expanding research and development efforts focused upon the indolinospirobenzoxazines and quinolinooxazines and their close structural relatives. In 1986 Dr. Crano become leader of a constantly enlarging team of organic, physical, polymer and photo chemists and engineers. The first generation plastic photochromic ophthalmic lenses, the Transitions® Comfort Lens, were manufactured in Ohio and test-marketed in June of 1989. Transitions Optical. Inc., a joint venture between PPG and the French lens manufacturer Essilor, was formed in 1990 and began manufacturing lenses early in 1991 in a new plant in Florida.

A second generation lens, the Transitions® Plus lens, was introduced in November 1992. In the years since, Transitions Optical has marketed a succession of new lenses. In September 1994 the EuroBrown™ lens appeared, formulated to give when activated a brown color, especially favored in the European market. The mid-index Transitions® III lenses were launched in the United States and in Europe during 1996, and the Transitions XTRActive™ lenses were introduced in the US in January 1997. The most recently introduced lenses are Transitions® III lenses in a standard index matrix. These use the latest technology in organic photochromic dyestuffs and polymer science and engineering, and maintain the company’s position of technical leadership in the field of plastic ophthalmic photochromic lenses. Transitions Optical now sells its various lenses in over 50 countries.

In his position as Associate Director of Research and Development, Optical Products, Dr. Crano managed the entire photochromics research program. He led the team of scientists that synthesized and evaluated hundreds of candidate photochromic dyestuffs, and directed all of the product and process development involved in the various Transitions®lenses. In addition, his responsibilities included R&D on non-ophthalmic photochromic applications, and on other optical coatings and resins.

He has a number of US patents in various areas of technology, including three during 1990–2 that cover the basic compositions and methods for producing the first generation of Transitions®lenses. These were important in establishing a strong proprietary position in photochromic plastic ophthalmic lenses. In addition, he had published several reviews and invited lectures on photochromism and photochromic polymers.

In 1985 he was General Chairman of the Central Regional Meeting of the American Chemical Society, and in September 1996 he was Co-Chairman of the 2nd International Symposium on Photochromism. This Symposium, which included participants from 16 countries, owed much of its success to Dr. Crano’s excellent organization.



John C. Crano (1936–1998)

Recent Publications and Presentations of J. C. Crano

Photochromic Systems for Plastic Ophthalmic Lenses, J. C. Crano, 1997 Gordon Conference on Organic Photochemistry.

Photochromic Compounds: Chemistry and Application in Ophthalmic Lenses, J. C. Crano, T. Flood, D. Knowles, A. Kumar and B. Van Gemert, Pure Appl. Chem, 68(7), 1395–1398 (1996).

Photochromic Materials, John C. Crano, in “Kirk-Othmer Encyclopedia of Chemical Technology,” 4th Ed., 1993,. J. Wiley & Sons, New York.

Photochromic Organic Compounds in Polymer Matrices, J. C. Crano, C. N. Welch, B. Van Gemert, D. Knowles and B. Anderson, in “Photochemistry and Polymeric Systems,” J. M. Kelly, C. B. McArdle and M. J. de F. Maunder, Eds., 1993, Royal Society of Chemistry, Cambridge.

Spirooxazines and Their Use in Photochromic Lenses, J. C. Crano, W. S. Kwak and C. N. Welch, in “Applied Photochromic Polymer Systems,” C. B. McArdle, Ed., 1992, Blackie and Sons.

R. Guglielmetti and R. Bertelson

Foreword

Experiments showing a rapid and *reversible* change of color seem to be magic and are always fascinating. This process called *photochromism,* has a few real and many potential applications. Photochromic glasses that darken in the sunlight (protecting eyes from excessive light intensity) and bleach in dim light are today a part of everyday life. *Organic Photochromic Compounds* in plastic ophthalmic lenses, more comfortable to wear, are now competing with silver salts glasses, despite the longer lifetime of the inorganic system. This successful commercial application has given a new impetus to research in the general field of photochromism that had its most recent revival in the early eighties.

The story of organic photochromism with its ups and downs, from the breakthroughs of the pioneering period in the fifties, through the hard times due to the drawbacks of photodegradation and the *recent successes* is in many ways a saga. The upsurges in the domain were marked by an increasing flow of articles in scientific journals and the publication of several *Books* (in *1971, 1990* and *1992*) which have collected the important accumulated knowledge. Over this period, a considerable number of patents have been issued. *International meetings* have accompanied this activity, the most recent being held in 1993 (*ISOP-93* at Les Embiez Island, France) and in 1996 (*ISOP-96* in Clearwater, Florida, USA). Remarkably, these meetings had a good representation from both academia and industry. The next ISOP is planned for 1999 in Fukuoka, Japan.

Since publication of the most recent Books, new areas have been explored and a large number of new results have been obtained and it seemed, therefore, timely to publish them. This was the endeavor of the chairmen of ISOP-93 and ISOP-96, Robert Guglielmetti and John Crano, respectively, who have acted as co-editors. R. Guglielmetti, a professor at the University of Marseilles is a recognized leader in the field and the late Dr. J. Crano, Associate Director of Research and Development for optical products at PPG since 1986, led research in the development of plastic ophthalmic eyewear. The efficient cooperation of a scholar and an industrial scientist has led to the Book entitled: “Organic Photochromic and Thermochromic Compounds” in two volumes of about 400 pages each.

Volume 1 includes nine chapters, the first six of these deal with the main *established* families of organic photochromes which have a few real and many potential applications. Their photochemical processes are based on pericyclic electrocyclic reactions. The three other chapters concern hydrogen or group rearrangement, and electron transfer. *Seven* out of the nine main authors, selected from all over the world, have not written chapters for previous books and importantly, *three* are from companies. Four chapters cover families not reviewed in the previous books while the other five have been *renewed* and *updated* (until 1995–1997). A useful initiative is the introduction of *detailed preparations* of some representative examples of spiropyrans, spirooxazines, chromenes, fulgides, spirodihydroindolizines, aryloxyquinones and perimidinespirocyclohexadienones. It should be noted that Volume 1 does not address thermochromism. Indeed, it will be obvious to the reader that this volume is *not a remake* of the preceding Books.

Organic photochromic systems have *actual applications* in variable transmission optical materials, authentication systems and novelty items. In addition, they offer *great potential* in erasable optical memories and many other fields where reversible changes of physical properties other than color are wanted. The domain is interdisciplinary and expanding.

Volume 1 can be read independently but the material contained in Volume 2 is intended to be complementary. The Book is strongly recommended to photochromism practitioners as well as anyone interested in Materials Science.

Henri Bouas-Laurent
University Bordeaux 1
April 1998

Alphabetical Contributors List

Name/Affiliation

Angelo Alberti, CNR (I.Co.C.E.A.) Bologna, Italy

Serguei Aldoshin, Academy of Sciences, Institute of Chemical Physics, Chernogolovka, Russia

Jean Aubard, Itodys, Denis Diderot University – Paris 7, CNRS–URA 34, Paris, France

Valeri Barachevsky, Academy of Sciences, Semenov Institute of Chemical Physics, Moscow, Russia

Robert Bertelson, Chroma-Chemicals, Inc., Dayton, Ohio

John Crano, PPG Industries, Monroeville, Pennsylvania

Heinz Dürr, Sarbrücken University, FR 11.2 Organische Chemie, Saarbrücken, Germany

Mei Gong Fan, Chinese Academy of Sciences, Institute of Photographic Chemistry, Beijing, China

Robert Guglielmetti, Méditerranée University, Faculté des Sciences de Luminy, Marseille, France

Kunihiro Ichimura, Tokyo Institute of Technology, Research Laboratory of Resources Utilization, Yokohama, Japan

Masahiko Inouye, Osaka Prefecture University, Department of Applied Materials Science, Osaka, Japan

Masahiro Irié, Kyushu University, Institute of Advanced Materials Study, Fukuoka, Japan

Shuichi Maeda, Mitsubishi Chemical Corporation, Yokohama Research Center, Imaging Materials Laboratory, Yokohama, Japan

Vincenzo Malatesta, Great Lakes Chemical Italia, s.r.l., Milano, Italy

Albrecht Mannschreck, Regensburg University, Institute für Organische Chemie, Regensburg, Germany

Jean-Claude Micheau, Paul Sabatier University, URA CNRS 470, Toulouse, France

Vladimir Minkin, Rostov/Don University, Institute of Physical and Organic Chemistry, Rostov/Don, Russia

Shinichiro Nakamura, Mitsubishi Chemical Corporation, Research and Development Division, Yokohama, Japan

Masata Nanasawa, Yamanashi University, Department of Applied Chemistry and Biotechnology, Yamanashi, Japan

André Samat, Méditerranée University, Faculté des Sciences de Luminy, Marseille, France

Barry Van Gemert, PPG Industries, Monroeville, Pennsylvania

Preface

This book, *Organic Photochromic and Thermochromic Compounds,* is the fourth major treatise on photochromism involving organic molecules and derived systems. The first such book was edited by G. H. Brown in the Weissberger series in 1971[1], the second was edited by H. Dürr and H. Bouas-Laurent in the Elsevier series in 1990[2].

A third book, edited by C. B. McArdle[3], should be added to the list, which focuses on the very important topic of the behavior of photochromic systems in polymer matrices.

The current book is an outgrowth of the large increase in the number of publications and patents concerning photochromic compounds and their use in various applications (e.g., ophthalmic lenses and security printing) during the past 10 years. As a result of this increased interest, two successful international symposia on photochromism have been held: the first was ISOP93, held in France on Embiez Island near Bandol (September 12–16, 1993) and the second, was ISOP96, held in the United States in Clearwater, Florida (September 8–12, 1996). The number of countries represented at each of these symposia (17 and 16, respectively) attests to the international scope of the photochromic research community. The increased international literature on syntheses and physicochemical investigations of photochromic phenomena led the Editors and the Publisher to divide "Organic Photochromic and Thermochromic compounds" into 2 volumes.

The first volume deals with the synthesis and specific photochromic properties of the best-known classes and their field of application; it contains 9 chapters. The aim of this new review, which is focused on organic photochromic compounds but also contains a brief survey on thermochromic compounds, is to give practical information involving selected series with the hope that this will lead to additional commercial applications for known photochromic families or to the discovery of new families.

To make this volume more useful, almost all the chapters covering specific families of photochromic compounds include general methods for preparing members of each family, along with synthetic procedures for specific examples.

Where possible, photochromic behavior (spectrokinetic parameters, photostability) in solution or in polymer matrices, and potential applications are described.

We did not emphasize the theoretical aspect of the different photochromic processes because of their coverage in a fairly recent treatise (Dürr, Bouas-Laurent[2]).

In general, the literature cited within the chapters covers publications through 1995. However, in several cases, publications from as late as 1997 are included.

Our thanks go to all the colleagues who volunteered to collaborate on this book and who had the patience and reliability to undertake all the steps required to prepare the final manuscripts. In addition to the chapter authors, several other people have contributed their time and talent to the completion of this book. Dr. A. Samat and Dr. V. Lokshin (Laboratory of Organic Chemistry and Materials of Marseille) must be acknowledged for many fruitful discussions during the entire process of assembling the book. We are deeply indebted to Diana Gronholm, PPG Industries, Inc., whose help in the revision and copying of manuscripts, communications with contributors and the publisher, and a variety of other tasks during the preparation of the book was invaluable. Dr. Anil Kumar, also with PPG, helped with the conversion of files into usable program formats and technical assistance in the preparation of files for the final manuscripts. Finally, we express our appreciation to Audrey Anderson, Denise Callihan and Beverly Weston with PPG Industries for their assistance in obtaining missing titles of several references and general assistance when it was needed to verify details of references.

1. *"Photochromism"* (G. H. Brown, ed.) Techniques Chem. Vol. III, Wiley Interscience, New York (1971).
2. *"Photochromism: Molecules and Systems"* (H. Dürr, H. Bouas-Laurent, eds.) Elsevier, Amsterdam (1990).
3. *"Applied Photochromic Polymer Systems"* (C. B. McArdle, ed.) Blackie, New York, 1992.

J. C. Crano and R. Guglielmetti

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Introduction

1. AIM AND ORGANIZATION OF THE BOOK

The principal aims of this book are to be complementary to the earlier volumes covering the phenomenon of photochromism[1,2,3] and to survey the main representative series of photochromic compounds having realized or potential industrial applications. In contrast to the previous book edited by H. Dürr and H. Bouas-Laurent[2] which was organized around the type of reactions involved in the photochromic phenomenon (cis-trans isomerization, electrocyclic reactions, cycloaddition reactions, tautomerisation, dissociation processes . . .), this collection of reviews is organized around the main categories of organic photochromic compounds which have real or potential uses in various applications. The many important developments of photochromic pigments and materials in recent years requires the book to be issued in 2 volumes.

Volume 1 describes the important developments in the synthesis and study of photochromic compounds and related devices over the past 10 years in industrial and academic laboratories. A brief survey of the contents, chapter by chapter, is useful. The first six chapters cover photochromic systems which are based on pericyclic electrocyclic reactions:

1. Spiropyrans – probably the most studied family of photochromics, accounting for the greatest number of papers until 1980;
2. Spirooxazines – a family of compounds proven quite useful because of their resistance to photodegradation, commonly called fatigue;
3. Benzo – and naphthopyrans (chromenes) – also of interest for their resistance to fatigue:
4. Fulgides and fulgimides – potentially useful for information storage in erasable optical disks;
5. Diarylethenes with heterocyclic rings – also potentially useful for information storage;
6. Spirodihydro indolizines.

Organic Photochromic and Thermochromic Compounds, Vol 1, edited by John C. Crano and Robert Guglielmetti, Plenum Press, New York, 1999.

The next three chapters cover very different families, which operate by mechanisms involving proton, group,or electron transfer:

7. Aryloxyquinones;
8. Perimidinespirocyclohexadienones;
9. Viologens.

2. BRIEF HISTORICAL SURVEY OF PHOTOCHROMISM

The first examples of the phenomenon of photochromism were discovered near the end of the nineteenth century in both inorganic or organometallic complexes and organic substances.[4,5] The terms *phototropy*[6] and *phototropism*[7] were employed to describe this phenomenon, but are now used largely for biological systems. The term *photochromism* was suggested by Hirshberg in 1950.[8]

Interest in the photochromism of organic materials began to increase substantially around 1940. The principal studies of photochromic compounds involved acquiring an insight into mechanisms of the photoprocesses, determining the structures of the uncolored and colored forms, and developing synthetic methods. The pioneering work by the Hirshberg and Fischer team in Israel[1,8,9] is worth a special mention. The development of time-resolved or flash spectroscopy by Porter[10] and, more recently, the use of laser photophysical means opened new approaches to the study of the excited states and transient species involved in the photoreactivity of photochromic molecules.

3. DEFINITIONS OF PHOTOCHROMISM

We could consider a photochromic organic compound as a reversible dye under photochemical control. Photochromism can be defined as a reversible transformation of chemical species, induced in one or both directions by electromagnetic radiation, between two states having observable light absorptions in different regions.

$$A(\lambda_1) \underset{h\nu_2,\Delta}{\overset{h\nu_1}{\rightleftharpoons}} B(\lambda_2)$$

Ordinarily, the photochromic reaction involves a reversible transformation between two species with B having at least one absorption band appearing at longer wavelength than those of A. The activating radiation generally is in the UV region (300 to 400 mm) but could be in the visible (400 to 700 nm). The most prevalent photochromic systems are established to be unimolecular reactions (A → B) and those described in this book correspond to this type.

Reversibility is the main criterion for photochromism. The back reaction (B → A) can occur predominantly by a thermal mechanism, as is the case with spiropyrans spirooxazines and chromenes. For these systems, the thermally driven back reaction can be accompanied by one that is photochemically driven but the thermal reaction normally predominates. For other systems, the photochemically induced forms (B) are thermally stable. For such systems, (e.g. fulgides or arylethenes) the back reactions (B → A) are predominantly photochemical.

The photochromic transformation and the observed spectral changes or changes in physical or chemical behavior are related to the modifications of the geometry of the system and its electronic distribution. This will be seen in the examples given below.

A recurring theme throughout the book is the importance of the medium in which the photochromic compound is incorporated. The medium can strongly influence or control the kinetics of the thermal back reaction when it occurs, the color of the species formed in the forward photochemical reaction, and other properties of the photochromic process.

Photochromism and its various characteristics can also be defined according to the type of application at which they are targeted. Two general types of applications can be defined:

1. Applications directly dependent upon the color change caused by the molecular and electronic structures of the two species (A, B) and their corresponding absorption or emission spectra.

Examples would be:

- variable-transmission optical materials such as the photochromic ophthalmic lenses or camera filters;
- fluid flow visualization;
- optical information storage;
- novelty items (toys, T-shirts, etc.);
- authentication systems (security printing inks);
- cosmetics

2. Applications dependent upon changes in the physical or chemical properties that occur along with the more easily observed color change during the photochromic reaction.

Examples of such properties are conductivity, refractive index, electrical moment, dielectric constant, chelate formation, ion dissociation, phase transitions, solubility, and viscosity. Certain physical changes that occur when the photochromic entity is chemically attached to the macromolecular backbone of polymers are of special interest (see Chapter 1, Volume 2).

Some examples of potential applications utilizing the physical or chemical changes that accompany the observed shift in the absorption maxima are:

- optoelectronic systems (semi-conductors modulated by photochromic pigments);
- reversible holographic systems;

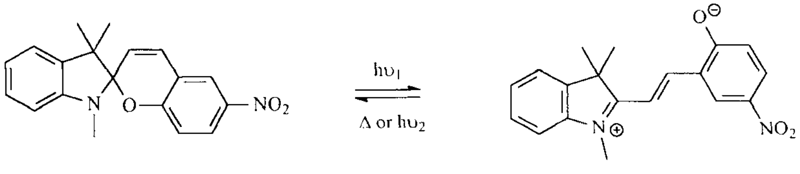
- optical switches;
- optical information storage;
- photochemically switchable enzymatic systems;
- nonlinear optical devices.

Of all these potential applications, a few have been commercially successful (polymer-based photochromic eyewear, novelty items and security printing inks) or demonstrated to be useful (fluid flow visualisation). Several others have shown considerable promise and may very well be utilized in commercial products in the future.

4. BRIEF ANALYSIS OF THE DIFFERENT CHAPTERS AND THEIR MAIN TOPICS

Chapter 1 (*Spiropyrans*) covers the most intensively studied families of photochromic compounds.

One of the families, the indolinospiropyrans (e.g. **1** in Scheme 1) is the most studied of all photochromic families and is at the center of this chapter in which are described their properties and syntheses as well as the syntheses of key intermediates.



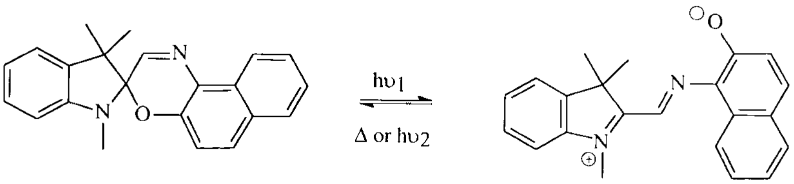
1

Scheme 1

This chapter, with over 200 references, is an extensive survey of the photochromic molecular and supramolecular systems involving the spiropyran entity. It also serves as an excellent introduction for the individual who does not have a comprehensive understanding of the phenomenon of photochromism.

Chapter 2 (*Spirooxazines*) covers close relatives of the spiropyrans which have been receiving increased interest during the past 15 years because of their excellent photochromic properties and their resistance to photodegradation or fatigue (Scheme 2). In general, the resistance to fatigue of the spirooxazines is much better than that of the spiropyrans. Their stability under conditions involving continuous irradiation has led to their use in various applications, including ophthalmic lenses.

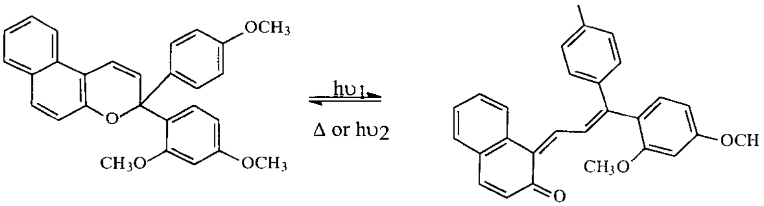
Chapter 3 (*Benzo and naphthopyrans or chromenes*). This chapter reviews another important type of thermoreversible photochromic compounds that have found application in the variable optical transmission materials field, specifically,



2

Scheme 2

ophthalmic lenses. Their development into commercially useful materials has been fairly recent. The broad absorption bands exhibited by the open forms of the naphthopyrans (Scheme 3) and heteroannellated naphthopyrans are somewhat complementary to the absorption bands of the naphthoxazines, leading to color neutralization when they are used together.

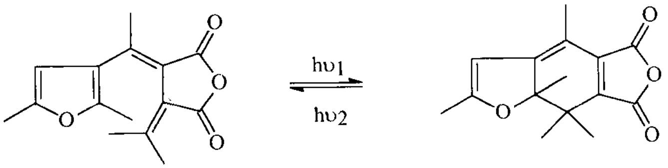


3

Scheme 3

Their resistance to photooxidation is also good relative to most other families of photochromic compounds. In this property they are comparable to the spirooxazines, which again adds to the complementary character of the two families. The color of the open forms can be tuned over a large range of the visible spectrum, by substituents on the naphthyl moiety or on the aromatic groups present on the sp^3 carbon atom of the pyran ring.

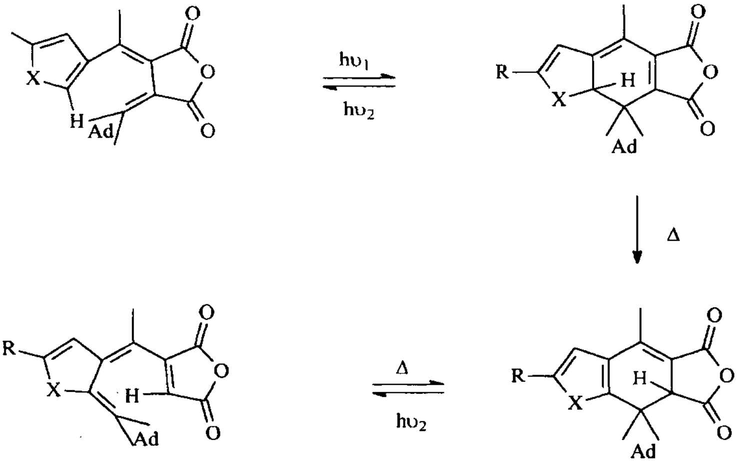
Chapter 4 (*Fulgides*). The fulgides are a class of photochromic compounds for which the thermal reversal or decoloration of the colored species is disallowed. Therefore, the reversion is largely driven photochemically as is illustrated with compound **4** (Scheme 4). Because of the stability of the colored species toward thermal reversion, the fulgides have potential application in the field of optical storage and security printing. Another use, in actinometry, is well known.



4

Scheme 4

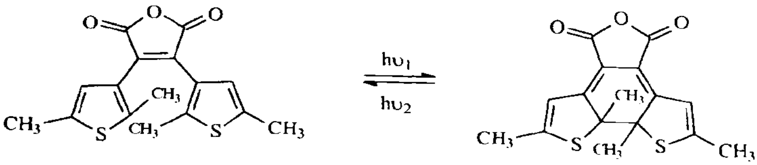
A related family of photochromics can be formed through a photochemical and thermal hydrogen shift of properly substituted fulgides. These compounds have been named heliochromes (e.g. **4'**, Ad = adamantylidene, Scheme 4'). In contrast to the fulgides, the heliochromes are thermally reversible.



4'

Scheme 4'

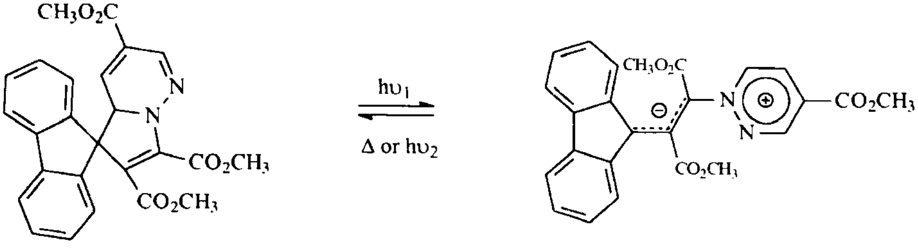
Chapter 5 (*Diarylethenes with heteroaryl groups*). The bis-heteroaryl ethenes (for example **5**, Scheme 5) are photochromic compounds similar to the fulgides in that the colored or cyclized forms are thermally stable. Decoloration is again driven photochemically. Increasing the thermal stability of the colored form has been a major goal of the research on this family; their targeted use is information storage.



5

Scheme 5

Chapter 6 (*Photochromism of dihydroindolizines and related systems*). The dihydro-, tetrahydro- and hexahydroindolizine compounds involving one, two or three nitrogen atoms make up another family of compounds that exhibits a generally thermoreversible photochromic system based on 1,5-electrocyclization reactions (Scheme 6). Photobleaching is sometimes superimposed on the thermal back reaction.

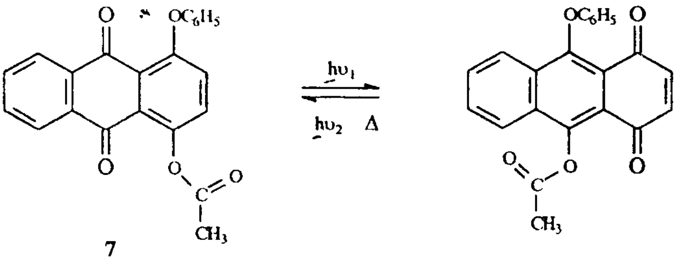


6

Scheme 6

They can be associated in supramolecular systems through interaction with inorganic salts or organic guests, in liquid crystalline phases or in polymer matrices (dissolved, absorbed or bound to a suitable polymer) or as bichromophoric units.

Chapter 7 (*Photochromic quinones*). The mechanism of the photochromic reaction of certain quinones involves proton or group transfer (Scheme 7).

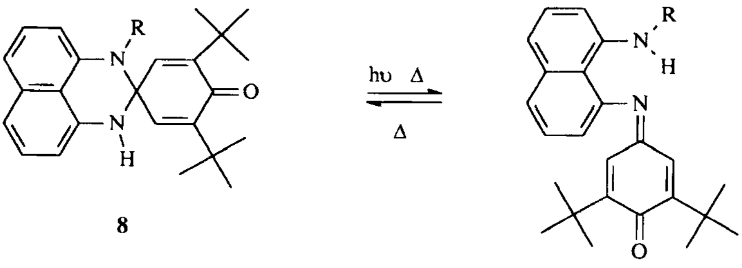


7

Scheme 7

In chapter 7, special emphasis has been placed on the synthesis of representative polycyclic quinones and their photochromic behavior, including the spectral, kinetic, and fatigue characteristics of such systems. Potential applications are focused on recording and multiplication of images, optical memories, and gradation masking.

Chapter 8 (*Perimidinespirocyclohexadienones*). This series constitutes a rather new photochromic or thermochromic system based on proton transfer involving valence and prototropic tautomeric intramolecular reactions (Scheme 8).

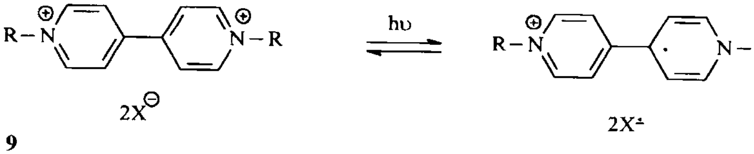


8

Scheme 8

The methods of synthesis, the spectral and photochromic properties in solution, in polymer film and in vacuum-deposited thin films, and the structural determinations by X-ray diffraction are reviewed as is the electrochemical behavior of this family of switchable materials.

Chapter 9 (*Photochromic viologens*). While photochromism quite common, via electron transfer, is in inorganic systems, fewer organic photochromic compounds operate by this method than by isomerization, heterolytic (or homolytic) cleavage or pericyclic reactions. This chapter is devoted to the photochromism of viologens (Scheme 9) and related thiazine systems, which do operate through electron transfer, in polymer matrices and in molecular assemblies involving long alkyl chains or with counter anions possessing long alkyl chains.



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Scheme 9

The formation of colored radical cations (and accompanying radical anions) and the possibility of oxidation (or reduction) by an electrochemical process indicates the possibility of erasable photo-electrochromic devices.

5. CONCLUSION AND FUTURE DEVELOPMENTS

This survey of organic photochromic and thermochromic compounds focuses on the main families that are involved in existing commercial applications, such as variable optical transmission materials (ophthalmic glasses and lenses), or in potential uses such as optical storage (optical disks or memories).

As always, the future direction of work on photochromism is difficult to predict. With regard to photochromic families, the spirooxazines, chromenes, fulgides, and arylethenes are the more advanced series for commercial applications and they will likely progress in the future through molecular design and understanding of the mechanisms of photocoloration and photodegradation. New series or modified "old" series could also be developed taking into account the results obtained in the other series.

Some of the major developments involving photochromism will very likely utilize other phenomena, in conjunction with photochromism, resulting in useful applications. Some of the work discussed in the chapters of this book illustrate the concept of coupling photochromism with another phenomenon. For example, combining the photochromic electron transfer reaction of viologens with electrochemistry shows promise in the development of electronic applications (Chapter 9).

The development of supramolecular systems involving a photochromic pigment and organic semi-conductor oligomers or polymers, is also of interest.

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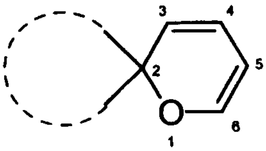
1

Spiropyrans

ROBERT C. BERTELSON

1.1. INTRODUCTION

“Spiropyrans” refers in general to a (substituted) 2*H*-pyran having a second ring system, usually (but not necessarily) heterocyclic, attached to the 2-carbon atom of the pyran in a spiro manner as shown in structure 1; i.e., a carbon atom is common to both rings. Compounds in which the second ring system is merely a saturated carbocycle such as cyclohexyl or adamantyl are better considered simply as 2,2-dialkylpyrans, and are discussed in Chapter 3.



The “pyran” portion of “spiropyran” usually refers to 2*H*-1-*benzo*pyran, as well as to its literal meaning of a single ring. The Russian literature often uses the less ambiguous (and therefore preferable) “spirochromene,” incorporating the common name for [2*H*]-1-benzopyran. The closely related spirobenzoxazines and spironaphthoxazines, in which the pyran ring includes an additional heteroatom, are discussed in detail in Chapter 2, and the 2,2-substituted benzopyrans (chromenes) and napahthopyrans (benzochromemes) that are not spiro compounds are discussed in Chapter 3. The compound from different heterocycles having the names “A” and “B,” and where the shared spiro carbon atom would be numbered “x” in heterocycle “A” and “y” in heterocycle “B,” should correctly be named “spiro(A-x,y'-B),” with the names in alphabetical order and the second name bearing the primed numbers; thus, spiro(2*H*-1-benzopyran-2,2'-2*H*-indole). A simpler name such as “indolino [or other heterocycle] spiropyran” is easily understood and often used informally as a general term. In much of the pre-1965 literature, substituents on the benzopyran

Robert C. Bertelson • Chroma Chemicals Inc. Dayton, OH, USA

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portion bore the primed numbers; thus the names of compounds in early papers must be examined carefully.

A very wide variety of possible spiropyran ring systems is implied by the above definition, and a considerable number of these systems have been prepared and examined for use in various practical applications. The spiropyrans, their photochromism, and their applications have been extensively reviewed.[1,2] This chapter surveys principally the literature appearing since the previous reviews, much of which concerns the indolinospirodipyrans because of their usefulness and ready availability. Little is said about spiropyrans or the many other known ring systems. Azaheterocyclic spiropyrans having benzothiazoline, benzoxazoline, thiazolidine, thiazine, oxazoline, oxazine, pyrrolidine, and piperidine moieties, which have been extensively studied by Guglielmetti *et al.*, have been reviewed.[2] Some of their recent work on synthesis, spectrokinetic behavior, and correlation of this behavior with electronic structure and geometry is given in this chapter.

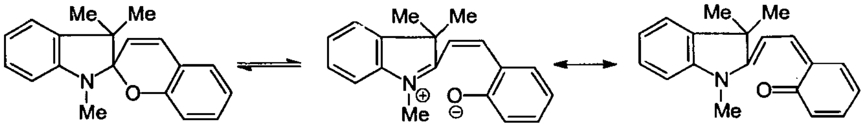
Many recent papers are ignored or mentioned only briefly because they are discussed elsewhere in this book. The biological applications of spiropyrans incorporated into membranes and their use as specific ion recognition sensors and signal transducers is discussed in Volume 2, Chapter 9. Spiropyran-modified artificial monolayer, bilayer, and multilayer membranes whose physical and chemical properties can be controlled by irradiation are discussed in Chapter 1 in Volume 2. The X-ray structures of numerous spiropyrans, the nature of the molecular packing, and the relationship between structure and photochemical behavior is reviewed in Volume 2, Chapter 7.

Following a suggestion of the editors, comments based on personal experience and unpublished research are included here. They chiefly concern practical aspects of synthesis. In this regard, reported product yields will usually be indicated.

Few new spiropyran-based chromophores have been reported recently. One present goal, discussed later, that is motivating the search for new chromophores is to find spiropyrans whose “colored” forms absorb strongly in the infrared but relatively weakly in the visible region. An earlier goal of finding spiropyrans giving intense yellow, orange, and red colors while also having thermal fade rates, quantum yields, and fatigue rates very close to the available blue and green dyes has been mostly met by spirooxazines and chromenes that cover these regions of the spectrum. Furthermore, computer programs can now calculate and display moderately accurate absorption spectra of proposed new chromophores, so only the most promising candidate dyestuffs need actually be synthesized.

Reversible photocoloration is attributed to an equilibrium between the spiropyran (“closed,” “colorless”) form and a merocyanine (“open,” “colored”) form, as shown in Scheme 1 for an indolinospirobenzopyran. The merocyanine itself is an equilibrium mixture of geometrical conformations, and its electronic distribution varies from highly zwitterionic to an essentially nonionic *ortho*-quinoidal structure.

The way in which authors consider these compounds seems to be influenced by the synthetic route they used. If an active methyl group is condensed with a hydroxyaldehyde (or an equivalent) compound, it’s a spiropyran; if the *same*



Scheme 1

compound is made by condensing a formylmethylene (or equivalent) group with a ketomethylene (or enol equivalent, e.g., 2-naphthol), it's a merocyanine, because these are the respective traditional synthetic routes.

The existence of the spirobenzopyran–merocyanine equilibrium implies that in principle a dimethinemerocyanine could be closed to a pyran isomer, thus exhibiting "reverse" photochromism (bleaching with visible light and thermally recoloring in the dark), but no systematic study of this large class of dyes appears to have been carried out. However, many merocyanines can be irreversibly photobleached by reaction with some added reagent, and have been surveyed for use in unconventional photographic systems. A few dimethinemerocyanines [e.g., those from naphthols, or 3,5-dinitrosalicylaldehyde, or 3-formyl-4*H*-1-benzo(thio)pyran-4-one[3]] exhibit extremely slow thermal fade in solution and films, and can be considered as "spiropyrans whose colored forms are stable"; they often exhibit reverse photochromism.[4]

The next section of this chapter reviews purely synthetic aspects of spiropyrans and their intermediates in some detail. A later section emphasizes studies of the properties of new (and some old) compounds.

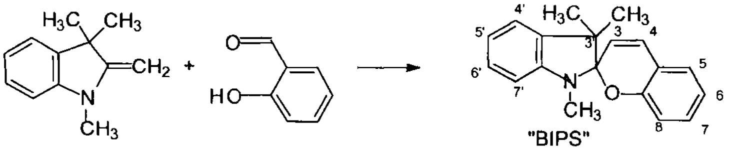
1.2. SYNTHESIS

1.2.1. General Summary

A spiropyran can be synthesized in several different ways. As indicated in Scheme 2, one can connect the two "halves" of the molecule by condensing an intermediate providing the C^2 and C^3 atoms of the pyran ring with an intermediate providing the C^4, C^5, C^6, and the oxygen atom of the pyran ring. In a second approach, one intermediate is the source of C^2, C^3, and C^4, while the other provides C^5, C^6, and the oxygen atom. In a third approach, one can prepare a spiropyran and then introduce new substituents, or transform substituents already present.

Scheme 2

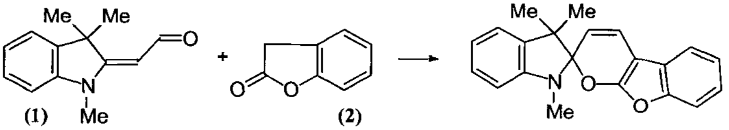
The first method is perhaps the most common, and is exemplified by the condensation shown in Scheme 3 of a 2-alkyl heterocyclic quaternary salt or the corresponding methylene base with a 2-hydroxy unsaturated aldehyde grouping (which usually is part of an aromatic ring, as in salicylaldehyde). These intermediates have given a broad assortment of spiropyran classes. The ready availability of 1,2,3,3,-tetraalkyl-3*H*-indoleninium salts and salicylaldehydes has led to a large number of spiro-(2*H*-1-benzopyran-2,2'-indolines) [this name will be used in preference to the "correct" 1',3'-dihydrospiro(2*H*-1-benzopyran-2,2'-(2 *H*)-indole)]. A common acronym for this class, "BIPS," will be used in this chapter as both singular and plural.



Scheme 3

In an unusual variation of this first method, 2-methyleneindolines condense with pyrylium salts to give photochromic spiroindolines with a carbocyclic rather than a pyran ring.[5]

The second method corresponds to moving the formyl group from the aldehyde intermediate to the methylene base, and is a standard method for preparing a merocyanine (the open form of a spiropyran). This method is useful for the reaction of the easily obtained and stable Fischer's aldehydes (2-formylmethyleneindolines) (**1**) with ketomethylene compounds such as "2-hydroxybenzofuran" (**2**) or "2-hydroxybenzothiophene" where the corresponding hydroxyaldehyde is difficult to obtain (Scheme 4). These two methods include the several routes to various symmetrical and unsymmetrical spiro(dipyrans).[6]



Scheme 4

The third approach is useful when the spiropyran itself (or, more correctly, its intermediates) is easily available, the necessary substituted intermediates are not, and the spiropyran tolerates the chemical transformations involved. Halogenation and nitration of BIPS and spiro(dinaphthopyrans) can be carried out by standard methods: bromo substituents replaced by cyano or lithium, nitro substituents reduced to amino, etc. For example, the aldehyde group in 6-formylBIPS can be reduced, oxidized, caused to react with organometallics, condensed with active methylene groups, converted to cyano, and derivatized to give a wide variety of 6-substituted BIPS. These reactions cannot be usefully carried out directly on 5-formylsalicylaldehyde to give the corresponding 5-substituted salicylaldehyde. However, the substituted BIPS can react with 3,5-dinitrosalicylaldehyde to liberate the 5-substituted salicylaldehyde.[7]

The synthesis of spiropyrans essentially reduces to the syntheses of the intermediates representing its halves, so it is necessary to discuss some aspects of obtaining these intermediates. An earlier review[1] tabulates many spiropyrans prepared during 1955–69 at The National Cash Register Co.; the preparation details reside in a series of technical reports. Starting about 1970, several groups in the former Soviet Union have been publishing much of their synthetic work, chiefly in the journal *Khimiya Geterotsiklicheskikh Soedinyenii* (*Chemistry of Heterocyclic Compounds*). Generally, the structures of the intermediates and dyes (and the often unexpected products!) were determined by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), which usually was more informative than infrared spectroscopy for this purpose.

1.2.2. Intermediates for Spiropyrans

The salicylaldehyde and hydroxynaphthaldehyde intermediates are often prepared by introducing a formyl group or an equivalent synthon next to the OH group (blocked, if necessary) of the corresponding phenol or naphthol; many formylation methods are known. Salicylaldehydes can easily undergo the common electrophilic substitution reactions, thus affording, for example, nitrated, halogenated, and chloromethylated products suitable for further transformations.

The two complications arise with simple substitutions, however. First, the aldehyde group is sometimes displaced (especially easily in the case of 2-hydroxy-1-naphthaldehydes) and the resulting phenolic compound undergoes additional substitution. Thus, for example, nitration of 4,6-dichlorosalicylaldehyde without very close control of temperature and acid concentration gives 3,5-dichloropicric acid instead of the expected 5-nitrodichlorosalicylaldehyde (both compounds have the same melting point and react with Fischer's base to give pale yellow solids of similar melting point; one is the authentic spiropyran, the other is merely the nonphotochromic dichloropicrate salt of Fischer's base).[7]

The second complication is that sometimes the incoming substituent does not go where expected; this is fairly common with naphthalene compounds, especially when replacing a sulfonate group or bromine atom via nucleophilic reactions, for example, with a cyano group (cine substitution). The structures of several multiply-substituted salicylaldehydes and naphthalene compounds reported in the literature in the period 1920–45 are wrong because of this complication and the circular reasoning following from it: the (incorrectly placed) cyano group was converted to carboxyl to provide the "authentic reference naphthoic acid" used in comparison with naphthoic acids obtained by other means.

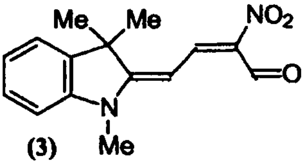
A more subtle case involves the bromonitrosalicylaldehydes. Bromination of 3- and 5-nitrosalicylaldehydes gives the expected 5-bromo-3-nitro- (62% yield) and 3-bromo-5-nitrosalicylaldehyde (56%), respectively. In the alternative route to these compounds, nitration of 3-bromosalicylaldehyde gives the expected 3-bromo-5-nitro compound. However, nitration of 5-bromosalicylaldehyde gives 3-bromo-5-nitro salicylaldehyde (44%) and only 25% of the expected 5-bromo-3-nitro isomer.[8,9] The former is the less soluble and crystallizes directly from the reaction mixture, and thus could understandably (but mistakenly) be assumed to be the desired isomer. Direct displacement of bromine by nitronium ion could possibly occur, and the resulting bromonium ion would then brominate the 5-nitrosalicylaldehyde also formed. Alternatively, an oxidation–reduction sequence could remove the bromine atom as bromide ion, which is then oxidized to elemental bromine by the nitric acid, which in turn effects the bromination.

Today an unequivocal determination of substituent positions on a phenol or naphthol or hydroxyaldehyde by infrared and NMR spectroscopy is usually straightforward and should always be performed routinely; the major or most easily isolated product is sometimes not the expected one! For example, the most easily isolated product (the first to crystallize) from a Reimer–Tiemann reaction of 3-chlorophenol is 6-chlorosalicylaldehyde, and not the 4-chloro isomer, which is the major product.

The salicylaldehydes commonly used have nitro, alkoxy, or halogen substituents, and need no further comment. Some unusual ones have cationic substituents: 3-, 4- and 5-methylthio- and dimethylaminosalicylaldehydes have been prepared and methylated to the corresponding dimethylsulfonium and trimethylammonium salicylaldehydes.[10–12] The salicylaldehyde substituted in the 4-position with a 3,5-diphenyl-2-pyrazolin-1-yl group gives a series of BIPS and spiro(dipyrans) having highly fluorescent spiro forms and nonfluorescent open forms, which is the reverse of the usual situation.[13]

The terms “salicylaldehyde” and “hydroxynaphthaldehyde” above are meant to include analogs having heteroatoms in the ring, especially the pyridine and quinoline analogs. Pyridoxal and related vitamin B6 compounds have an extensive literature concerning their synthesis. The direct introduction of a formyl group into azaheterocycles by the usual electrophilic methods generally proceeds poorly; however, methyl groups in the 2- or 4- position relative to a ring nitrogen atom can be efficiently oxidized in one or two stages to the formyl group by means of several different reagents.

Salicylaldehydes give spiro*benzo*pyrans, often referred to simply as spiropyrans. In principle, true monocyclic spiropyrans would be prepared from 3-hydroxyacrylaldehyde, which is the enol form of malonaldehyde. A reaction of Fischer’s base with malonaldehyde or its chloro derivative gave complex mixtures containing the open form, but nitromalonaldehyde sodium salt gave with Fischer’s base hydroiodide a 24% yield of beautiful orange crystals of the open form (**3**) ($\lambda = 483$ mm).[7] Recently a series of 2-substituted malonaldehydes (**4**) became



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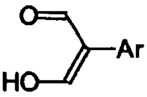


(4)

$$\text{Ar} = \begin{cases} \text{substituted phenyls} \\ \text{heterocyclics} \end{cases}$$

commercially available in which the substituents were ten differently substituted phenyls; four different pyridyls; two different quinolyls; and pyrazinyl, pyrimidinyl, quinoxalinyl, and benzoxazolyl. Pyran dyestuffs from these intermediates have not been reported as yet.

The heterocyclic alkyl quaternary salts used for preparing spiropyrans are usually obtained by N-alkylating the heterocyclic bases by standard methods. The common bases having an active methyl group of the indolenine, benzothiazole, benzoxazole, and quinoline series; some of their substitution products, and a few of their quaternary salts are commercially available. The pyrylium, thiopyrylium, 2-azaazulenium and benz[*c,d*]indolenium salts needed for potentially infrared-absorbing spiropyrans are not (as of the time of writing).

Many new heterocyclic salts are novel polynuclear compounds having multiple heteroatoms, and have been described during the past 20 years by research groups in the former Soviet Union, and more recently by groups in Egypt. These salts are primarily intermediates for cyanine and merocyanine dyes and have been converted to these dyes, but usually not to spiropyrans. New classes of spiropyrans should be obtainable from these salts.

1.2.2.1. Fischer's Base Syntheses

The Fischer's bases, 2-alkylidene-1,3,3-trisubstituted indolines, which may be further substituted in the indoline ring, are the most versatile and useful bases for preparing spiropyrans. For convenience, the name "Fischer's base" will be used hereafter in the general sense indicated above, as well as for the specific compound 2-methylene-1,3,3-trimethylindoline. Substituents in the 1- and 3-positions are methyl unless otherwise specified; thus "3-phenylFischer's base" denotes the 1,3-dimethyl-3-phenyl compound.

The preparation and chemistry of Fischer's bases have been reviewed several times.[1,14] In the first of the three classical methods for their preparation (Fischer synthesis), an aromatic amine is converted to the corresponding arylhydrazine, which is condensed with an isoalkyl methyl ketone to give the corresponding arylhydrazone; this may be isolated, but conveniently is cyclized directly to give a 2-methyl-3,3-disubstituted indolenine, which in turn is alkylated to give the *N*-alkylindolenium salt. The variation in which an *N*-alkyl-*N*-arylhydrazine is condensed to give the *N*-alkylindolenium salt directly is much less convenient in practice, because 1-alkylation of an arylhydrazine gives only moderate yields, as does the reduction of an *N*-nitroso-*N*-alkylarylamine, owing to the removal of the nitroso group to regenerate the secondary amine. If an *N*-arylFischer's base is the goal, however, the nitrosation of a diarylamine and subsequent reduction is the only practical route to the necessary *N,N*-diarylhydrazine. The Fischer synthesis is generally best for obtaining compounds unsubstituted on the aromatic ring but having alkyl groups other than methyl in the 2- or 3-positions, because phenylhydrazine and the required ketones are available. For example, methyl cyclohexyl ketone with phenylhydrazine gives an excellent yield of the 3,3-pentamethylene-[i.e., spirocyclohexyl]-2-methylindolenine.[7]

In a Fischer synthesis, the formation of the hydrazone and its cyclization to the indolenine in the crude reaction mixture can be monitored conveniently by IR spectra. The ketone C=O absorption near 1720 cm^{-1} disappears as the phenylhydrazone C=N absorption in the 1625–l640 cm^{-1} region appears, which in turn is replaced by the indolenine C=N absorption at 1570–l580 cm^{-1}. If a Fischer's base is formed directly, the IR spectrum exhibits two peaks near 1615 and 1650 cm^{-1}. All these absorption peaks are strong and sharp.

In the second classical method (Bischler synthesis), an aromatic primary or secondary (arylalkyl, but not diaryl) amine is condensed with an α-bromo (or better, hydroxy) ketone to give a 2,3-dialkylindole. This in turn is alkylated directly to the 1,2,3,3-tetraalkylindoleninium salt. Use of acetoin gives 2,3-dimethylindole, which is easily isolated and purified. The Bischler synthesis from a substitued aniline, and especially from anilines bearing one or more alkoxy groups, is much preferred in practice for indoles substitued in the 4–7-positions, since the substituted arylhydrazines needed for the Fischer synthesis are costly, unstable, or unavailable.

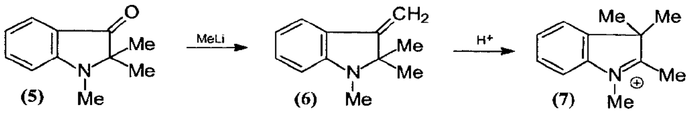
Any other synthesis that leads to a 2,3-dialkylindole can of course be considered, and several novel reported routes are mentioned later. Vigorous alkylation of a 2-substituted indole can introduce three identical alkyl groups; for example, the best route to 1,3,3-triethylFischer's base is exhaustive ethylation of 2-methylindole,[15] and methylation of 2-phenylindole also introduces three alkyl groups.

Methylation (and more generally, alkylation) of a Fischer's base itself occurs on the 2-methylene group, giving ethylidene and isopropylidene groups that can rearrange with the other alkyl groups present. However, the difficulty of separating the mixture of directly alkylated products and their rearrangement products makes this route a poor choice. The reaction of Fischer's base with iodomethane and with iodoethane to give various 1,3,3-trialkyl-2-alkylideneindolines has been studied.[16]

A Bischler synthesis can be monitored best by IR, following the disappearance of the sharp, single N–H absorption of the indole, or also by the appearance of *N*-alkyl peaks in the NMR spectrum.

In the Plancher arrangement, the third classical method of Fischer's base synthesis, a group larger than methyl in the 2-position of a 1,2,3-trisubstituted-3-methylindoleninium salt will exchange positions with the 3-methyl group, thus giving the 2-methyl compound [the salt of a (2-methylene) Fischer's base.] Groups larger than methyl in the 3-position also rearrange, but not so completely, and the rearrangements are reversible, leading to mixtures that are very difficult to separate. The synthesis is not really needed when all substituents are various alkyl groups, because the branched alkyl methyl ketone necessary for a Fischer synthesis is today either commercially available or easily synthesized. The Plancher rearrangement is the best route for introducing one aryl group in the 3-position of Fischer's base itself. Thus, 2-phenylindole can be caused to react with methyl iodide under conditions such that three methyl groups are introduced and the phenyl rearranges, giving 3-phenyl- 1,2,3-trimethylindoleninium iodide in one step (see Section 1.5.2).[7]

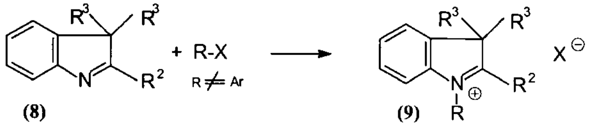
A Plancher rearrangement also occurs with an isomer of Fischer's base, as shown in Scheme 5. The addition of methyllithium to 1,2,2-trimethylindoxyl (**5**) gives 1,2,2-trimethyl-3-methyleneindoline (**6**). This base in acid solution at room temperature is completely converted over several hours to the 1,3,3-trimethyl-2-methyleneindoline salt (**7**). Even in the solid state the orange-colored perchlorate salt, which is stable for several months at –20°C, rearranges within 1 day at +20°C to the colorless Fischer's base perchlorate salt.[17] This route is useful for Fischer's bases having a phenyl or substituted phenyl on the N atom, because the starting material, *N*-phenylanthranilic acid (converted to the indoxyl by the standard routes of indigo syntheses), is much cheaper and safer to use than the *N*,*N*-diphenyl hydrazine required to prepare the same final compound by the Fischer synthesis.[7]



Scheme 5

1.2.2.2. Fischer's Base Salts by Alkylation of Indolenines

The Fischer synthesis gives a 2,3,3-trialkylindolenine (**8**) which is subsequently alkylated on the N atom to give the 1,2,3,3-tetraalkylindoleninium salt (**9**) (Scheme 6). Arylation, however, for example, with 2,4-dinitrofluorobenzene or 4-nitrohalobenzenes, has not been successful. [7]



Scheme 6

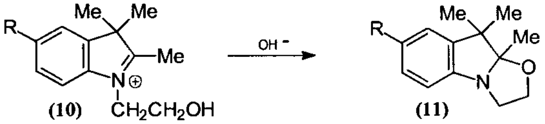
The N-alkylation can be carried out with or without a solvent, using alkyl halides, tosylates, sulfates, phosphates, and for difficult cases the very powerful but extremely toxic methyl fluorosulfonate. Excess methyl and ethyl iodides are convenient solvents; longer chain alkyl halides often are used with chloroform or tetrachloroethane as solvents. Ketones such as acetone and butanone have been used, and higher acyclic and alicyclic ketones have been claimed[18] to give high yields of substantially pure salts.

The reaction of an indolenine with an alkyl halide having the alkyl group ethyl or longer can also lead to elimination rather than alkylation, with the formation of the hydrohalide salt of the indolenine. This salt can be mistaken for the expected quaternary salt. In this case, treatment with base will merely regenerate the starting indolenine, which is easily distinguished by IR spectrum, as indicated earlier, from the Fischer's base formed from the quaternary salt. Often the solid isolated is a mixture of the two salts, and both components can be identified in the spectrum of the corresponding mixture of bases.

A detailed study of the N-methylation of 2,3,3-trimethylindolenine with methyl sulfate using triethylbenzylammonium chloride as a phase-transfer catalyst has appeared. The reported yields of high-purity (96–99%) Fischer's base were 90–92%.[19] N-alkylation is the most practical method for preparing a Fischer's base with alkyl groups having, for example, thienyl,[20] hydroxy, carboxy, or sulfonate substituents.

Reaction between butanesultone and 2,3,3-trimethylindolenine gave a 74% yield of the water-soluble *N*-(*n*-butylsulfonate) inner salt of Fischer's base; this salt and others from substituted indolenines were used as intermediates for cyanine and merocyanine dyes, but not specifically for spiropyrans.[21]

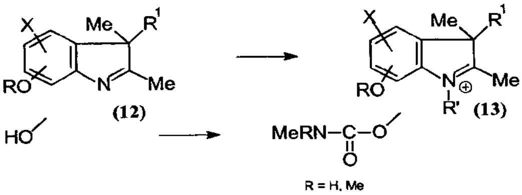
The preparation of 1-(2-hydroxyethyl)-2,3,3-trimethylindoleninium bromide and its 5-bromo (75% yield) and 5-nitro derivatives by alkylation of the corresponding indolenines with 2-bromoethanol has been described. As indicated in Scheme 7, these salts (**10**) with base gave the corresponding "cyclized" Fischer's base (**11**), 5-bromo-2,3,3-trimethylindolino[1,2- *b*]-oxazolidine.[22]



Scheme 7

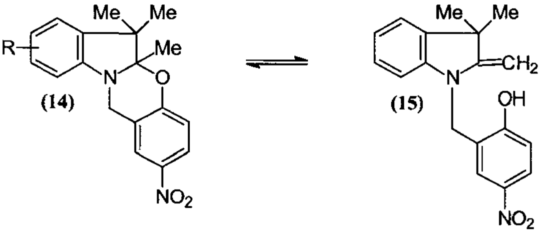
2,3,3-Trimethylindolenine can also be N-alkylated by α-haloketones such as bromoacetone (58% yield). For a series of 1'-acetonylBIPS, the thermal fade rate constant was several times larger than for the corresponding 1'-methylBIPS. The absorption spectra exhibited bathochromic shifts in ethanol, but negligible shifts in toluene.[23]

Sixteen indolenines (**12**) having a hydroxy group in the 6- or 7-position, and additional substituents in the 4- and 5-positions as shown in Scheme 8, were prepared and alkylated on the N atom to give the Fischer's base salts (**13,** R = H). The hydroxyindolenines were generally prepared by dealkylation of the corresponding methoxy compound with HBr or BBr_3. The 4,7-dimethoxy-2,3,3-trimethylindolenine was selectively demethylated at the 7-position. The OH groups of the indolenines were converted to the methylamino- and dimethylaminocarbamate esters (**12**), R = MeNHCO; Me_2NCO).[24]



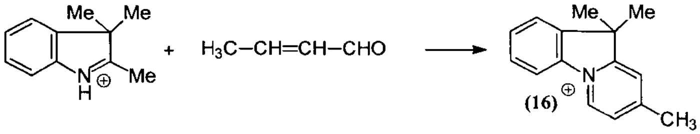
Scheme 8

Reaction of 2,3,3-trimethylindolenine and its 5- and 7-methyl analogs with 4-nitro-2-chloromethylphenol gives 2-nitro-5a,6,6-trimethyl-5a,6-dihydro-12*H*-indolo-[2,1-*b*][1,3]benzoxazine (60% yield) and its 8- (27% yield) and 10-methyl (15% yield) analogs (**14**). These could exist in equilibrium (Scheme 9) with the corresponding open-chain zwitterion and base [i.e., 1-(2-hydroxy-5-nitrobenzyl)-Fischer's base] (**15**), although the spectral evidence suggests only very small amounts of these open-chain forms. However, treatment with perchloric acid gave the hydroperchlorate of the Fischer's base, and aqueous alcoholic KOH gave the potassium salt of the phenolic function in the Fischer's base. No experiments have yet been reported in which these 1-substituted Fischer's bases were allowed to react with a salicylaldehyde.[25]



Scheme 9

The reaction between the perchlorate salt of 2,3,3-trimethylindolenine and crotonaldehyde involves Michael addition (at the 2-methyl group, not the N atom) and spontaneous cyclization to give 8,8,10-trimethyl-10*H*-pyrido[1,2-*a*]indolium perchlorate (**16**) in 26% overall yield. This can be considered a vinylog of a Fischer's base salt (and also a 4-picolinium salt). This salt has been condensed with aromatic aldehydes to give styryl dyes, but there is no report of reaction with salicylaldehydes. [26]



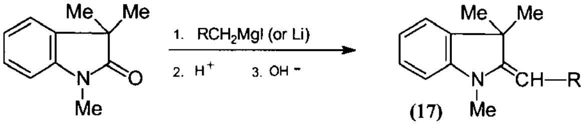
Scheme 10

Vilsmeier formylation of 1-(2-hydroxyethyl)Fischer's base (in its cyclic form as trimethylindolino[1,2-*b*]oxazolidine) (**11**) gave 1-(2-hydroxyethyl)Fischer's aldehyde in 82% yield when the reaction was performed at 35°C, but gave instead 66% of 1-(2-chloroethyl)Fischer's aldehyde at 60°C.[27]

The heterocyclic quaternary salt 1,3-diethyl-2-methyl-5-(*N*-trifluoromethylsulfonyl-*S*-trifluoromethylsulfoximido)-1*H*-benzimidazolium tosylate, containing the superstrong electron acceptor ($\sigma_p = 1.4$) group $CF_3S(O){=}NSO_2CF_3$, was prepared and used as an intermediate for carbocyanine, merocyanine, and styryl dyes. The spectra of these dyes showed a large bathochromic shift compared with the corresponding trifluoromethylsulfonyl dyes. The preparation of spiropyrans from such quaternary salts, for example, the 5-substituted trimethylindoleninium salt, has not yet been reported, but such spiropyrans should have interesting spectral properties.[28]

1.2.2.3. Fischer's Bases from Oxindoles

Another route to a Fischer's base involves the addition of a Grignard or lithium reagent to the carbonyl group of a 1,3,3-trisubstituted oxindole. This is useful to give, for example, an ethylidene or benzylidene group in the 2-position (**17**), leading to a BIPS bearing a methyl or phenyl substituent in its 3-position. The preparation of benz[*c,d*]indoleninium quaternary salts by the addition of Grignard reagents[29] or methyllithium[7] to a 1-alkylbenz[*c,d*]indol-2-one (*N*-alkylnaphthostyryl) is simpler than the original method[30] and succeeds where alternative methods do not.[31] The reported[32] cyclization of 1-acetamidonaphthalene to 2-methylbenz[*c,d*]indole could not be confirmed.[7,31]

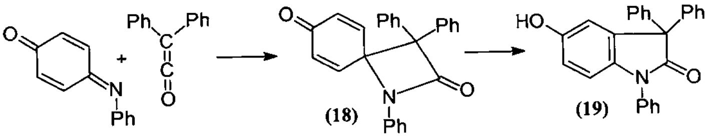


Scheme 11

The conversion of an oxindole to a Fischer's base by addition of an alkyllithium or Grignard reagent is useful in the preparation of 5-dialkylaminoFischer's bases. 5-AminoFischer's base itself overalkylates to the trialkylammonium salt and also alkylates on the methylene group, and direct preparations from *N,N*-dimethyl-4-phenylenediamine give complex mixtures affording negligible amounts of the desired material. 1,3,3-Trimethyloxindole gives a high yield of the 5-nitro compound, which is readily reduced to the amino compound. This amino compound can be dialkylated with trimethyl phosphate or, better, reductively with formaldehyde and sodium cyanoborohydride, and the resulting dimethylaminooxindole converted to the Fischer's base.[7]

Phenylmagnesium bromide can be added to N-methylisatin to give either the 3,3-diphenyloxindole (95% yield of crude) or the 2,2-diphenylindoxyl (91% yield of crude);[33,34] this is a more convenient route to a 3,3-diarylFischer's base than the alternative Friedel–Crafts reaction of 3,3-dichlorooxindole with benzene using aluminum chloride. However, the Friedel–Crafts reaction is satisfactory with more reactive aryl groups, for example, the condensation of anisole with an N-alkylisatin using phosphoryl chloride as condensing agent.

A unique oxindole synthesis is the addition of diphenylketene to the mono-*N*-phenylimine of benzoquinone; the resulting spiro-β-lactam (**18**) rearranges to give a 62% overall yield of 5-hydroxy-1,3,3-triphenyloxindole (**19**), which can be methylated to the 5-methoxy compound,[35] which in turn could be converted to the Fischer's base.

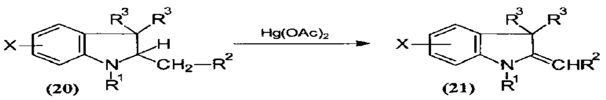


Scheme 12

Trimethyloxindole is usually prepared by permanganate oxidation of Fischer’s base.[36] Cyanine, merocyanine (including spiropyran), and styryl dyes made from Fischer’s base also give the oxindole upon thermal or photodegradation in air.[36a] The accumulated pot residues from the distillation of Fischer’s base and the concentrates from dye preparations can be recycled by simply treating these chemical wastes with air (or better, hydrogen peroxide), preferably in the presence of visible light. The trimethyloxindole is recovered by a simple vacuum distillation in about 50% yield (from Fischer’s base still residues).[7]

1.2.2.4. Fischer’s Bases by Oxidation of Indolines

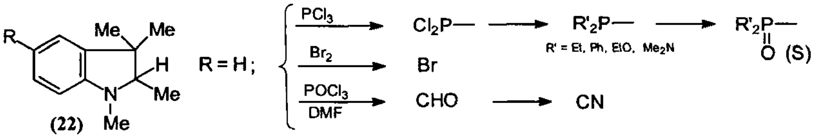
A route to a Fischer’s base (**21**) useful in some cases involves the oxidation with mercuric acetate of its reduced form, a 1,2,3,3-tetra-substituted indoline (**20**). Since the indoline is merely a substitute aniline it may be more efficient to prepare this intermediate. A number of examples are presented in Scheme 13.



Scheme 13

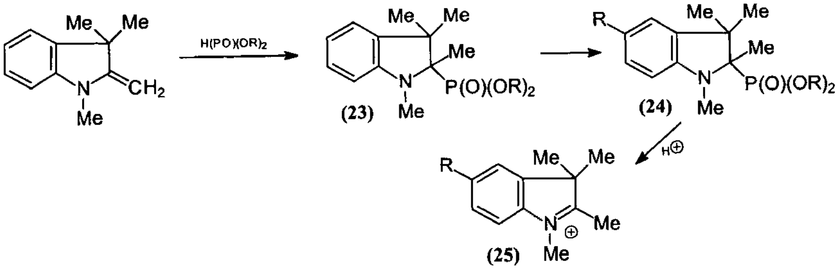
This route can be useful in controlling the orientation of a substituent. Nitration of Fischer’s base gives the 5-nitro compound, whereas the nitration of the reduced Fischer’s base gives the 6-nitroindoline. Its easy oxidation is the best preparative method for the useful 6-nitro Fischer’s base. Fischer’s base is conveniently reduced to 1,2,3,3-tetramethylindoline (**22**) simply by stirring with sodium borohydride pellets in methanol at room temperature (72% yield).[36a]

Fischer’s base can also be reduced catalytically over Raney nickel at 50 atm and 100°C to give the tetramethylindoline in 93% yield. This was brominated and formylated in the 5-position in 65 and 89% yields, respectively. Thiocyanation, however, gave only the bis(indoline-5-yl) disulfide in 51% yield after the workup. The 5-formyl group was converted into a cyano group in 78% overall yield by successive treatment with hydroxylamine and trichloroacetyl chloride. Phosphorus trichloride gave the dichlorophosphinoindoline in 96% yield, whose chlorine atoms could be replaced by ethyl, phenyl, ethoxy, and dimethylamino groups in good yields. These R_2P– compounds were further transformed into a series of $R_2P(=X)$– compounds (X = O,S). The various tetramethylindolines were oxidized by mercuric acetate to the corresponding Fischer's bases (usually isolated as their salts). However, the $Et_2P(=S)$ and $Ph_2P(=S)$ groups were hydrolyzed to the corresponding P=O compounds, and the $(EtO)_2P(=O)$ and $(Me_2N)_2P(=S)$ groups were also hydrolyzed, possibly to the corresponding acid.[37]



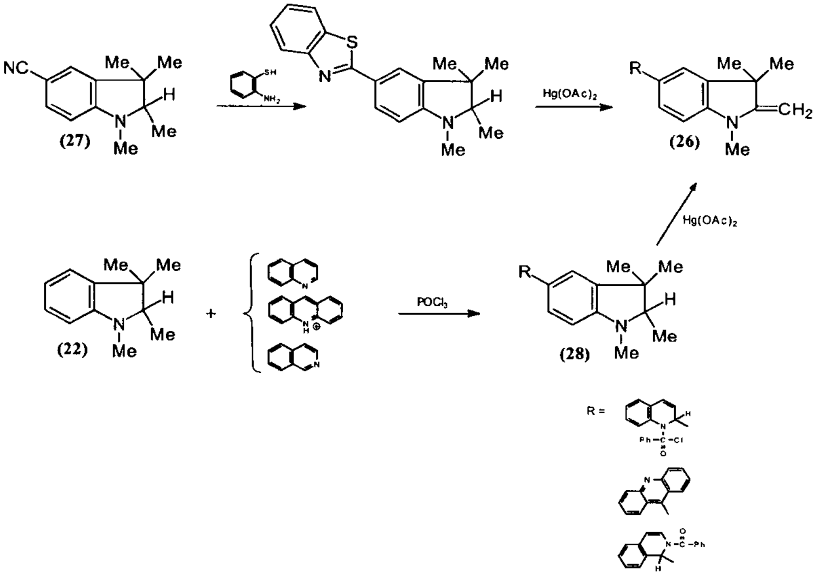
Scheme 14

The oxidation of substituted 1,2,3,3-tetramethylindolines with mercuric acetate cannot be used if the substituents are susceptible to oxidation. An alternative method for protecting the methylene group of Fischer's base is the addition of dialkyl phosphites to give the 2-phosphorylated tetramethyleneindoline (**23**); the addition is easily reversed by acid. In the presence of a base such as triethylamine, these can undergo electrophilic substitution with, for example, thiocyanogen to give the 5-SCN derivative, or bromine to give the 5,7-dibromo compound. Acidic electrophiles such as the Vilsmeier reagent cannot be used. The substituted phosphorylated indolines (**24**) are reconverted to the Fischer's base salt (**25**) upon treatment with acid, unless the indoline is rendered very weakly basic by having in the 5-position strongly electron-attracting substituents such as tricyanovinyl or 4-nitrophenylazo. This route appears best by far (69% yield overall for three steps) for the preparation of 5-thiocyanatoFischer's base, a precursor to the 5-mercapto compound.[38]



Scheme 15

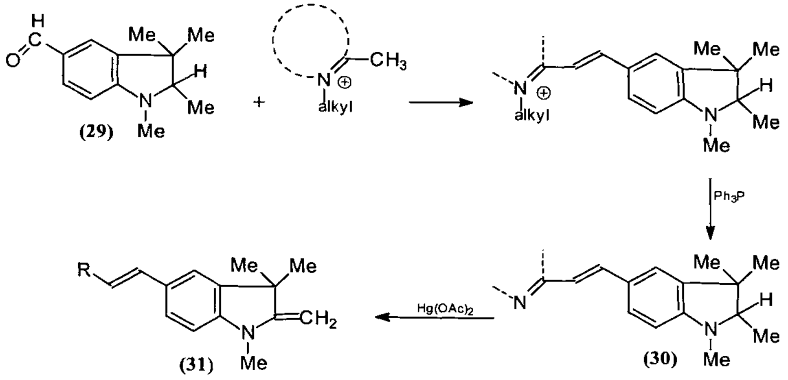
The oxidation of indolines is useful for preparing Fischer's bases having heterocyclic substituents in the 5-position. 5-CyanoFischer's base, which is difficult to obtain and is unstable, was condensed with 2–OH, –SH, and $-NH_2$ anilines to give the corresponding benzoxazol-2-yl, benzothiazol-2-yl, and benzoimidazol-2-yl substituted Fischer's bases (**26**). However, 2-mercaptoaniline was condensed with the easily obtainable 5-cyano-1,2,3,3-tetramethylindoline (**27**) and the product was subsequently oxidized with mercuric acetate to give the Fischer's base (**26**). Similarly, oxidation of the corresponding indolines (**28**), prepared by the condensation of (**22**) with a heterocycle, gave Fischer's bases having in the 5-position the following heterocyclic substituents: acridin-9-yl, quinolin-2-yl, isoquinolin-1-yl, 3,4-dihydroisoquinolin-1-yl, *N*-benzoyl-1,2-dihydroquinolin-2-yl, and *N*-benzoyl-1,2-dihydroisoquinolin-1-yl. The Fischer's bases were converted to various polymethine dyes, but not spiropyrans. [39,40]



Scheme 16

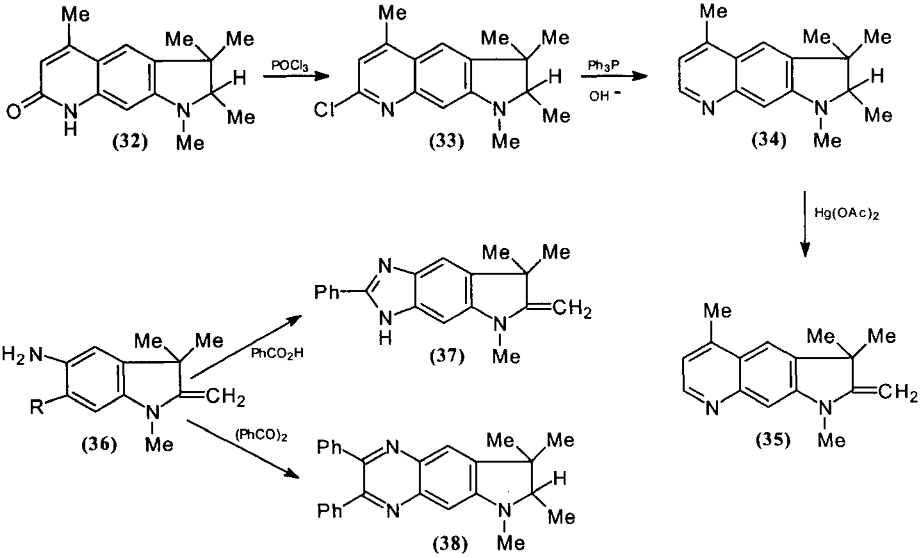
5-Formyl-1,2,3,3-tetramethylindoline (**29**) was converted to various 5-(β-heterocyclylvinyl) indolines (**30**) via condensation with heterocyclic quaternary salts and subsequent N-dealkylation by triphenylphosphine. The resultant indolines were oxidized with mercuric acetate to the 5-substituted Fischer's bases (**31,** R = benzoxazol-2-yl; quinolin-2-yl; quinolin-4-yl; pyridin-4-yl; 1,3,3-trimethylindolen-2-yl). These were used as intermediates for cyanine dyes; their conversion to spiropyrans was not recorded. [41]

Fischer's bases having an additional heterocyclic ring fused in linearly (i.e., in the 5,6-position) were prepared from 6-amino-1,2,3,3-tetramethylindoline by reaction with acetoacetic ester to give an 86% yield of the 1,2,3,3,5-pentamethyl-2,3,7,8-tetrahydro-1*H*,8*H*-pyrrolo[3,2-g]quinolin-7-one (**32**), converted to the corresponding 7-chloroquinoline (**33**) in 80% yield with phosphorus oxychloride. Both the chloroquinoline and its precursor quinolone gave the corresponding Fischer's base upon oxidation with mercuric acetate. The chloroquinoline was hydrodechlorinated by fusion with triphenylphosphine followed by base hydrolysis to give a 54% yield of pentamethyl-2,3-dihydro-1*H*-pyrrolo[3,2-g]quinoline (**34**). Oxidation of this with mercuric acetate, even in 100% excess, gave an (apparently) inseparable mixture containing only 30% of the desired Fischer's base (**35**).



Scheme 17

5-Amino-6-nitro-Fischer's base (**36**, R = NO_2) was reduced to the 5,6-diamino compound (**36**, R = NH_2) in 80% yield, which (as its hexachlorostannate salt) was condensed with benzoic acid and with benzil to give, respectively, a 68% yield of 5,7,7-trimethyl-6-methylene-6,7-dihydro-5*H*-pyrrolo[2,3-*f*]-benzimidazole (**37**) and a 62% yield of 6,8,8-trimethyl-7-methylene-2,3-diphenyl-7,8-dihydro-6*H*-pyrrolo[2,3-*g*]quinoxaline (**38**).[42] Spiropyrans from these linearly annellated Fischer's bases were not reported; they likely would color upon irradiation with blue light.



Scheme 18

1.2.2.5. Substitution in Fischer's Bases

Some electrophilic substitutions can be carried out on Fischer's base. Practical ones for introducing substituents in the ring are nitration, sulfonation, bromination, and amidomethylation. Vilsmeier formylation occurs at the methylene group to give Fischer's aldehydes. A nitro group goes into the 5-position and gives a small amount of 6- and a negligible amount of 7-substitution. The nitro group can be readily reduced to amino without reducing the methylene group. Thus, nitration of Fischer's base (60 g) gave 54.8 g of the 5-nitro and 1.6 g of the 6-nitro compound. The 5-nitro compound was reduced to 5-aminoFischer's base with stannous chloride in 71% yield.[43] This Fischer's base is a versatile intermediate, especially for attaching to polymers. However, it preferentially reacts with salicylaldehydes at the amino group to give anils rather than 5'-aminospiropyrans.

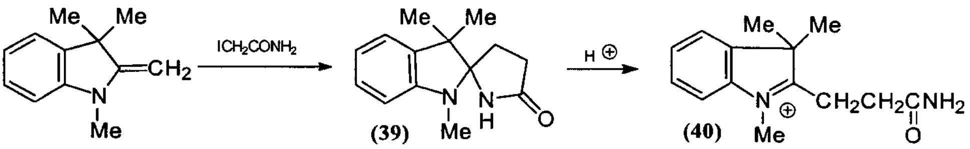
Sulfonation of Fischer's base in 30% oleum gives a 97% yield of the 5- and not the 6-substituted derivative, according to NMR spectral evidence. The compound was used to prepare cyanine and styryl dyes, but no spiropyrans were reported.[44]

5-AminoFischer's base was benzoylated in 74% yield to the amide, which upon nitration gave the 6-nitro-5-(3-nitrobenzoyl)amido derivative, hydrolyzed with acid in 64% yield to the desired 5-amino-6-nitroFischer's base. Aminomethylation of Fischer's base with *N*-hydroxymethylphthalimide[45] gave the 5-substituted product in 40% yield with only a trace of the 6-isomer, hydrolyzed with acid to give 51% of the 5-aminomethyl compound. Nitration of the 5-phthalimidomethyl compound occurred in the 6-position (53% yield), and after hydrolysis the 5-aminomethyl-6-nitroFischer's base was obtained in 59% yield. Amidomethylation of tetramethylindoline, however, occurred in the 6-position in 63% yield, and after mercuric acetate oxidation, 6-phthalimidomethylFischer's base was obtained in 67% yield. Nitration (79%) and hydrolysis gave the isomeric 6-aminomethyl-5-nitro compound.[46] The aminomethyl group is a useful link to polymers, sensitizers, initiators, etc.

Fischer's aldehydes having a 2-hydroxyethyl or 2-chloroethyl substituent on the N atom and a 5-nitro substituent were prepared by formylation of the corresponding 2,3,3-trimethylindoline[1,2]-*b*]oxazines. According to the NMR and IR spectral evidence, the aldehydes, both in solution and the solid state, existed entirely in the open chain form rather than as 2-formylmethyl-2,3,-dimethylindolino[1,2-*b*]oxazines.[47]

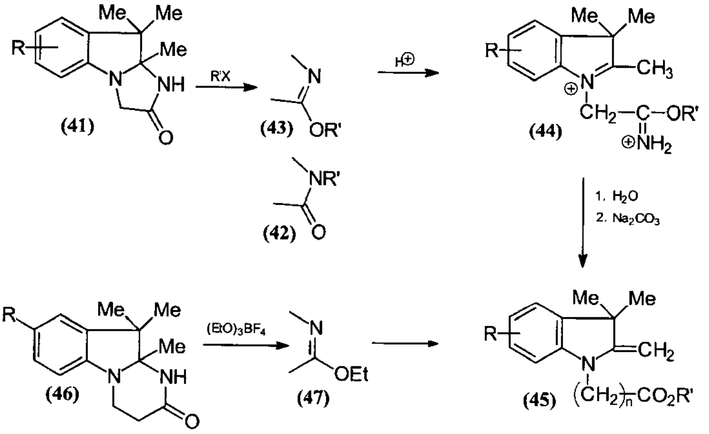
Alkylation of Fischer's base generally occurs on the methylene group. Reaction with α-iodoacetamide gave a 26% yield of the spiro product, 5'-oxo-1,3,3-trimethyl-1,3-dihydrospiro-[2*H*-indole-2,2'-pyrrolidine] (**39**). Treatment with perchloric acid opened the pyrrolidone ring and gave in 80% yield the Fischer's base salt having a 2-(2-carbamoylethyl) substituent (**40**). No information is given as to whether the spiro compound is photochromic, or whether the Fischer's base salt can be further condensed with salicylaldehydes.[48]

Alkylation of 7-(un)substituted-9,9,9a-trimethyl-1,2,3,9a-tetrahydro-9*H*-imidazo[1,2-*a*]indol-2-ones (**41**) gave a mixture of the N- (**42**) and O-alkylated (**43**) products; the latter can easily be separated from the mixture in ether by



Scheme 19

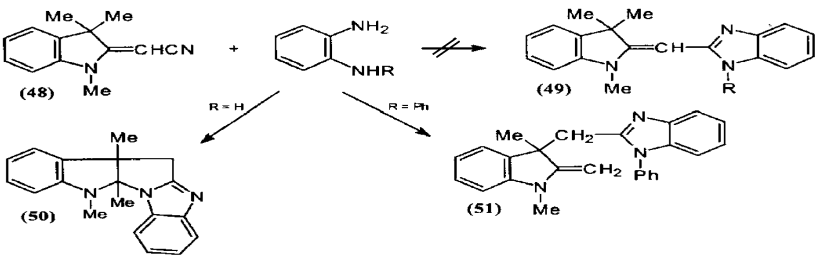
extraction with 0.5% HCl. Strong acid cleaves the ring of these O-ethers to give iminoester salts (**44**), which are readily hydrolyzed to the 1-alkoxycarbonylmethyl-2-methylene-3,3-dimethyl-5-substituted indolines (**45**, *n* = 1).[49]



Scheme 20

Alkylation of 8-(un)substituted-10,10,10a-trimethyl-1,2,3,4,10-10a-hexahydro-pyrimido[1,2-*a*]indol-2-ones (**46**) gave (unlike the five-membered ring case) chiefly the O-ethers (**47**), and gave them exclusively when triethyloxonium fluoroborate was the alkylating agent. Upon treatment with acid, these similarly gave the 1-alkoxy-carbonylethyl-2-methylene-3,3-dimethyl-5-substituted indolines (**45**, *n* = 2).[50]

In the condensation of 1,3,3-trimethyl-2-cyanomethylene indoline (**48**) with 1,2-phenylenediamine, the product (68% yield) was not the expected 2-(benzimi-

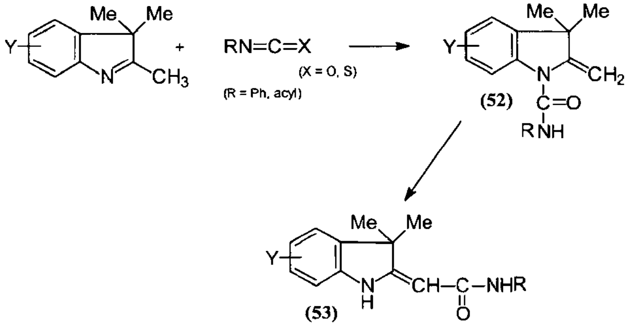


Scheme 21

dazol-2-yl)methyleneindoline (**49**, R=H), but instead 6,6a, 11a-trihydro-6a, 11,11a-trimethylindolo[2',3':1,2]pyrrolo[1,2-*a*]benzimidazole (**50**). This product resulted from a Plancher rearrangement followed by ring closure. The condensation with 2-aminodiphenylamine gave in 35% yield only the rearrangement product, 1,3-dimethyl-2-methylene-3-(1-phenylbenzimidazol-2-ylmethylene) indoline (**51**), which cannot cyclize further.[51]

1.2.2.6. Preparations of Indolenines

2,3,3-Trimethylindolenine and its 5-methyl-, 5-chloro- and 7-chloro derivatives react with phenyl isocyanate and various acyl isocyanates and isothiocyanates to give 75–97% of the corresponding 1-carbamoyl-2-methyleneindolines (**52**), which isomerize to the 2-(carbamoylmethylene) indolines (**53**) (41–85% yield).[52] Whether these Fischer's base derivatives after further N-alkylation will condense with salicylaldehydes to form spiropyrans is not known.



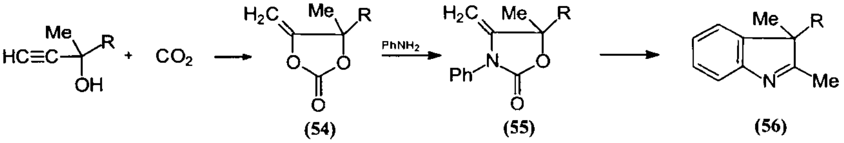
Scheme 22

The condensation of 2,3,3-trimethylinolenine with aryl aldehydes gave the corresponding 2-styrylindolenines. Condensation with 5-nitrosalicylaldehyde and its 3-bromo, 3-methoxy, and 3-nitro derivatives similarly gave the 2-(2-hydroxy-styryl)indolenines (46, 73, 68 and 91% yields, respectively), rather than the corresponding merocyanine or spiropyran forms. These indolenines were neither photochromic nor solvatochromic.[53]

An exceptionally facile route to 2,3-dimethyl-3-methoxyindolenine, an intermediate for Fischer's bases having only one rather than the usual two alkyl groups in the 3-position, consists of brominating 2,3-dimethylindole in the presence of methanol.[54]

A convenient synthesis of 3-alkyl-2,3-dimethylindolenines consists of treating the 2,3-dimethylindole with BuLi to give the Li salt, followed by addition of the alkyl iodide. Yields ranged from 45 to 70% for straight-chain alkyl groups, but fell to 36% with isopropyl iodide.[55] N-alkylation of the resulting indolenines with a different alkyl will lead to Fischer's bases in which the 1-alkyl and one of the 3-alkyl groups are different from each other and also are not methyl.

A synthesis of 3,3-disubstituted indolenines suitable for industrial use involves the addition of CO_2 under pressure to a 3-alkyl-1-butyn-3-ol to give nearly quantitative yields of the 4-alkyl-4-methyl-5-methylene-2-oxo-1,3-dioxolane (**54**). This upon heating with an arylamine in the presence of $ZnCl_2$ in an aromatic solvent with azeotropic removal of the water formed gives nearly quantitative yields of the 4-alkyl-4-methyl-5methylene-2-oxo-1-aryl-1,3-oxazolidine (**55**). Heating this compound with $ZnCl_2$ in a high-boiling mineral oil causes cyclization and loss of CO_2 to give 75–85% of the corresponding indolenine (**56**)[56]; details are given in a patent.[57] The intermediate methyleneoxazolidine (**55**) does not condense with 5-nitrosalicylaldehyde.[7]



(**54**) (**55**) (**56**)

Scheme 23

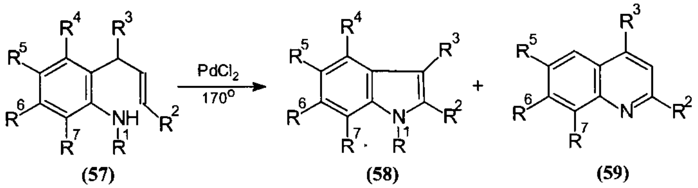
1.2.2.7. Preparations of Indoles

Although the Fischer synthesis can give an indolenine directly, it is best known as an indole synthesis.[58] The synthesis of 1,2,3,4,7-pentamethylindole is typical.[59] The Fischer synthesis has also provided 5-(2-pyridyl)indole, whose longest wavelength absorption band is at 302 nm, which is 19 nm longer than the corresponding band in the spectrum of 5-phenylindole.[60] A 5-pyridylFischer's base therefore might give a spiropyran sensitive to violet or blue light, but such a base or BIPS has not been reported.

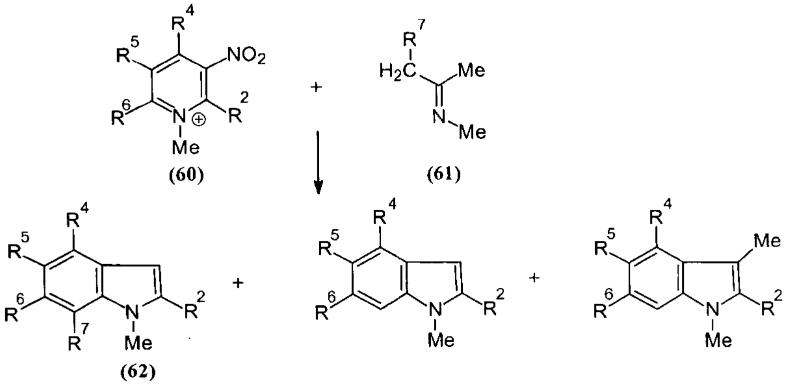
Details of the preparation of 2,3-dimethylindoles from acetoin and aromatic amines have been reported.[61] This variation of the Bischler synthesis is general, usually gives good yields, avoids the use of the lachrymatory bromoketone, and is convenient to carry out. It is the method of choice for ring-substituted-1-alkyl-3,3-dimethylFischer's bases (especially if the substitutents are one or more alkoxy groups), since the ring-substituted aniline can be used directly, and need not be first converted to the corresponding phenylhydrazine. In the reaction between an arylamine and an a-hydroxyketone, a crucial step is the rearrangement of an imino-*tert*-alkanol to an anilinoketone.[62]

The intramolecular cyclization of substituted 2-alkenylanilines (**57**) catalyzed by $PdCl_2$ affords a novel route directly to 1,2,3-trialklylindoles (**58**), which can be further methylated to Fischer's base salts. The cyclization reaction is complex, and the reaction mixture contains much of the corresponding quinoline compound (**59**). The composition of the crude product and its yield depend strongly upon the nature of the substituents. The yields of pure indoles are moderate.[63]

An unusual indole synthesis consists of reaction between a 1-methyl-3-nitropyridinium salt (**60**) and the *N*-methylimine of a dialkyl ketone (**61**).



Scheme 24



Scheme 25

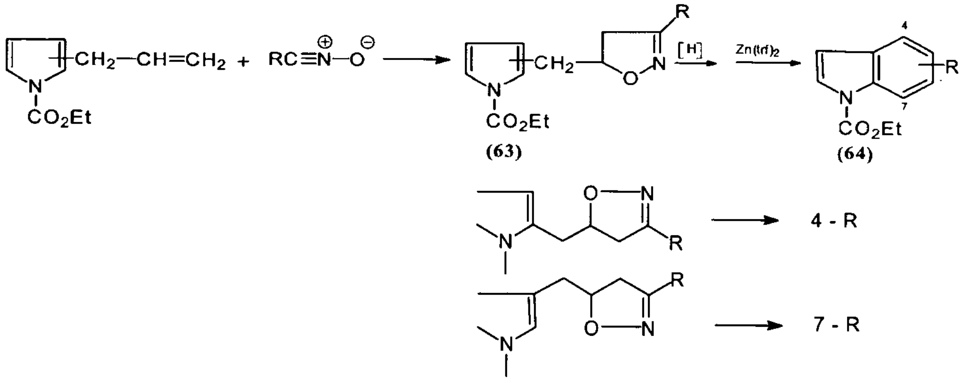
A mixture of three products is obtained, in which the 7-methylated indole (**62**, R^7 = Me) predominates (when methyl ethyl ketone is the ketone used), and predominates greatly when a substituent is present at position 4.[64] The reaction mechanism is extremely complex, and the 7-methyl group is claimed to arise from the *ethyl* group of the ketimine. The synthesis is general, but gives a mixture of polyalkylated indoles in poor yield. Instead of a preformed alkylimine, a simple mixture of a dialkyl ketone and a primary alkylamine can be used. The N atom of the indole is provided by the alkylamine; the N atom of the pyridinium salt is eliminated, along with the nitro group.[65–67]

Another novel indole synthesis consists of the addition of a nitrile oxide to 1-carbethoxy-2-(or 3-)allylpyrrole, reduction of the resulting isoxazoline (**63**) to a β-hydroxyketone, and regiospecific cyclization using zinc or magnesium triflate to a 4-(or 7)-substituted indole (**64**).[68] The overall yields are excellent.

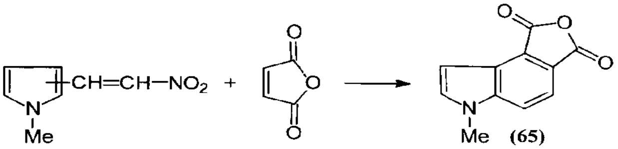
Yet another novel indole synthesis involves a Diels–Alder addition of a dienophile to a 2- (or 3-) (2-nitrovinyl)pyrrole to give in 46–50% yield indoles (**65**) in which the dienophile moiety appears in the 4,5- or 6,7-positions, respectively.[69]

1.2.3. Preparations of Spiropyrans

The condensation of the two "halves" of a BIPS or other spiropyran involving a nitrogen heterocycle generally goes rapidly and smoothly. In most cases the



Scheme 26



Scheme 27

hydroxyaldehyde and the Fischer's base, or the quaternary salt and an equivalent of a base such as triethylamine, are refluxed in ethanol or isopropanol and the relatively poorly soluble spiropyran precipitates from the reaction mixture. If the spiropyran is easily soluble in low-polarity solvents, the above reactants may be refluxed in heptane with azeotropic removal of the water formed, and the triethylammonium salt removed by filtration. The product isolated from the hepfane may be contaminated with significant amounts of triethylammonium salts, which are easily observed in the NMR spectrum.

The methylene bases of most heterocycles generally dimerize instantly upon formation, and the quaternary salts must be used. However, Fischer's Bases are reasonably stable as the monomers, and even those of relatively high molecular weight, such as the 1- or 3- phenyl compounds, can be distilled. The essentially colorless base should always be used immediately after distillation for preparing a BIPS; the product spiropyran will be obtained in a state of high purity after merely washing on the filter. Using old, colored Fischer's base will contaminate the desired product with the cyanine dye and other colored degradation products that are very difficult to remove. The extinction coefficients for the cyanine dyes are 5–10 times those of the colored spiropyran in the same wavelength region. If the crude Fischer's base cannot be distilled, or is heavily contaminated with indoles, indolenines, and tars from its synthesis, spiropyran formation serves as a separation method.

Normally the hydroxyaldehyde and Fischer's base or corresponding quaternary salt are used in equimolar amounts. Some hydroxyaldehydes readily form the poorly soluble, nonphotochromic "dicondensed" 3,4-dihydroBIPS having a second Fischer's base moiety as a substituent in the 4-position. Salicylaldehyde itself does this, as do many 3-alkoxy (especially methoxy) salicylaldehydes containing additional substituents. To minimize the formation of the dicondensed product, add the Fischer's base slowly to a 5–10% excess of the aldehyde. The readily soluble excess aldehyde is easily removed from the (usually) poorly soluble desired BIPS.

If the desired BIPS is much less soluble in the reaction solvent than the reactants and side products, as is often the case, it can be obtained highly pure and in high yield. Thus, for example, the procedure described in section 1.5.1 gives a 95–98% yield of 8-ethoxy-6-nitroBIPS of 99+% purity. More typically, this procedure has given 70–85% yields with dozens of different BIPS.[7]

The BIPS will be poorly soluble in lower alcohols if it is prepared from parent or halogen-substituted Fischer's base, or if the salicylaldehyde used has a 5-nitro substituent alone or with additional methoxy, ethoxy, or halogen substituents (isomeric dyes from a 3-nitrosalicylaldehyde are significantly more soluble). Fischer's bases having longer-chain alkyl groups or phenyl groups in the 1- and/or 3-positions give BIPS having greater solubility.

Although ethanol is the usual reaction solvent, lower ketones such as 2-butanone are also useful solvents if an intermediate contains a group reactive to alcohols, e.g., 1-(2-carboxyethyl)Fischer's Base hydroiodide.[70] In aromatic solvents such as toluene, the condensation proceeds well and the water formed may be removed by azeatroping, but the product generally is easily soluble, requiring concentration of the reaction mixture. Separation of pure spiropyran from colored impurities of similar solubility may then be tedious.

The preparation, filtration, washing, and drying of the spiropyran should, of course, be carried out in the absence of direct or diffuse daylight, and if possible under incandescent or "gold" (minus blue) fluorescent lamps. There is sufficient UV radiation available from ordinary fluorescent lamps to significantly color a still-damp filter cake of a sensitive compound.

If the highly polar methanol or "wet" ethanol is the reaction solvent, the position of thermal equilibrium is shifted to the colored form, and the crystallized product is significantly colored. In anhydrous ethanol or isopropanol, the spiropyran is less contaminated with the colored item. The crystallization should take place as fast as practical in order to get small, easily washed crystals. Slow cooling gives large crystals that occlude the colored mother liquor and that cannot be simply washed clean. Most simple BIPS are white or pale yellow solids when entirely pure; traces of the usually blue-colored form will impart a bluish or greenish tint to the solid. A dirty maroon or red-brown (rather than bright magenta) color indicates impurities from oxidized Fischer's base.

Recrystallization of 6-nitroBIPS and its simple (methoxy, lower alkyl, halogen) substituted derivatives is often best carried out from *pure* ethyl acetate (i.e., free of ethanol and acetic acid) with use of decolorizing charcoal. Most dyes have a large temperature coefficient of solubility and crystallize beautifully.

The melting point behavior observed in a capillary tube is an excellent indicator of purity. A *pure* BIPS exhibits no (thermal) coloration until just a few degrees below its melting point, and then colors rapidly and intensely. The melt in most cases is pure blue and not violet (even if the irradiated solution color is violet). More significantly, the vapor space in the tube above the melt will be colorless. Impure compounds generally show the pinkish vapor of Fischer's base even if the melting point is not lowered.

High-performance liquid chromatography (HPLC) can be ambiguous in indicating purity; a pure spiropyran may thermally equilibrate in a polar mobile phase and the open and closed forms will appear as two peaks.

The *N*-heterocyclic quaternary salts of nonaromatic enamines, such as the tialkyl-3,4,5,6-tetrahydropyridines, Δ-1-pyrrolines, and 5,6-dihydro-2*H*-thiazines, are very sensitive to water, and molecular sieves need to be used in conjunction with azeotroping to keep the reaction mixture anhydrous. Preparing and handling these intermediates and spiro compounds[2] from them requires great care.

For the preparation of spirobi(pyrans), the pyrylium salt (preferably the easily purified perchlorate or fluoroborate) may be used, but it is often more convenient to merely condense the appropriate hydroxyaldehyde(s) with the requisite aliphatic ketone either directly using gaseous HCl in ethanol, or via a base-catalyzed condensation to first give a 2-hydroxychalcone intermediate.[5]

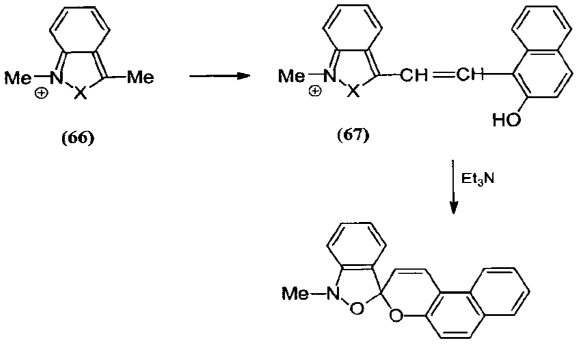
Preparative details, typical for their respective classes of compounds, have been disclosed for several spiro(4*H*-1-benzopyran-4,3'-[3*H*]naphtho[2,1 -*b*]pyran)s ("β-naphthoisospiropyrans")[71]; for 3-methyl-6-nitrospiro(2*H*-1-benzopyran-2,3'[3 *H*]-naphtho[2,1 -*b*]pyran)[72]; and for 3-phenyl-6'-nitrospiro(2*H*-1-benzopyran-2,2'[2'*H*-1'-benzopyran).[73]

Detailed directions for preparing 26 spiropyrans having a piperidine or tetrahydrothiazine ring are given in a patent.[74]

A summary of synthetic methods for obtaining spiropyrans from benzodithioles, benzoxathioles, and 1,3-dithioles is given elsewhere.[75]

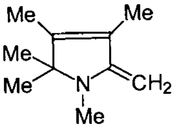
1,3-Dimethyl-2,1 -benzisoxazolium perchlorate (**66**, X = O) condensed with 2-hydroxynaphthaldehyde to give an 87% yield of the red (λ_{max} = 520 nm) styryl salt (**67**, X = O). Treatment of this salt with base (Scheme 28) gave an 80% yield of the spiropyran (**68**), which was thermochromic, turning red (λ_{max}not given) at 155°. Photochromic behavior, if any, was not mentioned. The analogous 1,3dimethyl-2,1 benzisothiazolium (**66**, X=S) and 1,2,3-trimethylindazolium (**66**, X = NMe) salts were condensed with aromatic aldehydes to give styryl dyes, but their conversion to the corresponding spiropyrans was not mentioned.[76]

Not all heterocyclic methylene bases give spiropyrans (at least under the usual conditions). 1,3,4,5,5-Pentamethyl-2-methylene-2,5-dihydropyrrole (**69**)[77] did not condense with 5-nitrosalicylaldehyde to give any photochromic material.[7] However, 1-methyl-2-methylene-3,3,4,5-tetraphenyl-2,3-dihydropyrrole (**70**), prepared by reaction of methyllithium with 1 -methyl-3,3,4,5-tetraphenylcrotonolactam, did condense with 5-nitrosalicylaldehyde to give a product exhibiting reverse photochromism: the unexposed form was red and the exposed form yellow. This behavior probably represents a trans to cis isomerization of the open form.[7]



(66) (67) (68)

Scheme 28



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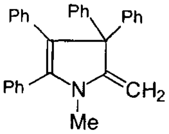

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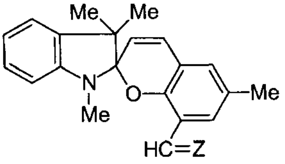
The preparation of 8,10, 10-trimethyl-10*H*-pyrido[1,2- *a*]indolium salts has been described.[78] These Fischer's base analogs condense with salicylaldehydes in the same manner as other aromatic aldehydes to give styryl dyestuffs rather than spiropyrans.[7]

The preparation of 2-hydroxy-3 -pyridinecarboxaldehyde and its 6-acetamido derivative, and their condensation with Fischer's base to give the corresponding spiropyridopyrans have been described. The acetamido spiro compound selectively recognizes guanine, which traps the open colored form by triple hydrogen bond complementarity, thus signaling the presence of guanosine derivatives.[79]

6-Methyl-8-formylBIPS (**71**, Z = O) was condensed with amines to give in 36–61% yields the 8-anils (Z = N–R) (R = benzyl and 4-X-phenyl, [X = acetyl, nitro, and methyl]), and with aldehydes to give in 62–76% yields the 8-styryl ketones (Z=CH–R') (R' = methyl, phenyl, and 2-hydroxyphenyl). The styryl ketones were shown by their NMR spectra to be the cis isomers. Of the anils, only the 4-nitrophenyl

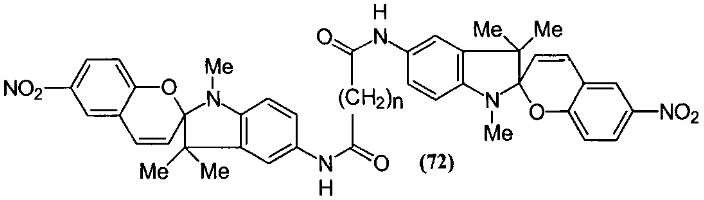


(71)

derivative was photochromic (in 2-propanol at –70°; λ_{max} = 587 nm.) All three styryl ketones were photochromic (λ_{max} = 628, 615, and 617 nm, respectively.)[80]

A BIPS having hydrogen rather than alkyl on the 1'-nitrogen atom could possibly be formed from the reaction between a 2,3,3-trialkylindolenine and a salicylaldehyde. However, the reactions between 4-nitro-2,3,3,7-tetramethylindolenine and five different substituted salicylaldehydes (3-methoxy-5-nitro; 5-nitro; 3-bromo-5-nitro; 3-nitro-5-methoxy; and 3-nitro) gave only the 2-hydroxy(substituted)styryl dyes, which were not solvatochromic or photochromic. The yields were 3–7% based on 5-nitro-2-methylphenylhydrazine, the precursor of the indolenine used. The NMR, UV, and mass spectrometry (MS) evidence excluded spiro or open zwitterionic structures for these products.[81]

5-AminoFischer's base was condensed with the diacid chlorides of glutaric, pimelic, and azelaic acids to give in 70–92% yields the bis-amides, which upon reaction with 5-nitrosalicylaldehyde gave 70–88% of the bis-spiropyrans (**72**, *n* = 3,5,7). The alternative route, reaction of the acid chlorides with 5'-amino-6-nitroBIPS, is impractical because of the difficulty of obtaining this BIPS. The bis-BIPS exhibit strong photochromism. The open forms precipitate in nonpolar solvents, which is apparently due to intra- or intermolecular π-stacking.[82,83]



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1.2.4. Substitution in Spiropyrans

The spiropyrans can be brominated with *N*-bromosuccinimide (NBS) in chloroform to give various substitution patterns that are dependent upon the nature of the two halves of the molecule. In the case of 5-methylspiro-[5,6-dihydrophenanthridine-6,2'-(2*H*-1-benzopyran)], *two* bromine atoms enter only the chromene but not the phenanthridine portion to give the 6',8'-dibromo derivative (λ_{max} 540nm). In the case of the BIPS compounds, more possibilities occur. Bromination of the unsubstituted BIPS occurs first only in the indoline ring to give a 77% yield of the 5'-bromo compound, then threefold simultaneously in the indoline and chromene rings to give 60% overall yield of the 5',7',6,8-tetrabromo compound. To obtain the di- or tribromo compounds, it is necessary to start with 6- or 6,8-dibromoBIPS. Bromination of 6-nitroBIPS with one or two equivalents of NBS takes place only in the indoline ring, giving 80 and 83% yields of the 5'-bromo- and 5',7'-dibromo-6-nitroBIPS, respectively.[84] This is the best route to these spiropyrans.

Bromination of 6-nitroBIPS to the 5'-bromo derivative could be carried out in excellent yield with bromine in chloroform (95%), *N*-bromosuccinimide in carbon tetrachloride (95%), cuprous bromide in acetonitrile (87%), or bromine in chloroform with boron trifluoride added (92%). Similarly, chlorine in chloroform or cuprous chloride in acetonitrile gave the 5'-chloro compound in very good yield. (Although 5-chloroFischer's base is commercially available, this direct chlorination is useful when the Fischer's Base bears alkyl groups other than methyl in the 1- and 3-positions.) Nitration of 6-nitroBIPS in the 5'-position can be carried out using nitric acid in acetic anhydride (43% yield) or concentrated sulfuric acid (60%), or better (87%), by adding sodium nitrite to the spiro compound in glacial acetic acid, followed by simply stirring in air to oxidize the initially formed nitroso compound. Treatment of the 6-nitroBIPS with the double salt of 4-nitrophenyldiazonium chloride and mercuric chloride in acetone gave a 89% yield of the orange-red 5'-azosubstituted compound, which was not photochromic. The 5'-bromo-6-nitroBIPS could be converted in moderate (21%) yield to the corresponding cyanoBIPS by reaction with cuprous cyanide in pyridine.[85] Direct chlorination, bromination, nitration, and azo coupling with 4-nitrophenyldiazonium salts introduce the substituent into the 5'-position of a BIPS in 83–95% yields.[81]

Since aminosalicylaldehydes are very labile substances, the reductions of 6-nitro and 6-nitro-8-methoxyBIPS were examined as routes to the corresponding 6-amino compounds. The amino group is a versatile function for linking the spiropyran to polymers, sensitizers, etc. Reduction with hydrogen and Raney nickel in benzene gave the aminoBIPS derivatives (yield crude, 97%; purified, 48%), whereas in ethanol solution the products were the 3,4-dihydro-6-aminoBIPS, possibly because the open (merocyanine) form is present and the chain adds hydrogen faster than the nitro group.[84]

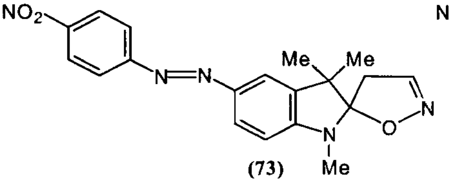
A method for preparing silica gel having BIPS groups bonded to it consists of metallating 6-bromoBIPS with butyllithium and causing the 6-lithioBIPS to react with silica. In a less efficient route to the same material, 4-methoxyphenyllithium (from the metallation of 4-bromoanisole) was coupled with silica gel. The resulting 4-methoxyphenylated silica was demethylated with boron tribromide and the resulting hydroxyphenyl groups were formylated by the Duff reaction to give the corresponding salicylaldehydes; they were then treated with Fischer's base. The first lithiation method was also carried out with 5'-bromoBIPS and 1'-(4-bromobenzyl)-BIPS.[86] This method should be generally useful for a wide variety of substituted BIPS, since the lithio function could be converted to numerous groups; a substituent such as nitro that is incompatible with an organolithium function can be introduced in a subsequent step.

1.3. NEW MATERIALS. PROPERTIES AND STRUCTURE–PROPERTY RELATIONSHIPS

1.3.1. Spiropyrans in Fluid Solutions

In the search for new photochromics, the spirobenzopyran–merocyanine structure suggests many variations. The size of the rings and the nature and placement of the hetero atoms can obviously be varied, for example. Some of the earlier suggestions[87] have been examined.

The oximes of 2-acylmethyleneindolines (Fischer's aldehyde and ketones) can be obtained in the spiro (31–82% yields) and open forms, as shown by ^{1}H and ^{13}C NMR spectra, and by X-ray diffraction analysis of the open form of the aldehyde oxime.[88] The thermal and acid–base reactions of these compounds were reported, but nothing was said about photochromic properties. The spectral change on treatment with acid is given only for the case of 3',4'-dihydro-5-(4-nitrophenylazo)-1,3,3-trimethylspiro[indoline-2,3'-isoxazole] (**73**): λ_{max} 425nm; open form (**74**), 595 nm.[88,89] When the substituent in the 5'-position of the spiro[indolineisoxazole] was hydrogen (**75**, R = H), treatment with acid gave the starting oxime by cleavage of the spiro–O bond; when R was methyl or chloromethyl, the isoxazole was recovered unchanged, or hydrolized to the original acylmethyleneindoline. However, when the 5'-substituent was (un)substituted phenyl, acid cleaved the spiro C–N bond rather than the spiro C–O bond, giving a 3-aryl-5-[1-methyl-1-(2-methylaminophenyl)ethyl]isoxazole (**76**). Upon heating, this partly reformed the starting (**75**) to give the thermodynamic equilibrium mixture of the two forms (60% spiro form in the case of the 5-phenyl substituent).



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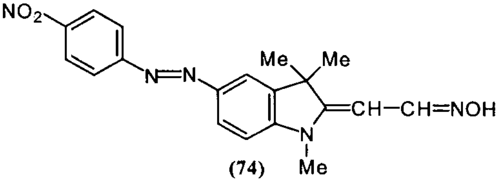

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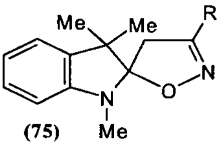

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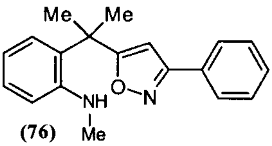

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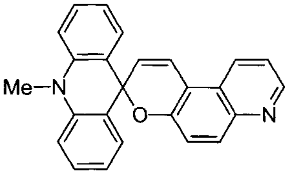
Balli, in summarizing[90] a series of earlier papers, described the preparation and properties of compounds having variations of the spiropyran structure, assembled from 9 different "left-hand sides" and 19 different "right-hand sides," as shown in Figure 1.1.

The original objective was to obtain materials exhibiting reverse photochromism (photobleaching with visible light and recoloration in the dark). The thermochromic properties and coloration with acids were also of interest for applications in thermal recording papers and carbonless copy papers. The thermodynamic parameters, equilibrium constants, and absorption maxima for the reversible coloration reactions of a large number of compounds in several different solvents were tabulated. To summarize the thermochromic results, the compounds with oxygen linked to the spiro carbon atom behaved very similarly to the known spiropyrans, whereas the compounds with nitrogen in a five- or six-membered ring linked to the spiro atom underwent thermally irreversible bleaching or showed no measurable thermochromism. The absorption maximum of the 1',3',3'-trimethylspiro(4*H*-imidazo[4,5,1-*ij*]quinoline-4,2'-[2*H*]indole (**77**, structure shown in Figure 1.1) is 550nm. An unusual solvatochromic shift was observed for the compound spiro(*N*-methylacridinepyridinobenzopyran) (**78**), which reportedly has a λ_{max} at 710nm in benzyl alcohol and 600nm in xylene. All of the other compounds showed a shift less than 60nm, and usually much less.[90]



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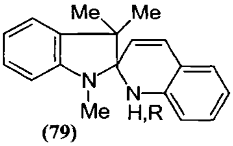
Authentic N-analogs of spirobenzopyrans, the 1,2-dihydrospiro-2*H*-quinolines (**79**) (or their open forms), have never been isolated, despite many attempts during the past 35 years. In reactions with Fischer's base, 5-nitro-2-aminosalicylaldehyde gave no reaction, whereas 2-aminobenzaldehyde gave only a polymer.[7] The open form of the desired compound could be considered a quinone monoimine and therefore be expected to have poor stability.

Attempts to prepare spiro(1,3-oxazines) (**80**) by using the 2-imino analogs of Fischer's bases gave in 67–77% yields only nonphotochromic anils (**81**), which were apparently stabilized by hydrogen bonding. Such anils from indoline bases are not thermochromic either, but the corresponding anils from 2- or 4-iminopyridine or quinoline are thermochromic, changing from orange to red in boiling chlorobenzene.[91] Condensation of 2-imino-3,5-dimethylthiazolidine (**82**)[92] or 2-imino-3-methylbenzothiazoline[90] with various substituted salicylaldehydes gave no spiro(1,3-oxazines), but rather gave in 25–52% yields the corresponding bis(2-ylidenamino)-2-hydroxyphenylmethane derivatives (**83**), as shown by NMR and X-ray structure analysis. These compounds also were thermochromic but not photochromic.[92,93]



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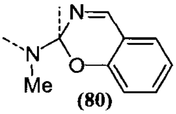

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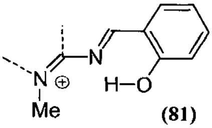

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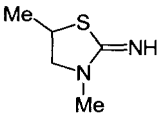

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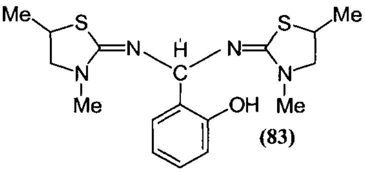

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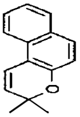
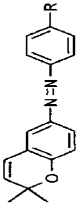
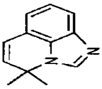




R = H, CN, CF_3, NO_2



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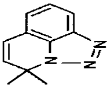
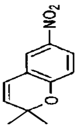
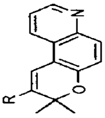
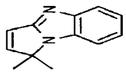
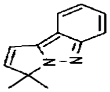


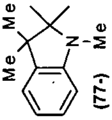




R = H, Me







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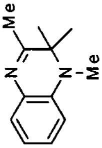
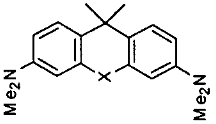
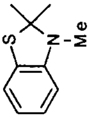
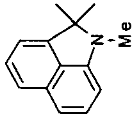
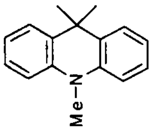




X = O, S, NMe, NH







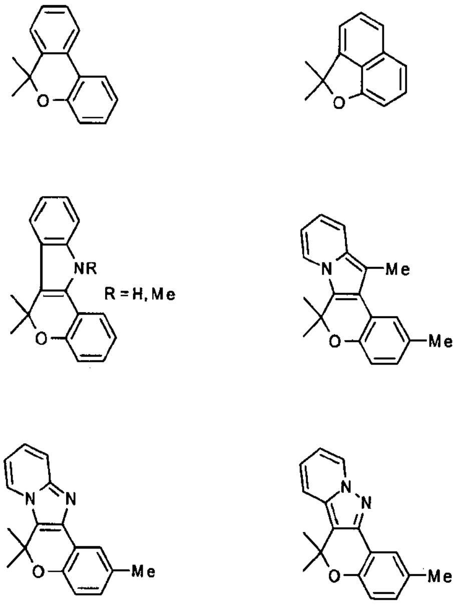
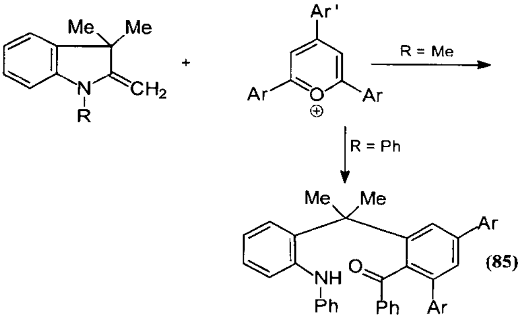


Figure 1.1. Component moieties of some photo-, thermo-, and acidochromic spiropyrans and analogs.

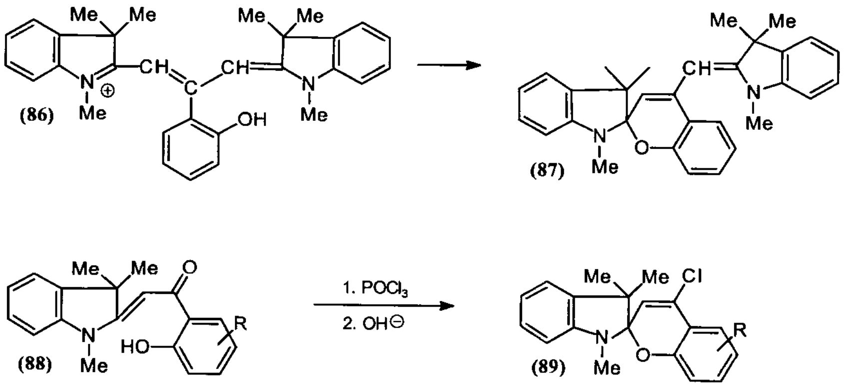
"Carbon analogs" of BIPS were formed in 35–88% yields by the reaction between Fischer's bases and 2,4,6,-triarylpyrylium salts.[5] The resulting 6-aroyl-3,5-diarylspiro(cyclohexa-2,4-diene-1,2'-indolines) (**84**) were reportedly photochromic, but details of their photochromic behavior had not been published at the time of writing. Such spiroindolines, whose structures were confirmed by X-ray analysis, represent a new class of photochromics. Since a wide variety of tris(substituted aryl)pyrylium salts is readily obtainable, reports of many more examples of these photochromics may be expected. The compounds having a methyl group on the indoline N atom were relatively stable to acids, whereas those having a *N*-phenyl substituent were unstable, easily aromatizing the cyclohexadiene ring by displacing the indoline group with the concomitant ring opening, as shown in Scheme 29, giving the corresponding 4,6-diaryl-2-[1-methyl-1-(2-phenylaminophenyl)ethyl]-benzophenone (**85**).



Scheme 29

Cyanine dyes having a 2-hydroxyphenyl substituent on a β-position of the polymethine chain, proposed earlier[94] as salts of the open form of spiropyrans, have been prepared[95] and treated with base. The symmetrical indocyanine from Fischer's base (**86**) gave the (yellow) 4-(Fischer's base)-substituted spiropyran (**87**) (Scheme 30), but the unsymmetrical indocarbocyanines having one lepidine or quinaldine end group did not undergo ring closure.

In a search for 4-substituted BIPS, Fischer's base was acylated with substituted 2-acetoxybenzoyl chlorides, and after removal of the acetoxy group via base hydrolysis, the resulting (2-hydroxyphenacylidene)indolines (**88**) were treated with phosphorus oxychloride followed by treatment of the resulting salts with aqueous base to give the colorless spiro forms of the 4-chloroBIPS (**89**, R=H;8-Me;6-NO_2;6,7-benzo) in low (14–39%) yield (Scheme 31). In contrast to the analogs unsubstituted at position 4, these new compounds do not show any solvatochromic effect and are not usefully photochromic. Examined by laser photolysis in benzene, only the 6-nitro compound gave a visible absorption band (λ_{max} about 570 nm), and its half-life was 50 ns, compared with the nonchlorinated 6-nitroBIPS half-life of 100 s under the same conditions. The chlorinated BIPS exhibit irreversible thermo-

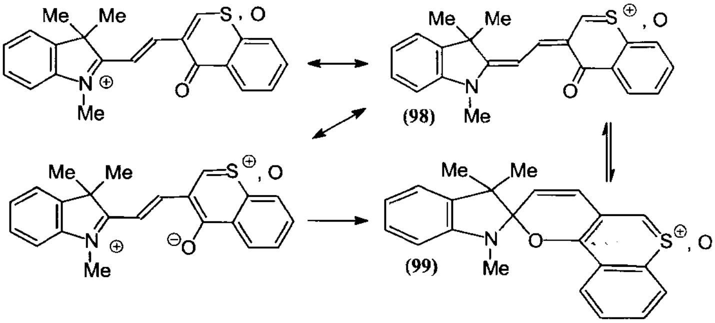


Schemes 30 and 31

chromism when heated in dimethyl sulfoxide solution. The chlorine atom appears to provide sufficient steric hindrance to prevent the ring closure.[96]

The series of spiropyrans (**90**) was prepared in 54–65% yield from 4-methyl-7-hydroxy-8-formylcoumarin and cationic salts. The absorption maximum of the colored forms of the dyes shown in Figure 1.2 were (Z, nm given): (**91**), R = Me;Pr;n-C_6H_{13};n-C_8H_{17};CH_2Ph, 560–565; (**92**), 570; (**93**), 600; (**94**), 650; (**95**), 630; (**96**), 620; and (**97**), 660. The spiro forms although coumarins, show either no fluorescence or weak (quantum yield $<10^{-3}$) fluorescence in the 380–420-nm region. The coloration efficiencies of the indoline derivatives were an order of magnitude greater than those of the oxazolidine and the oxaindene compounds, and two orders of magnitude greater than those of the other four compounds.[97]

Condensation of indoleninium quaternary salts with 3-formyl-4*H*-1-benzothiopyran-4-one and its pyran analog gave the cationic merocyanine dyes (**98**) (λ_{max} = 403–435 nm) in 32–75% yields. In solution these decolorize reversibly (Scheme 32) to the spirothiopyran (**99**) upon irradiation with visible light. The corresponding dyes having a dimethylaminovinyl or 4-dimethylaminophenylvinyl substituent in the 2-position have a λ_{max} of 556–725 nm, and decolorize in a polyester film but not in solution.[3]



Scheme 32

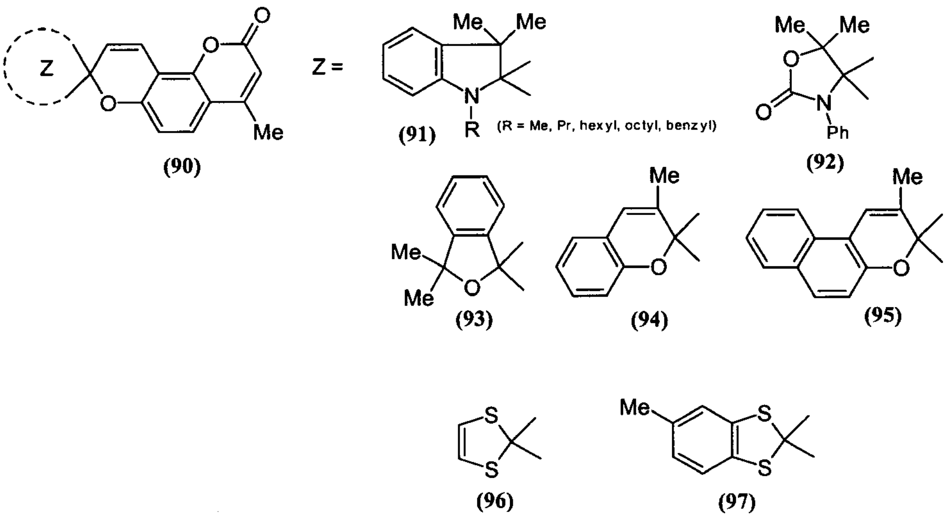


Figure 1.2. Some spiropyrans containing a coumarin moiety.

The five spiroimidazodihydroquinoline compounds shown in Figure 1.3 exhibit reverse photochromism and were studied in detail by both stationary illumination and nanosecond time-resolved laser flash spectroscopy.

The quantum yields and kinetics of the photobleaching of these compounds were determined, and their thermal coloration rates and activation energies were measured. The pH dependence of the spectral absorption changes, due to both the shift in the position of the protonation equilibrium between the spiro form and its salt, and the equilibrium between the salts of the spiro form and the open form, were also measured. A detailed analysis of the extensive data led to the spectroscopic identification of the short-lived ground-state cis conformers of the open forms of the five compounds studied. The photobleaching process is a photo trans–cis isomer-

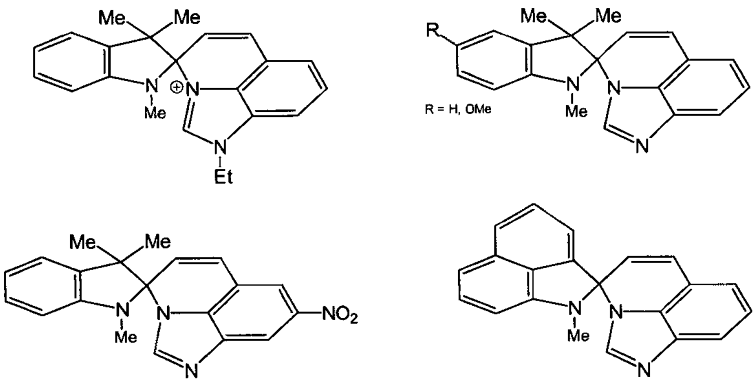
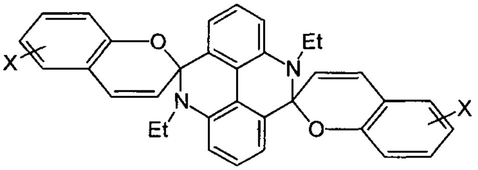


Figure 1.3. Spiroimidazodihydroquinolines that exhibit reverse photochromism.

ization having a quantum yield of about 0.5, followed by a thermal ring closure having a rate constant of typically $10^7\ s^{-1}$ and an activation energy of about 30 kJ-mol^{-1} at room temperature. The rate of the thermal cis → spiro ring closure is more than 10^{10} times the rate of the cis → trans isomerization of the open form.[98]

A molecule containing more than one spiropyran group, provided they are not merely insulated from one another, for example, by a saturated alkyl chain spacer, could possibly open the rings selectively or successively, and thus give different colors with different irradiation wavelengths or intensities. The interesting dispiropyrans (**100,** X=6-NO_2; 6,8-Br_2), from the twofold condensation of a salicylaldehyde with 5,10-dimethyl-4,9-diethyl-4,9-diazapyrenium ditosylate in 35–54% yields exhibited observable photochromism only during flash photolysis, because the thermal fading of the colored forms was very rapid. They were thermochromic, however, and also pH sensitive, opening first one pyran ring to give the mono salt of the spiro-substituted styryl dye, and then the second pyran ring at higher acid concentration to give the (bis-styryl) dye. Similarly, the monospiropyrans (**101**) with acid open the pyran ring, and at higher acid concentrations protonate the 9-N atom.[99]



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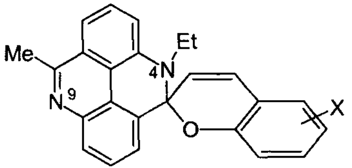
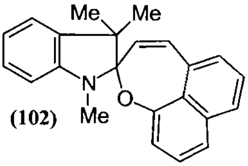


(101)

The calculated spectrum of the open form of a spiro(indolino-2,2'-naphth[1,3-*bc*]oxepine) (**102**) indicates absorption in the near infrared region. Experimentally, however, the reaction of Fischer’s base with 8-hydroxy-1-naphthaldehydes gave, according to the ^1H and ^{13}C NMR spectra, different types of products, depending upon the substituents present in the aldehyde. The unsubstituted aldehyde gave a 51% yield of the “dicondensed” seven-membered ring product (**103**); the 5-nitro, 5-bromo, and 5,7-dibromohydroxyaldehydes gave 75–89% of the naphthofuran compounds (**104**); and only the 5,7-dinitroaldehyde gave the desired product, but only in the open form (dark red, λ_{max} not given). None of these compounds showed any detectable photochromic properties upon nonpulsed irradiation with UV light.[100] Whether the furan compounds which could be considered Fischer’s bases substituted on the methylene group, would condense with a salicylaldehyde to give the 3-substituted BIPS are not known.



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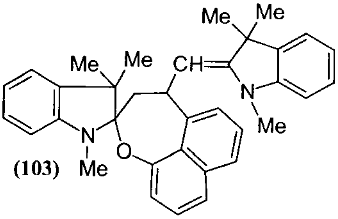

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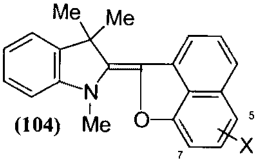
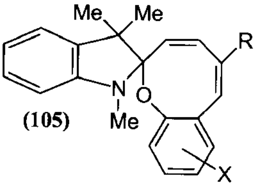


(104)

In attempts to prepare a spiro-2*H*-oxocine (**105**), Fischer's base was allowed to react with 2-hydroxycinnamaldehyde and its α-ethyl-5-nitro, 5-bromo, 3,5-dibromo, 3-bromo-5-nitro, and 3,5-dinitro derivatives. As with the oxepines, the "dicondensed" product (**106**) was formed in the first four cases listed (36–72% yield), and the black, crystalline open form (**107**) of the desired product was formed (69%) with the dinitro derivative. The bromonitro intermediate gave a mixture of the dicondensed product and the open form of the desired monocondensed product. In this series also, none of the compounds exhibited any photochromic properties.[101]



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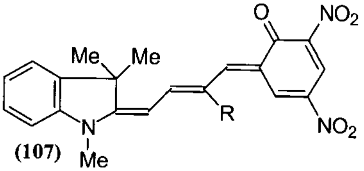

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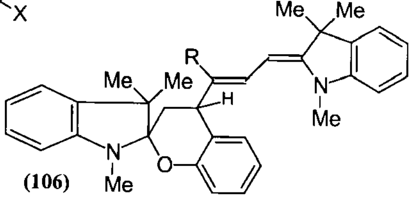
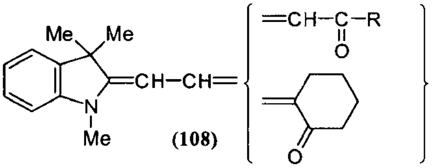


(106)

In an alternative approach to spirooxocines, three vinylogs of Fischer's base were allowed to react with salicylaldehyde and 5-nitrosalicylaldehyde. Salicylaldehyde itself gave only the nonphotochromic dicondensed products (**106**) in 24% yield, whereas the nitroaldehyde gave simply 6-nitroBIPS. Apparently the Fischer's base vinylogs were cleaved to Fischer's base and the alkyl aldehyde (the reverse of their syntheses) by the rather acidic nitrosalicylaldehyde.[102]

Attempts to obtain spiro(pyrans) (not *benzo*pyrans!) by the condensation of Fischer's base with simple 1,3-carbonyl compounds have failed for a long time. For example, dibenzoylmethane and similar enolized β-diketones did not react under the usual condensation conditions,[7] and experiments with malonaldehyde and its derivatives have already been mentioned. With ketoaldehydes such as aroylacetaldehydes, 2-formylcyclohexanone, and 2-formyl-1-tetralone, the products formed in 40–64% yield were the corresponding open-chain dimethinmerocyanines (**108**); no thermal or photobleaching of these materials was observed.[103] This agrees with an earlier calculation[104] that 1,3,3-trimethylindolinospiro-2,2'-pyrans should exist in the open merocyanine form. The Fischers's base cyclic analog, 4a,9-dimethyl-2,3,4,4a-tetrahydrocarbazole, gave with salicylaldehydes 36–73% yields of the corresponding spirobenzopyrans (**109**), which could be colored with a UV pulse but faded extremely rapidly. With all the ketoaldehydes tried, the carbazole derivative gave as the only isolable product the open merocyanine form. Condensation with 4-nitrobenzoylacetaldehyde in toluene, however, gave a photochromic and solvatochromic solution having two absorption peaks and an isosbestic point, indicating the presence of the spiro form (**110**).[103]



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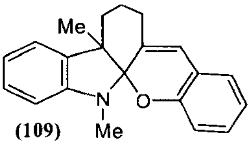

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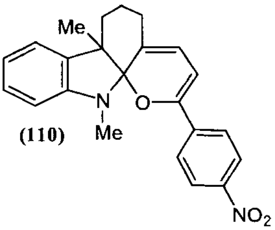
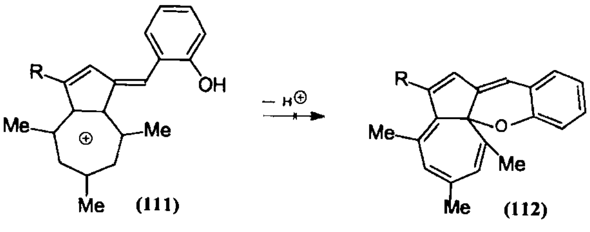


(110)

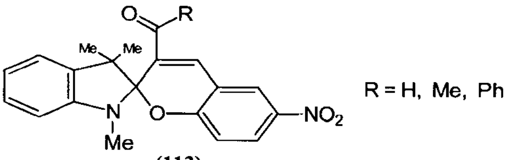
The condensation of 4,6,8-trimethylazulenium and 1-ethyl 4,6,8-trimethylazulenium perchlorates with salicylaldehyde gave the hydroxybenzylidene salts (**111**, R = H,Et) (λ_{max} 504 and 511 nm) in 26 and 48% yields, respectively. However upon deprotonation (Scheme 33), neither the merocyanine nor the Spiro form (**112**) could be isolated.[105]



(111) **(112)**

Scheme 33

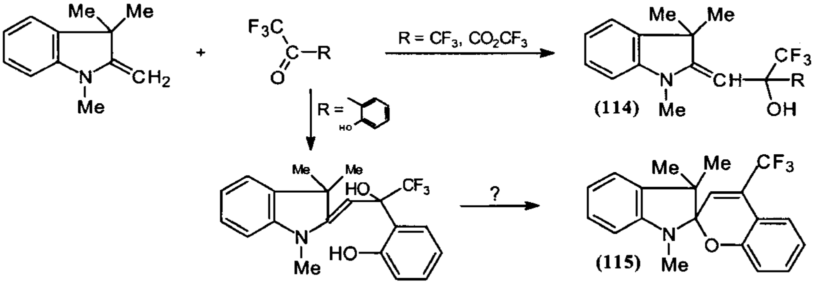
In attempts to prepare 3-acyl-substituted BIPS (**113**), various salicylaldehydes were condensed with 1,3,3-trimethyl-2-formylmethyleneindoline (Fischer's aldehyde). In alcohol, dimethylformamide, tetrahydrofuran, *N*-methylpyrrolidone, and hexamethylphosphoramide as the sole solvents, decarbonylation occurred and the only products were the BIPS compounds. However, in dimethyl sulfoxide, 5-nitro- and 3-bromo-5-nitrosalicylaldehydes gave 11 and 5.6% of the desired 3-formyl-BIPS, respectively. The structures were assigned from their IR and NMR spectra.



(113)

Alternatively, direct electrophilic acylation of a BIPS also occurred in the 3-position. Vilsmeier formylation of 6-nitroBIPS gave 22% of the 3-formyl derivative (**113,** R=H); acetic anhydride with boron trifluoride etherate in chloroform solvent gave 56% of the 3-acetyl compound (**113,** R=Me); and benzoyl chloride with aluminium bromide in carbon disulfide solvent gave 26% of 3-benzoyl-6-nitroBIPS (**113,** R=Ph). None of the 3-acyl BIPS showed any coloration upon UV irradiation in any solvent.[106]

Fischer's base reacts with perfluorocarbonyl compounds to give in 67 and 96% yields the carbinols (**114**) shown in Scheme 34.[107] Use of 2-trifluoroacetylphenol could possibly result in a spiropyran bearing a trifluoromethyl group in position 4 (**115**).



Scheme 34

5-Acetylindole and methyl iodide at 150°C for 15 hr gave the unstable 5-acetylFischer's base, which upon immediate reaction with the appropriate salicylaldehyde was converted to 5'-acetyl-6-nitroBIPS and its derivatives containing bromo, methoxy, and nitro groups in the 8-position. Compared with the corresponding compounds without the acetyl substituent, the positions of the absorption maxima were 2–8 nm longer, the quantum yields of coloration were significantly less (0.24 vs. 0.61 for the 6-nitro-8-methoxy case), and the thermal fading kinetics were not simple first-order, but rather the sum of two first-order processes having rate constants differing by about one order of magnitude.[108]

The nitration of 5-chloromethylsalicylaldehyde in the absence of water gave the 3-nitro derivative in 43% yield, which was very easily converted to the hydroxymethyl and acetoxymethyl compounds. These gave the corresponding photochromic 8-nitro-6-substituted BIPS, which had λ_{max} 590 and 600 nm, respectively. Compared with 8-nitroBIPS itself, the thermal fade rates of the compounds having the additional 6-substituents were slightly faster in toluene and slightly slower in dioxane.[109]

A wide variety of 3-(substituted)methyl-5-nitrosalicylaldehydes were prepared in 50–95% yields from the 3-chloromethyl compound, the isomer of the compound described in the preceding paragraph. The substituents were piperidino, hydroxy, methoxy, ethoxy, 2-methoxy-ethyl, 2-(2-methoxyethoxy)ethyl, mercapto, thiomethyl, thioethyl, thioisopropyl, and thiopropyl. These were condensed with Fischer’s base and its 1-isopropyl and 1-phenyl analogs, and also with 3-methyl-2-methylenebenzothiazoline and its analogs having methyl, phenyl, methoxy, ethoxy, isopropoxy, and propoxy substituents on the methylene group, to give 34 different spiropyrans in yields ranging from 20 to 86%. Their spectral, kinetic, and “colorability” data have been tabulated.[110]

A series of Fischer’s bases having additional rings (2,3-benzothiophene, 2,3-indene; 2,3-inden-1-one, and cyclohexyl) annellated to the 4,5- and 5,6-positions of the indoline (giving angular and linear annellation, respectively) was prepared in very poor yields via the Fischer synthesis and condensed with 5-nitro, 5-nitro-3-bromo-, 5-nitro-3-methoxy-, and 3-nitro-5-methoxy salicylaldehydes. All of the resulting BIPS were photochromic. The annellated rings caused a bathochromic shift of up to 20 nm in both the long- and short-wavelength band of the colored form, compared with the corresponding 5'-phenyl-substituted BIPS. However, the annellation did not change the thermal fading rates significantly.[111]

Because spiropyrans (and especially BIPS) are relatively easy to prepare, a variety of compounds are available from which to deduce correlations (usually semiempirical Hammett-like equations) between structure and photochromic parameters in dilute fluid solutions. The photochromic behavior of a single dye in a variety of solvents can also be correlated with a solvent parameter such as E_T. In applications, however, the dyes are almost always relatively concentrated in a bulk polymer or a polymeric binder film, and various other additives such as antioxidants, surfactants, fire retardants, plasticizers, and other colorants are also present. Under these conditions, the observed photochromic behavior is often very different from that predicted by the dilute fluid solution correlations.

The absorption maxima in toluene and ethanol, the thermal fade rate constants in toluene and dioxane, and the kinetic parameters ΔH and ΔS for a series of 1'-phenyl- and 1'-carbethoxymethyl-6-nitro BIPS having also methoxy, bromo, or nitro substituents in the 8-position have been recorded. The effects of the substituents on the λ_{max} and the rate constants are discussed. The preparation of 1-carbethoxymethylFischer’s base is given in detail.[112]

The thermal fading rates were measured in toluene at 10°C for a series of 6-nitroBIPS having additional substituents (nitro, methoxy, chloro, bromo, carbomethoxy, and carboethoxy) in the 5'- and 8-positions. The rate constants were fitted to an equation of the form log $(k/k_0) = \rho_1\sigma_1 + \rho_2\sigma_2$ with a correlation coefficient $r = 0.85$. This relatively low correlation coefficient, which is not improved by attempts to include the specific steric effects of the 8 substituent or by including the cross-term $\rho_{12}\sigma_1\sigma_2$, implies the complexity of the substituent effects on the fading rate.[113]

In a search for visible-light photoinitiators for stereolithography, the 6,8-diiodo-, 6-nitro-8-iodo-, and 6-nitro-7-methoxy-8-iodo- and 1'-benzyl-6-nitro-7-methoxy-8-iodoBIPS [respective λ_{max} (nm) and first-order half-lives for thermal fading (s): 606, 35; 572, 330; 568, 70; and 578, 15] were converted to their colored forms by heat or UV irradiation in solution in trimethylolpropane triacrylate containing added coinitiators. The benzyl compound with added *N*-phenylglycine was the best initiator when irradiated with a 632-nm laser beam.[114,115]

A series of indolino- and benzothiazolino-spirobenzopyrans was prepared (69-88% yield) and the thermal fade rates in ethanol and toluene solutions determined. The indolino compounds had isopropyl and phenyl substituents on the indoline N atom, hydrogen and methoxy in the 8-position, and a 4-X-phenylazo substituent in the 6-position, where X was hydrogen, methoxy, and nitro. The benzothiazolino compounds all had methyl groups on the benzothiazolino N atom and methoxy in the 8-position, the 4-nitro or methoxyphenylazo substituent in the 6-position, and a methyl or methoxy group in the 3'-position. The presence of the phenylazo substituent shifted the λ_{max} of the spiro compound to the 370–410-nm region. This substituent efficiently absorbed the irradiating light, so that the coloration rate was very slow.[116]

8-Bromo-6-nitro-BIPS having F, Cl, and Br substituents in the 5'-position, and 1'-(4-R-phenyl)-5'-R-8-bromo-6-nitro-BIPS, where R=H, F, Br, and Me, were prepared and their photochemical kinetic behavior in toluene solutions determined. Analysis of the data gave the kinetic parameters of thermal decoloration rate, coloration quantum yields, and decoloration quantum yields. The Hammett-type correlation between structure and thermal decoloration rate agreed with that found earlier by Berman *et al.*[117] A similar correlation for the two quantum yields was very tentative. Qualitatively, the photocoloration quantum yields increased in parallel with the thermal decoloration rates. Notably, the quantum yields for coloration were larger than the quantum yields for decoloration when the indoline nitrogen of the spiropyran carried a methyl group, but the reverse was true when the nitrogen carried a phenyl or substituted phenyl group.[118] In the correlations involving the substituent on the *N*-phenyl group, an apparent reduced influence of the substituent was attributed to the rotation of the phenyl ring out of the plane of the chromophore.[119]

When formed on cellulose [thin-layer-chromatography (TLC) plates], the colored forms of 6-nitro-8-methoxyBIPS and of trimethylindolinospironaphthoxazine are stabilized against thermal or photoerasure by interaction with nickel or zinc salts of hydroxycarboxylic acids or dicarboxylic acids. The zinc salts of 1-hydroxy-and 3-hydroxy-2-naphthoic acids were most effective in retarding the fading. Presumably the amphoteric or zwitterionic nature of the zinc salt permits its complexation with the zwitterionic form of the colored dye, as in the similar case of the color reactants used in carbonless copy paper.[120]

The thermal fade rates of 6-nitroBIPS and its 8-bromo, 8-iodo, and 8-methoxy derivatives were measured in 13 solvents of varying polarity. Plotting the log of the rate constants vs. the E_T values of the solvents gave linear plots, not double-branched ones as found later by this research group. The ring closure involves a zwitterionic transition state. Semiempirical molecular orbital (MO) calculations predict that the most stable merocyanine configuration is the cis-trans-trans-cis form.[121,122]

The thermal fading rates and the absorption maxima of the colored forms of three different 6-substituted 5'-chloro-8-nitroBIPS (6-H, 6-Me, and 6-Br) were determined in 20 different solvents of widely differing polarity. The plot of log k vs. E_T of the solvent was linear (with a negative slope) in the case of the 6-Br compound, but was doubly branched in the other two cases. One branch had a negative slope for high-polarity solvents ($E_T > 40$), whereas the other branch had a zero slope for low-polarity solvents $E_T < 40$). Similarly, a plot of absorption maxima (in wavenumbers) vs. $E_T$of solvent was linear (with a positive slope) in the case of the 6-Br compound, and doubly branched in the other two cases. One branch had a positive slope for high-polarity solvents, whereas the other branch had a zero slope for low-polarity solvents. These observations were attributed to a change in the ground-state structure of the open form from zwitterionic to quinoidal as the solvent polarity changes: this change in structure causes the mechanism of ring closure to change from an ionic process to a concerted electrocyclic process, and the spectral behavior to change from a hypsochromic shift to a negligible shift.[123,124]

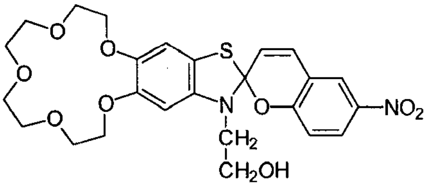
BIPS giving a negligible coloration upon irradiation (“nonactivated”), such as the 6-phenyl and 6-phenylazo derivatives, were treated with HCl to give the salt of the colored form. This was then treated with a tributylamine solution to give the colored form whose thermal ring closure rate back to the spiro form was followed in a stopped-flow apparatus. Measurements using the “activated” 5'-chloro-6-nitro-8-methoxyBIPS gave rate results comparable to those obtained by the usual photokinetic method. As in the earlier studies, the plot of the log of the rate constant vs. the E_T value of the solvents employed gave for the 6-phenylBIPS a linear plot of zero slope, and for the other two compounds, doubly branched plots having a zero slope for low-polarity solvents and a negative slope for polar solvents. This is further evidence for a dual mechanism involving a transition state with zwitterionic character in the more polar solvents and an electrocyclic process with an isopolar transition state in the less polar solvents.[125]

Extending these studies further, the absorption spectra of 6-nitro- and 6-bromoBIPS, and the indolinospiro(naphthopyran), (naphthoxazine) and (phenanthroxazine) were measured in 12 solvents of widely varying polarity, having E_T values ranging from 32.4 (CCl_4) to 55.4 (MeOH), at several temperatures from 10 to 60°C. The effects of solvent polarity indicate that the colored form is quinoid-like if unsubstituted, and zwitterionic if substituted with an electron-withdrawing group. The enthalpy change between closed and open forms decreased as the solvent polarity increased. The long-wavelength absorption band of the colored forms could be resolved into three Lorentzian–Gaussian component bands, and the solvent dependence of the relative contribution of each band was determined.[122]

A series of seven substituted BIPS were treated in toluene and ethyl acetate with phenol and with 4-nitrophenol as proton donors. The changes in absorption spectra indicated the presence of H-bonded complexes with the colored form. The equilibrium constants and thermodynamic parameters for their formation were determined. The complex formation slowed the thermal fade rate significantly.[126]

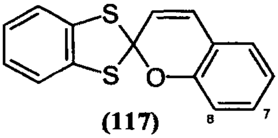
8-(Methacryloyloxymethyl)-6-nitro-3-octadecylspiro(2 *H*-1-benzopyran-2,2'-benzoselenazoline) and analogs having 5'-methyl, 5'-methoxy, and 5',6'-dimethoxy substituents were prepared and found to exhibit negative photochromism in various solvents. The half-lives for recoloration of the photobleached forms were approximately 2–3 min in chloroform and 4–6 min in dimethyl sulfoxide at 25°C. In dimethyl sulfoxide as solvent, the dye without a 5'-substituent could be cycled more than 800 times before the absorbance decreased to 50% of the initial absorbance, but in chloroform this degree of fatiguing occurred after only 40 cycles. In this solvent, the fatigue products that were isolated included several chloro and trichloromethyl adducts.[127]

Several spirobenzothiazolinopyrans (**116**) incorporating a crown-ether portion were prepared in 74–90% yields. These were stable as the open form (λ_{max} 488–579 nm in various solvents), as were the HCl salts in two cases not containing a nitro group (λ_{max} 537–538 nm in methanol, 607–610 nm in *N*,*N*-dimethylformamide). All compounds exhibited reverse photochromism, bleaching to some extent with 2–5 s of exposure to sunlight, and recovering in about 10 min in the dark or upon heating. Photobleaching upon exposure to an “IR lamp” is also claimed, but this is undoubtedly due to the visible light from the (unfiltered) lamp. No experiments were reported on the effects of introducing cations into the crown–ether moiety.[128]



(116)

Twenty-two derivatives of spiro[(2*H*-1-benzopyran)-2,2'-benzo-1',3'-dithiole] (**117**) were prepared (35–80% yield) and studied. Most existed in solution only in the spiro form, and were fast faders so that photochromism was observable only in frozen solutions at 77 K. The colored forms (λ_{max} usually in the 550–600-nm region) were stabilized by 7-diethylamino and 7,8-benzo groups. The benzodithiolane and benzoxathiolane spiropyrans exhibit positive solvatochromism, rather than the negative solvatochromism that is usual for spiropyrans.[129]



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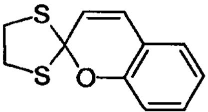


(118)

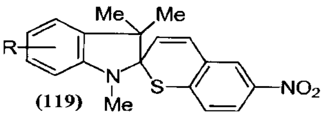
Fourteen derivatives of spiro[(2*H*-1-benzopyran)-2,2'-1',3'-dithiolane] (**118**) were prepared (64–81% yield) and studied. They existed in solution as the spiro form, exhibiting observable photocoloration only at –100°C. The colored forms (λ_{max} usually in the 600–615-nm region) were readily decolorized upon heating or irradiating with visible light. Their spectra underwent hypsochromic shifts upon introduction of a donor (alkoxy) substituent in the 7-position, annellation of a benzene ring to the 5,6- positions, or replacement of the sulfur atoms with oxygen atoms.[130]

All of the protons in each of 12 thermo- and photochromic BIPS were assigned through a combination of homonuclear decoupling experiments and correlation spectroscopy. The relative stereochemistry of the gem-dimethyl groups could be assigned on the basis of Nuclear Overhauser Effect (NOE) experiments.[131]

A pairwise condensation of Fischer's base and 5-nitroFischer's base with salicylaldehyde, 5-nitrosalicylaldehyde, 2-hydroxy-1-naphthaldehyde, and 6-nitro-2-hydroxy-1-naphthaldehyde gives six spiro compounds containing at least one nitro group. These were reduced electrochemically in acetonitrile or chemically with potassium *tert*-butoxide in dimethyl sulfoxide or with tetrabutylammonium borohydride in tetrahydrofuran (THF). The electron paramagnetic resonance (EPR) spectral parameters showed that in all the radical anions the unpaired electron is localized in the moiety bearing the nitro group, indicating no significant conjugation between the two halves of the molecule. The two compounds bearing a nitro group in each half of the molecule gave striking results: under mild reduction conditions, the electron was localized in the nitrochromene half; under vigorous conditions, the electron appeared to be localized on the nitroindoline half.[132]

1.3.2. Spiropyrans with Long-wavelength Absorption

Spiropyrans whose open forms absorb strongly in the infrared and whose closed forms absorb only weakly in the visible are of interest for several applications. In one approach to such dyes, the pyran oxygen atom is replaced by a sulfur atom to give spiro(2*H*-1-benzothiopyran-2,2'-indoline) compounds.[133,134] Few of these are known because of the general difficulty of preparing the 2-mercaptobenzaldehyde intermediate. However, its 5-nitro derivative is easily available (64% yield) via the displacement of chlorine from 2-chloro-5-nitrobenzaldehyde by Na_2S[135] or Na_2S_2, and has been condensed with several different Fischer's bases,[134,136] leading to novel spirothiopyrans (**119**) that absorb above 800 nm.[137] The corresponding selenopyrans have not been reported. However, selenochromenes (2*H*-1-benzoselenopyrans) (**120**) are known and are photochromic compounds absorbing beyond 900 nm, but are very unstable.[138]



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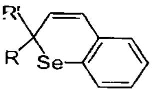
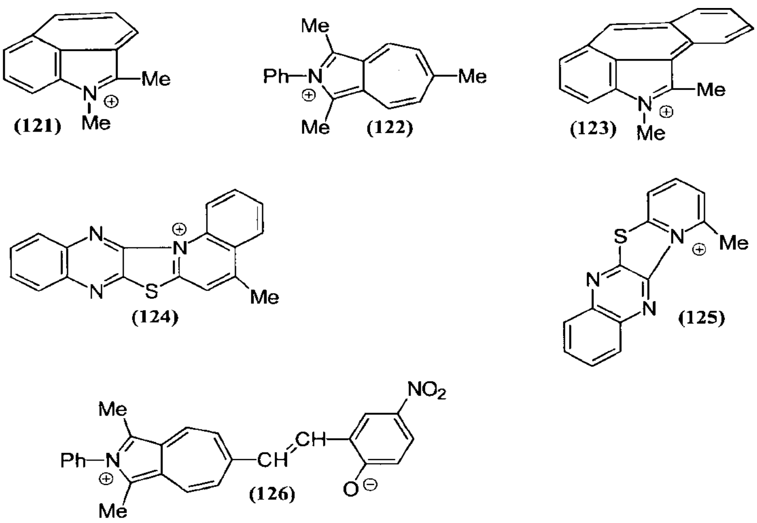


(120)

Another approach to obtaining spiropyrans whose colored forms absorb in the infrared is to use a heterocyclic base, such as those displayed in Figure 1.4, based upon benz[*cd*]indole (**121**), 2-azaazulene (**122**),[139–141] pyrroloanthrone (**123**),[142] and other ring systems (**124, 125**)[143].

Thus, the condensation of 2-phenyl-1,3,6-trimethyl-2-azaazulenium perchlorate with 5-nitrosalicylaldehyde gave the cationic styryl dye (λ_{max} 510 nm) in 56% yield.[139] This dye is the salt of the open form of the corresponding spiropyran, and upon treatment with base, a reaction which was not originally reported, was found to give the expected dye (**126**), which absorbs at 733 and 536 nm. This material did not thermally fade or photobleach to any significant extent with visible light in either polar or nonpolar solvents.[7]

In a third approach to obtaining absorption at longer wavelengths, the chromophore can be extended, as evidenced by the bathochromic shift of 43 nm in going from 6-nitro- to 6-(2-nitrovinyl)BIPS.[144] Accordingly, styryl and substituted styryl groups were placed in the 6-position of BIPS. The 5-chloromethyl derivatives of salicylaldehyde and 3-nitrosalicylaldehyde were prepared and converted to their triphenylphosphonium salts. The former salt underwent the usual Wittig reaction

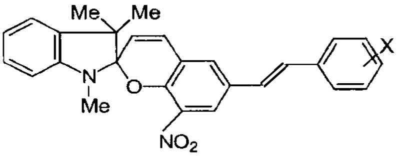


(121) **(122)** **(123)** **(124)** **(125)** **(126)**

Figure 1.4. Heterocyclic quaternary salts that should give dyes absorbing in the infrared.

with benzaldehyde and 4-nitrobenzaldehyde to give 5-styryl- and 5-(4-nitrostyryl)-salicylaldehydes in 55 and 28% yields, respectively.

The latter salt gave 5-methyl-3-nitrosalicylaldehyde in 44% yield under the usual conditions, presumably because of hydrolysis of the poorly reactive phosphorane; with moisture excluded and dry toluene as solvent, the desired 3-nitro-5-styrylsalicylaldehyde was obtained in 10% yield. The 5-styrylsalicylaldehyde was also prepared in 44% yield by the alternative route from 5-formylsalicylaldehyde and triphenylbenzylphosphonium chloride. Nitration of 5-formylsalicylaldehyde gave its 3-nitro derivative in 47% yield. These variously substituted salicylaldehydes were condensed with Fischer's base and its 3-phenyl analog to give in 20-34% yields a series of styryl-substituted BIPS, e.g., (**127**). The BIPS having a 6-formyl group also underwent the Wittig reaction, giving a further alternative route to the styryl-substituted compounds. All the styryl compounds had the trans configuration, according to IR, UV, and NMR spectra. The 8-nitro-6-formylBIPS was negatively photochromic: its intensely colored solution in ethanol, λ_{max} 530 nm, bleached with visible light irradiation. The 6-styrylBIPS did not color under UV irradiation. With the exception of 6-(4-nitrostyryl)BIPS, all the other spiropyrans were photochromic. One might have expected the nitrostyrylBIPS to color, considering it merely as a vinylog of 6-nitroBIPS. The BIPS having a phosphonium salt substituent were soluble in water to give intensely colored (λ_{max} 525 nm) solutions. The response of these solutions to irradiation with UV or visible light was not reported; one would expect some photobleaching with visible light. The introduction of the styryl substituent in the BIPS gave rise to a bathochromic shift of about 80 nm in the long-wavelength band of the colored form; the formyl group, as expected for an electron acceptor, gave rise to a hypsochromic shift.[145]



(127)

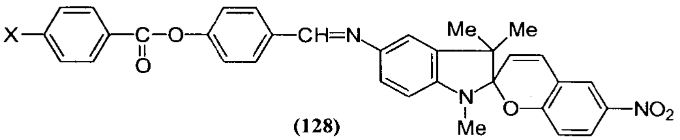
In an attempt to obtain spiropyran colored forms absorbing at relatively long wavelengths but not having a nitro group, 6-methyl-8-formylBIPS (λ_{max} 590 nm) was prepared (56% yield) and condensed with benzylamine and anisidine to give the corresponding azomethines (36 and 61% yields, respectively); neither of these were photochromic in 2-propanol at –70°C. The formylBIPS was also condensed with acetone and acetophenone to give the corresponding 8-acetylvinyl- and benzoylvinylBIPS compounds in 62 and 76% yields, respectively. These were photochromic, having a λ_{max} at 628 and 615 nm, respectively.[146]

A recent review discusses the synthesis, spectral properties, and photochemical behavior of novel spirobenzopyrans, Spiro-1,4-oxazines, and 2*H*-chromenes. It emphasizes the structural features needed for infrared-absorbing photoisomers, luminescent stable forms, improved fatigue resistance, and spiropyrans exhibiting photochromism in vacuum-deposited films.[147]

1.3.3. Spiropyrans as Vapor-Deposited and Amorphous Films

Vacuum-deposited films of 6-nitroBIPS having in the 1'-position *n*-alkyl chains of 1, 7, 12, and 18 carbon atoms are amorphous and colorless, but crystallize upon standing. The films color with UV exposure, and the colored film bleaches upon exposure to visible light.[148]

6-NitroBIPS having in the 5'-position (4'-X-benzoyloxy)-benzylidenamino substituents (**128**), where X is cyano, methoxy, and *n*-hexoxy, form amorphous films exhibiting birefringence when colored. The bulk materials exhibit quasi-liquid crystalline properties, intermediate between supercooled liquids and mesophases, which are attributed to the interactions between small ordered domains of the spiropyran molecules.[149]



(128)

Vacuum-deposited films of 6-hydroxyBIPS are glassy and colorless. Ultraviolet irradiation gives a deep blue color which, upon irradiation with visible (>500 nm) light or heating changes to a pale blue color. The original colorless state is never attained. A study of infrared spectra suggests that two cisoid open forms, H-bonded together, are responsible for the deep blue color, whereas the light blue color can be attributed to one cisoid open form H-bonded to one closed spiro form. No cis–trans isomerization is involved, as in the case of 6-nitroBIPS.[150]

Ordinary vacuum deposition of 6-nitroBIPS gives a film lacking mechanical strength and having mixed amorphous and crystalline phases, which rapidly crystallizes further and is then not significantly photochromic. If the vapor is irradiated with intense UV light during the deposition, the resulting film is completely amorphous, highly colored (its infrared spectrum shows that it is completely the colored form, without any decomposition products), and thermally stable for over 3 months at room temperature; heating decolorizes the film. The usual incompletely colored film is obtained if the heated dye source or the receiving substrate but not the vapor path is irradiated. This result strongly suggests that the spiropyran is undergoing ring opening in the gas phase. This light-assisted deposition is a useful method for preparing stable photosensitive films.[151]

In another alternative to the simple evaporation of 6-nitroBIPS, a plasma polymerization process was used to prepare a highly adherent, smooth, transparent film having good photochromic properties. However, after 1 week of storage, the film lost its photochromic properties, probably through crystallization.[152]

The photocoloration and photobleaching behaviors of vacuum-deposited and spin-coated poly(methyl methacrylate) films of 6-hydroxyBIPS, and of the 6-nitroBIPS having 1, 7, 12, and 18-carbon alkyl chains on the indoline N atom, were studied at 50K. The 6-hydroxy BIPS was photobleached both in deposited and cast films. The 6-nitro compounds could not be photobleached in the deposited films below their glass transition temperature, which decreased from +37°C for the 1'-methyl compound to –48°C for the 1'-octadecyl compound. The nitro compounds also could not be decolored in concentrated (30 and 50 wt.%) acrylic films, but did bleach in dilute (5 and 10 wt.%) films. These differences were attributed to interactions between the open, colored transoid forms in the nitro cases when concentrated. There was no interaction between the open forms in the hydroxy case because they are cisoid, and no interaction in the nitro cases when diluted because they are not in close proximity.[153]

Three spiropyrans, each molecule having a long alkyl chain located in a different relative position (1'-hexadecyl, 3-decyl, and 8-dodecanoyloxymethyl), were spread as monolayers on water under irradiation and the changes of surface area and surface pressure with time were measured both when the lamp was turned on and after it was turned off. The results were especially striking observations of a reversible and an irreversible photoconversion of a surface-inactive system into a surface-active one.[154]

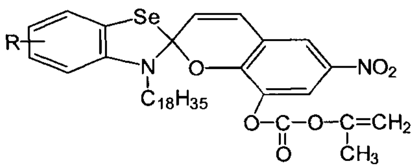
Amorphous films of 13 spironaphthoxazines having various substituents in the 1'- and 5'-positions were prepared by melting and undercooling these compounds. The spectra and thermal fading kinetics of the colored forms and the glass transition temperature (T_g) of the films were determined. The photochromic behavior was very similar to that in polymers. Above T_g, the fading kinetics were first-order (half-lives of 2–9 s); below T_g, the kinetics were complex: there was an initial fast decay, a subsequent slower decay, followed by a still slower decay. These complex kinetics can be attributed to a random distribution of free volume in the glassy state. The preparation of the substituted Fischer's bases is outlined, but no yields are given.[155]

Polyelectrolyte glasses can be cast as optically clear films from a solution of poly(dimethylalkylamines) and BIPS-6-sulfonate as the counterion. The films and solutions of the polymer exhibit negative photochromism, the colored form (λ_{max} = 408–430 nm) bleaching significantly by irradiation or heating.[156]

1.3.4. Polymeric Spiropyrans

6-Nitro-8-methacryloxymethyl-3'-octadecylspiro(2*H*-1-benzopyran-2,2'-benzoselenazole) (**129**) and its 5'-methyl, 5'-methoxy and 5'-6'-dimethoxy analogs, which exhibit negative photochromism, were copolymerized with methyl methacrylate to give colored polymers whose solutions in chloroform or spin-coated films (λ_{max} 579 and 569 nm, respectively, for the compound without substituents in the 5'- and 6'-positions) rapidly bleached to about 15% of their original absorbance upon exposure to visible light. The solution recolored in the dark at room temperature within a few minutes, but the solid film recolored only upon heating. The activation energy for the thermal recoloration was 17 kcal-mol^{-1} for the copolymer, and 14 kcal-mol^{-1} for a film cast from a solution of the monomeric dye in poly(methyl methacrylate) (PMMA).[157]

Cyclic siloxanes bearing cholesterol and biphenyl groups as mesogens and 6-nitroBIPS as a photochromic group (Figure 1.5) were prepared by first esterifying 4-



(129)

(allyloxy)- and 4-(pentenyloxy)benzoic acid with cholesterol, 4-hydroxybiphenyl, and 1'-(2-hydroxyethyl)-6-nitroBIPS using *N*, *N*'-dicyclohexylcarbodiimide and 4-dimethylaminopyridine, and attaching the resulting esters to pentamethylhydrocyclopentasiloxane via hydrosilylation with a dicyclopentadienylplatinum(II) chloride catalyst.[158]

Poly(L-glutamic acid) bearing 6-nitroBIPS side chains exhibited reverse photochromism in hexafluoro-2-propanol containing added trifluoroacetic acid. About half of the original absorption at 415 nm was restored during about 6 hr. There was no change in the random coil conformation of the polymer when the acid was present. Upon the addition of methanol as cosolvent, the coils change to α-helices upon irradiation, the extent depending upon the solvent composition.[159]

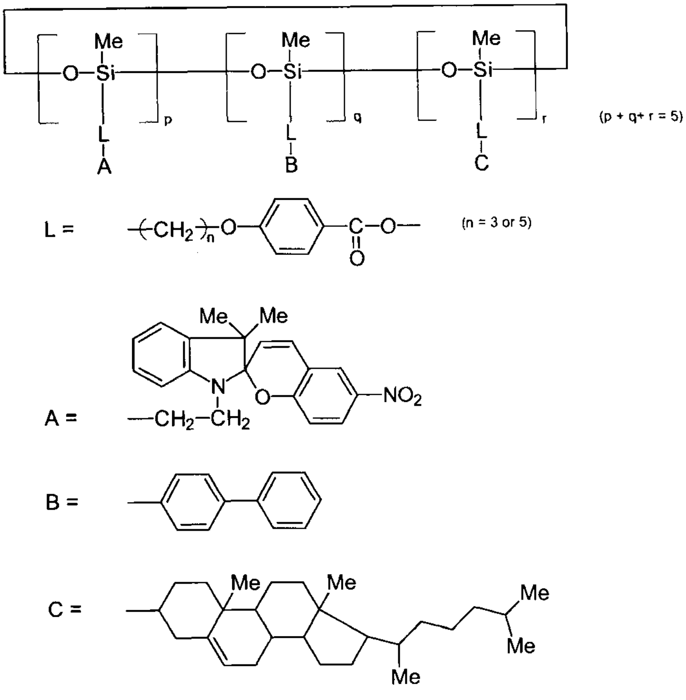


Figure 1.5. A cyclic siloxane framework having a spiropyran and two different liquid crystalline groups attached to it.

In order to obtain three-dimensional networks of photochromic polymers, BIPS containing two polymerizable groups were prepared. A reaction between methacryloyl chloride and 5-amino-2,3,3-trimethylindolenine and subsequent methylation gave 5-methacrylamidoFischer's base hydroiodide; a reaction of the chloride with 1-(2-hydroxyethyl)Fischer's base gave its methacrylate ester. A reaction between 3-chloromethyl-5-nitrosalicylaldehyde and silver methacrylate gave the corresponding 3-methacrylate ester, which was condensed with the two Fischer's bases to give BIPS having 6-nitro and 8-methacryloyloxymethyl groups, and in addition a 5'-methacryloylamido- or a 1'-(2-acryloyloxyethyl) group.[160]

Conjugated poly(thiophene) chains and spiropyrans together in a poly(methyl methacrylate) film demonstrated that the coloration of the dye could be sensitized by the excited state of the poly(thiophene). Accordingly, in attempts to achieve an intramolecular transfer between an excited conjugated chain and a spiropyran group pendant on such a chain, indolinospiropyrans (and spironaphthoxazines) having a 3-(3-thienyl)propyl group on the indoline nitrogen atom were prepared. However, all attempts to polymerize the thiophene to a conjugated chain failed.[20]

1.3.5. Spiropyran Aggregates

In cyclohexane and heptane, the colored form of 6-nitroBIPS undergoes aggregation, giving absorption near 700 nm. An observed anomalous (nonexponential) thermal decoloration can be attributed to the deaggregation to the dimer (λ_{max} 620 nm) and monomer (λ_{max} 580 nm),[161]

The resonance Raman spectrum of the colored aggregate of 6-nitroBIPS was compared with those of 8-nitroBIPS (which showed little aggregation) and the unsubstituted BIPS (which exhibited no aggregation). The spectrum showed the presence of several different transoid conformers, stabilized by coordination of a negatively charged oxygen atom of the nitro group in its acinitro form to the positively charged nitrogen atom of the indoleninium moiety.[162]

The time-resolved resonance Raman spectrum of the colored species produced during a 30-ns laser pulse indicated that a short-lived intermediate, almost certainly the cis form, is a precursor to the stable trans form of the merocyanine.[163]

The 6-nitro BIPS having a long alkyl chain in the 1'-position and a $-CH_2OCOR$ substituent in the 8-position, where R is also a long alkyl chain, form J-aggregates having sharp absorption peaks in Langmuir–Blodgett membranes. Layering a series of these having slightly different λ_{max} permits selective excitation of a particular layer and thus multiplex recording. Avoiding energy transfer between the layers is a major difficulty.[164,165]

Molecular modeling was used to compute the structure of the aggregates and the nature of their interactions with a water surface; they were formed from 1'-octadecyl-6-nitroBIPS and its derivative having a docosoyloxymethyl group in the 8-position. The results were in agreement with experiment; J-aggregates are more stable than H-aggregates by 1.35 kcal-mol^{-1} for the first BIPS and 6 kcal-mol^{-1} for the second. A water surface stabilizes the J-aggregates even more, and thus only these are obtained during the formation of Langmuir–Blodgett films of these spiropyrans.[166]

1.3.6. Mechanistic Studies: Photocoloration, Photodecoloration, Fatigue, and Photodegradation

The various techniques of Raman spectroscopy have recently been applied to the spiropyrans, and this is discussed more extensively in Chapter 8 in Volume 2. BIPS and its 6-nitro-, 6-nitro-8-methoxy-, and 6-nitro-5,7-methoxy derivatives were studied by surface-enhanced (SERS) and resonance-enhanced Raman spectroscopy in neutral, acidic, and basic solutions. The complex results are too numerous to summarize here, but two unusual ones are that even in acid solutions the tested compounds gave the SERS spectra of the unprotonated open forms, and that an aged solid sample of 6-nitroBIPS gave results very different from a fresh sample. This was attributed to the existence of two enantiomers of the spiro form, which are slowly interconvertible in the solid state and which have greatly different photocoloration quantum yields.[167]

A similar SERS study was carried out on indolinospironaphthopyran, its aza analog spironaphthoxazine, and the model compounds, 1,2,3,3-tetramethylindoline and 3,3-dimethylnaphthopyran. The orientation of the adsorbed spiro compounds and their indoline and chromene portions on the silver surface was determined. A goal of the work was to develop methods for using the high sensitivity and selectivity of SERS to study the photochromics and their fatigue products in polymer matrices.[168]

Nanosecond time-resolved resonance Raman and absorption spectra of 6-nitroBIPS in deoxygenated cyclohexane were obtained in the 20–100-ns time region, extending an earlier study[169] in the 200–2000-ns time region. A sequence of three transients was observed: (1) the lowest triplet state T_1, λ 435 nm, of the spiro form; (2) the open merocyanine form, λ 580 nm, formed from the triplet (1); and (3) a dimer of the merocyanine, λ 540 nm.[170]

In a laser flash photolysis study of 1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*]pyran and its 5-nitro, 8'-nitro, and 5,8'-dinitro derivatives in toluene solutions, the coloration of the unsubstituted compound proceeded only through a singlet pathway, with a quantum yield of coloration of about 0.2, whereas the coloration of the 8'-nitro compound proceeded essentially only through a triplet pathway, with a relative quantum yield of about 0.9. The coloration of the two compounds having a 5-nitro substituent went through both pathways, with quantum yields of about 0.5. Thus the triplet pathway induced by the nitro group is much more efficient than the singlet pathway for opening the naphthopyran ring.[171]

The implication of singlet oxygen in the early photodegradation studies of spiropyrans led to a reinvestigation carried out in the presence of the efficient singlet-oxygen quencher 1,4-diazabicyclo[2,2,2]-octane (DABCO). The unsubstituted trimethylspiroindolinonaphthopyran, the unsubstituted trimethylspiroindolinonaphthoxazine, and 6-nitro-8-methoxyBIPS were irradiated continuously in toluene, and the degradation products identified by gas chromatography. The presence of

DABCO increased three- to ninefold the relative amount of 3,3-dimethyloxindole, which is proposed to arise from the reaction between the open form and triplet oxygen. The quencher also considerably increased the "fatigue resistance time," the time in minutes necessary to reduce the value of the initial absorbance by half. For the BIPS compound, the increase varied up to nearly tenfold, depending upon the DABCO concentration.[172]

Among the photodegradation products of 1-alkyl-3,3-dimethylindolinospironaphthoxazines in toluene solution in air are the 1-alkyl-3,3-dimenthyloxindole and 3,3-dimethyloxindole; the latter compound is not formed simply by subsequent photodealkylation of the former. Also, the 1-phenyl compound does not give any 3,3-dimethyloxindole, but does give 1-phenyl-3,3-dimethyloxindole. These observations indicate that the homolytically cleaved C–O bond of the spiro form, previously identified by trapping with nitroxide, reacts with oxygen to give a peroxy radical, which can abstract a hydrogen atom from an alkyl substituent on the indoline N atom. This mechanism also accounts for the appearance of naphth[1,2]*d*]oxazole among the isolated fatigue products.[173]

A similar study of the photooxidation of some spiropyrans and spironaphthoxazines indicates that the spiro and open forms of these dyes are singlet oxygen quenchers and that the colored form does not act as a sensitizer. A mechanism is proposed that involves the formation of a superoxide radical anion by photoinduced electron transfer to oxygen from a merocyanine form of the dye, followed by nucleophilic attack of the radical anion on the radical cation of the dye.[174]

In a study of the thermal fading rate of 27 different spirophotochromics, which included naphthoindolinospiropyran, its 5- and 8'-nitro, and 5,8'-dinitro derivatives, there was a good correlation between the initial fading half-life $t_{1/2}$ and the change in the fading half-life $\Delta t_{1/2}$ during irradiation. Curiously, however, the value of $\Delta t_{1/2}$ (%) went from negative to positive as $\Delta t_{1/2}$ increased. The faster the initial fading rate, the more the fading rate tended to increase during irradiation; the slower the initial fading rate, the more it tended to decrease during irradiation. This modification of the rate was not due to any of the identified photoproducts of the spiropyran, but may be related to the photodegradation of the toluene solvent. Irradiating the pure solvent first and then adding it to a fresh solution of the dyes also caused changes in rates.[175]

The usual kinetic equations for the calculation of quantum yields and thermal fade rate constants have been extended by taking into account the information contained in the experimentally recorded absorbance vs. time curves recorded under continuous irradiation and by adding additional kinetic terms representing photodegradation or other mechanistic complications. The extraction of the rate constants and quantum yields from the experimental curve requires numerical integration and iterative calculations.[176]

1.3.7. Reactions of Spiropyrans with Inorganic Reagents

6-Nitro-8-methoxyBIPS in acetone solution in the dark forms a chelate with copper(II) chloride ($\lambda = 400$ nm). In tetrahydrofuran, the copper salt has poor solubility, but the chelate (λ 500 nm) is formed from the colored form (λ 600 nm) if the solution is irradiated. The thermal decoloration rates of the chelated and unchelated colored forms in tetrahydrofuran are nearly the same. The rate and equilibrium constants are given. No X-ray structural data are given, but the ESR spectrum of the chelate in acetone indicates a square or square pyramidal structure, rather than a trigonal bipyramidal one.[177]

The merocyanine form of numerous BIPS compounds in solution complex with many transition and rare-earth metal ions. The complexation between 6-nitro-8-methoxyBIPS and several ions was studied by spectrophotometric, luminescent, stopped-flow, and nanosecond laser flash photolysis techniques. The absorption maximum of the dye, 580 nm, is shifted to the 480–500 nm region, and the relatively weak fluorescence shows a similar hypsochromic shift. The kinetics of the complexation involved a fast reaction between the components, followed by a slow equilibrium of the complex to its most stable isomer. The photoreactions of the complexes include formation of a short-lived triplet state (lifetime about 2×10^{-5} s, λ = 430 nm) and slow reversible photobleaching.[178]

The 6-nitroBIPS having a 4-butylsulfonic acid salt group in the 1'-position, when intercalated into the interlayers of an Li-Al-layered double hydroxide, showed reversible photochromism in both the presence and absence of cointercalated 4-toluenesulfonic acid. When the acid was present, the absorption peak (λ, ca. 520 nm) was sharpened and split into two peaks, and the fluorescence intensity was increased.[179]

Two methods of bonding a spiropyran to the surface of silica gel have already been mentioned: the reaction of silica-bound salicylaldehyde with Fischer’s base, and the reaction of 6-lithioBIPS with silica. Silica-bonded spiropyrans exhibited properties (reverse photochromism, visible light photobleaching, and color changes upon acid treatment due to salt formation) very similar to those of spiropyrans merely adsorbed onto silica. The differences in behavior were attributed to the different extent of absorption and desorption of atmospheric water caused by the difference in the number of free SiOH groups available in the two cases.[86]

Upon treatment with acid (or on contact with an acidic surface), many spiropyrans give the salt of the open form or the open form itself, depending upon the relative base strengths of the spiro and open forms. Thus, treatment of several BIPS (7-diethylamino, 6-nitro, and 5'-nitro) with trifluoroacetic acid in the nonprotic solvents acetonitrile and chloroform gave the protonated merocyanine form, which upon neutralization with base gave the open colored form.[180] This sequence of operations causes coloration by a non–thermal, non–photochemical route; the adsorption coloration was utilized in the early applications of spiropyrans in carbonless (pressure-sensitive) copy papers. In this application, dialkylamino-substituted spirodi(benzopyrans) were preferred; paper containing BIPS compounds turned pink on storage.

1.3.8. Spiropyrans in Sol–Gel Matrices

Three different 6-nitroBIPS having as additional substituents 1'-phenyl, 1'-phenyl-8-methoxy, and 5'-chloro-8-methoxy, exhibited complex photochromic and kinetic behaviors in aluminosilicate sol–gels. Fresh gels prepared by the hydrolysis of [(diisobutoxy)aluminoxy]triethoxysilane were transparent and highly photochromic. As the gels aged, dried, and shrank, they first became colored but remained transparent; then they became more deeply colored and translucent; and finally they became transparent again and were permanently colored a deep maroon. They then were neither photochromic nor photobleachable. These changes were followed by absorption and emission spectroscopy, and several possible explanations were proposed for this behavior.[181]

When various BIPS compounds were trapped in a polymerizing silicon tetramethoxide system, their photochromic behavior varied during the course of the reaction, proceeding from "ordinary" photochromism (stable colorless form coloring with UV light) to "reverse" photochromism (stable colored form bleaching with visible light). The point at which this reversal takes place is dependent upon the substituents in the BIPS. This reversal in behavior was attributed to a shift in equilibrium between dissolved and adsorbed photochromic molecules within the silica cage.[182]

1.3.9. Quantum Mechanical Calculations

Quantum mechanical calculations on the $2H$-pyran ring opening and closing agree with the different mechanisms for photocoloration and photodecoloration experimentally observed in spiropyrans. The photobleaching proceeds from the T_1 state, and mechanistically is very different from thermal bleaching, which proceeds from the S_0 state and has a much lower activation of energy barrier.[183]

In a recent calculation of the properties of spiropyrans and spironaphthoxazines, MOPAC/AM1 calculations with full geometry optimization gave heats of formation and dipole moments for the ground, first excited singlet and first excited triplet states of the spiro and the four most stable isomers of the merocyanine form. The results indicated a quinoidal structure for the colored form. The absorption spectra were calculated using complete neglect of differential overlap (CNDO)S method), and were in good agreement with the experimental data for the spiro forms and the UV portion of the spectra of the colored forms.[184] The same calculations on the same structures, as well as 11 additional spirooxazine open forms, were independently performed using AM1 and GenMol programs for the structures and five different methods for absorption spectra. Here also, the calculated spectra of the spiro forms correlated well with experiment, but those of the open forms were significantly different in the visible region.[185]

For the trimethylspironaphthoxazine, *ab initio* molecular orbital (MO) calculations indicated that the most stable colored form is the trans-trans-cis- form – about 7 kcal-mol^{-1} endothermic relative to the spiro form. Measurement of the proton NMR nuclear Overhauser effect experimentally confirmed this calculated result. The structural calculations indicate that the colored form is essentially quinoidal, rather that zwitterionic.[186]

The electronic spectra of spiropyrans of many kinds and those of the related $2H$-chromenes have been reviewed.[187] The relative energy levels of the ground and excited states, their multiplicities and nature, electron density distributions, and bond orders have been calculated by various quantum-mechanical methods [Self-consistent field Pariser-Parr-Pople (SCF PPP) and CNDO/S]. The relationship between the molecular structure of the dyes and their photochemical and thermal behavior is important for developing applications.

1.3.10. Optically Active Spiropyrans

Little has been reported about the preparation and photochromic behavior of optically active spiropyrans, despite an old suggestion[188] to examine photocoloration with circularly polarized light.

Mannschreck *et al.*[189–193] have studied the preparation, separation, and thermal and photo racemization of the chiral chromenes and spiropyrans shown in Figure 1.6.

The enantiomers were separated by high-performance liquid chromatography (HPLC) on triacetyl- and tribenzoylcellulose, using a polarimetric detector.[190] The rates of thermal isomerization, which must involve a ring opening and reclosing, were determined by polarimetry, and the activation energies for the thermal ring opening were calculated and compared with the activation energies for the thermal ring closing after photocoloration. The results and mechanistic implications of this and earlier[191,192] work have been briefly reviewed[193] and are treated in detail by Mannschreck in Volume 2, Chapter 6.

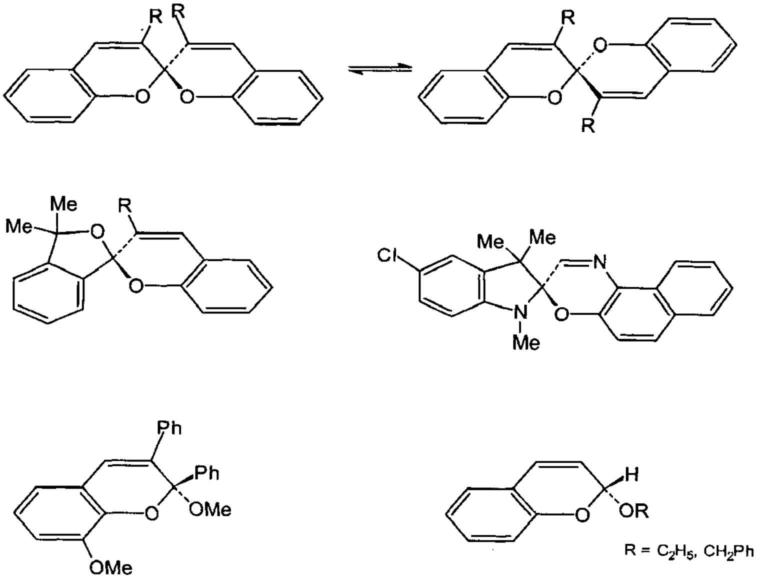


Figure 1.6. Some chiral spiropyrans and chromenes that have been resolved.

1,3-Dimethyl-3-ethyl-2-methyleneindoline, prepared by Plancher rearrangement of 1,3,3-trimethyl-2-ethylideneindoline, was resolved by a tedious fractional crystallization of its 1:1 salt with (–)-O,O'-dibenzoyl-L-tartaric acid monohydrate. D-(+)-10-camphorsulfonic acid failed to resolve this base. The circular dichroism spectrum of the (*S*)-(–)-enantiomer, as the tetrafluoroborate salt, shows a weak, negative Cotton effect near its longest wavelength absorption band at 278 nm, and a second weak negative Cotton effect near 220 nm. The chiral Fischer’s base was converted to optically active trimethinecyanine dyestuffs, but not to spiropyrans.[194]

Chiral 2,4-dimethyl-3-(1-phenylethyl)thiazolium perchlorates were prepared from the available chiral 1-phenylethylamines and used to prepare optically active monomethinecyanines, but not spiropyrans.[195]

3'-Phenyl-6-nitroBIPS was easily resolved (at the 3'-carbon atom, not the 2'-spiro position) by reaction in ethanol with either (+) or (–) 10-camphorsulfonic acid. The first fraction to crystallize in each case was the salt of the open form. Both salts had a mp of 237°C and their solutions, after standing to thermally equilibrate at the 2'-carbon atom, showed equal but opposite rotations, $[\alpha]_D^{25} = -201°$ for the salt from the (+) sulfonic acid and +201° for the salt from the (–) acid. After treatment of these salts with aqueous sodium acetate and benzene, the respective spiropyrans, having melting points of 201–202°C and specific rotations of –11° and +11° for thermally equilibrated solutions, were recovered from the benzene extract. Similar attempts to resolve several other 3'-phenylBIPS with the camphorsulfonic or 3-bromocamphor-8-sulfonic acids were only partly successful.[7]

The resolution of 3-phenylFischer’s base itself would make available the chiral base for the preparation of not only indolinospiropyrans, but also for cyanine, merocyanine, and styryl dyes. Several attempts to effect this resolution using the camphorsulfonic, bromocamphorsulfonic, and dibenzoyltartaric acids in lower alcohols, 1,2,-dimethoxyethane and tetrahydrofuran, were unsuccessful in giving a clean resolution.[7] Perseverance and luck are of prime importance.

1.4. APPLICATIONS AND FUTURE TRENDS

Practical applications of photochromism at first (*ca.* 1955–70) concentrated on the spiropyrans, and especially on BIPS compounds, because of their ready availability, photosensitivity, convenient thermal fade rates, and good color contrast when perceived by the human eye. However, applications in which the dye was required to cycle very many times (e.g., an optical binary switch for a photochemical computer memory) or be irradiated continuously (e.g., sunglasses, vehicle windshields) were impractical because of the rapid fatigue of these dyes.[196]

Photochromic plastic ophthalmic sunglasses are the largest volume and value application for photochromics, but the indolinospiropyrans originally used generally underwent photodegradation (“fatigued”) rapidly in sunlight, a serious deficiency for this application. The emphasis then shifted to the spironaphthoxazines (see Chapter 2), which generally were more resistant to fatigue.[197] More recently, the 2,2-

disubstituted pyrans (which are not spiro compounds, see Chapter 3) are in turn displacing the spirooxazines for use in sunglasses. These pyrans are replacing the spiropyrans in several applications because of their (generally) greater resistance to fatigue and photodegradation.

At present, spiropyrans are commercially used in moderate quantities as exposure indicators in photolithographic plates, in small quantities for microimage recording, and in a most interesting application, fluid-flow visualization.[198–207a] For these uses, fatigue is not an important limitation. In addition, relatively small amounts are used in printing inks for T-shirts and in toys and novelties having a limited lifetime.

One recent trend has been away from using a photochromic dye itself merely as an individual component of a solution, polymer film or bulk polymer matrix. Instead, the photochromic is chemically linked to a polymer, which may be a natural polymer such as a cellulose derivative, an enzyme, a protein, or synthetic polymers from acrylates, urethanes, and vinyl compounds. The properties of the polymer can then be modified by external irradiation, and conversely, the properties of the photochromic are modified by the polymer. A recent biochemical example is the photocontrolled binding of monosaccharides to concanavalin A (Con A) modified with spiropyran units.[208]

To a polymer chemist or biochemist, a spiropyran-linked polymer is a polymer having photosensitive side chains; but to a dyestuff chemist, it is a spiropyran with a substituent that happens to be a polymer. The polymer modifies the properties of the spiropyran, and the behavior of the spiropyran gives information about the polymer. That the thermal fade rate of a spiropyran open form is much lower when it is bound to a polymer than when it is unbound is well–known. As a recent example, the colored form of monomeric 1'-octadecyl-6-nitro-8-(methacryloxymethyl)-spiroindolinobenzothiapyran in acetone solution at 25°C had a half-life of 0.86 min; when cast in a PMMA film ($\lambda_{max} = 680$ nm), it bleached “slowly,” but when copolymerized with MMA ($\lambda_{max} = 655$ nm), it was stable for more than 200 days after a slight initial fading lasting several hours. Conversely, a graph of fading rate constants vs. temperature showed breaks that may be attributed to a relaxation mode of the polymer chain.[209]

For biochemical applications in particular, there are still plenty of things to be done by merely tinkering with the substituents of a few well-known spiropyrans: attach a polymer, attach an ion-binding group, or modify its solubility. Note that the “photocontrol unit” for concanavalin A, poly(L-glutamic acid), poly(L-lysine) and the selective signaling receptors all referred to earlier, is in each case merely that old workhorse molecule, 6-nitroBIPS. Indolinospiropyrans are especially useful for tinkering because a 2-hydroxyethyl or 2-carboxyethyl (more generally, an ω-substituted alkyl) substituent is easily placed on the N atom of the indoline and serves there as a convenient link to the polymer or crown ether. Furthermore, a hydroxyethylated compound can be converted into a methacrylic ester suitable for copolymerization. The early[210,211] and more recent[212] efforts along these lines have been reviewed, and the current work is presented in Chapters 1 and 9 in Volume 2; a few other examples have been presented here.

Photochromic control of the polymer properties leads to potential applications involving the mechanical properties of a solution (viscosity, photogelation), polymer fiber (extensibility, "photomuscle"), or membrane (porosity). More important, however, the ability to control the activity of enzymes and other biologically important macromolecules leads to potential applications in clinical phototherapy.

Polymer control of the photochromic properties may significantly lower the rate of fatigue, probably by sterically hindering the approach of oxygen to the dye moiety. The powerful molecular modeling capabilities now available could suggest the polymer structures that are the most effective in protecting the spiropyran. Thus, many applications impractical 25 years ago because of the fatigue of the simple spiropyrans might now be practical by using polymer-protected versions of the same dyes.

Current research also uses a spiropyran as an orientated species. Dye in Langmuir-Blodgett films, in bipolar membranes, in liquid crystalline solvents, and adsorbed or vapor deposited on crystalline surfaces exhibits photochromic behavior significantly different from its behavior in dilute fluid solutions or amorphous polymer films or bulk matrices. In an indirect technique for controlling orientation, a silica surface is treated with a photochromic silylating reagent (again, a 6-nitroBIPS derivative) to give a "command surface" that when exposed to linearly polarized UV light causes the homogeneous alignment of adjacent nematic liquid crystals.[213] This orientation, and several other aspects of photochromic polymer behavior that have been mentioned in this chapter, are discussed further in Chapter 1, Volume 2.

In the future, spiropyrans most likely will be used chiefly in biochemistry and image technology or optical physics, in ways in which their inherent "fatigue" can be neglected (not overcome – merely neglected). The potential applications of properly designed spiropyrans as biosensors specific for cations and nucleotides has already been described.

Spiropyrans show promise for optical recording, three-dimensional optical memories,[214] and holography.[215] The dyes currently under study for these applications very probably will not be used merely dissolved in a bulk polymer matrix, but will be oriented in films and membranes, or adsorbed or vapor deposited on solid substrates to take advantage of the nonlinear optical properties of the colored forms. For example, thick (0.5 mm) PMMA films of 6-nitro-thiaBIPS can be used to record wavelength-multiplexed volume holograms with an infrared diode laser. This system is impractical at present because of fatigue and poor diffraction efficiencies.[216]

In a promising approach to high-density recording for optical memories, thin films of aggregates of five different 6-nitroBIPS derivatives, each absorbing sharply at a different wavelength, are layered on a substrate and independently recorded in each layer at one spot by linearly polarized laser lights of wavelengths matching each absorption band. Two mutually perpendicular polarized lights will act independently, thus permitting a total of ten different recordings in the same volume.[217]

The dream of 40 years ago of a "self-developing, instant, reusable photographic system" has evolved from impractical to promising, not only by improving the molecule, which is what organic chemists did for many years, but also by being more sophisticated about its use, which is what biochemists and optical physicists and molecular engineers[218] do now.

1.5. SOME REPRESENTATIVE PREPARATIONS

The original literature records the preparation of many hundreds of spiropyrans and is the place to look first for a specific compound. Some generalities about the best choice of intermediates and reaction conditions have been given in Section 1.2. Presented here, with an emphasis upon manipulative details, are descriptions of preparations of a typical BIPS on a large laboratory scale (in which the condensation intermediates can be observed); a Fischer's base via a Plancher rearrangement, where the reaction and purification are complex; and a salicylaldehyde having a group useful for various further transformations.

1.5.1. 6-NitroBIPS

Approximately 897.3 g (see Note 1) of 5-nitrosalicylaldehyde (see Note 2) is placed in a 50-L round-bottomed flask equipped with a powerful paddle stirrer, reflux condenser, and heating mantle. To this, 18 liters (5 ga) of anhydrous ethanol (see Note 3) is added and the mixture stirred and heated to about 74°C (Note 4). The aldehyde dissolves at about 65°C. Then 929 g (Note 5) of freshly distilled 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) is added over about 45 s to the solution, which turns orange for a fraction of a second (Note 6) and purplish-gray immediately thereafter and gives a thick slurry (Note 7). The solid dissolves in 10–15 min, and the resulting intensely purple solution is refluxed for 3 hr, allowed to cool with stirring, and then let stand overnight. During all these steps the flask is protected from light (covered with a black cloth).

The mixture is filtered through a large (4- or 6-liter) fritted funnel (conveniently, much of the supernatant can first be siphoned off) and pressed and sucked as dry as practical. The solid is washed three times each with 2–3 L of ethanol, slurrying it well each time to remove purple streaks. The last runnings of the filtrate will be lightly colored. The solid is air dried in the dark to give 1481 g (85.6% of 1729 g theoretical) of small, dense, light tan sandy crystals, mp 175–7°C (uncorr.) (Notes 8 and 9).

Note 1. The amount used is adjusted to correspond to the amount of freshly distilled Fischer's Base available; see Note 5.

Note 2. A high-purity material, preferably prepared from 4-nitrophenol, is necessary in order to obtain a directly pure product. Material made by nitration of salicylaldehyde usually contains small amounts of the 3-nitro isomer and gives a reddish-brown BIPS product. The 8-nitroBIPS contaminant will impart a background color to solutions and coatings made from the contaminated spiropyran.

Note 3. The alcohol must be denatured with other alcohols or hydrocarbons, and not with ketones or aldehydes, which can react with Fischer's Base.

Note 4. On this scale, the heat of reaction upon adding the base brings the mixture just to boiling (why waste electricity or steam when nature provides free energy?), but on larger-scale runs, either a lower temperature or slower addition rate would be needed.

Note 5. One liter of commercial Fischer's Base is distilled (in the morning) in a simple pot-to-pot still at 2–5 mm pressure to give 960–970 g of distillate, which often is water-white, but usually pale yellow. It is always used the same day it is distilled, and then gives directly a pure product. Using "red" Fischer's Base gives a brown product that requires multiple recrystallizations with charcoal to clean up, with great loss.

Note 6. This is the proton-transfer reaction that gives the (orange-colored) anion of the nitrosalicylaldehyde (and the colorless indoleninium cation).

Note 7. This is the initial aldol-like condensation product, indoleninium$^+$ $–CH_2–CHOH–C_6H_3(O^-)NO_2$ in which the chromophoric moieties are still isolated. It loses water relatively slowly to give the intensely colored dye.

Note 8. The yield of product in runs on this scale is 83–87%. This preparation also has been carried out more than 20 times on twice the scale described with the same range of yields. Concentrating the filtrates and washings gives highly colored material that is impractical to purify. The tan product of this preparation is quite pure, but can be recrystallized from toluene, ethyl acetate, or methyl ethyl ketone with charcoal to give light yellow material. Product contaminated with the somewhat more soluble 8-nitro isomer suffers considerable loss if complete removal of this impurity is attempted.

Note 9. As indicated in section 1.2.3, this exact procedure on this approximately 5-mol scale gives ca. 95% yield of 8-ethoxy-6-nitroBIPS. Scaled down it is the usual laboratory preparation for dyes that are significantly less soluble than their starting components.

1.5.2. 3-Phenyl Fischer's Base and its Hydroiodide

A 45-ml bomb is charged with 5.25 g of 2-phenylindole (Note 1), 7.5 ml of methanol, and 15 g (6.6 ml) of methyl iodide (4.15 moles MeI/mol indole). The bomb is kept at 135°C for 8 h (Note 2) and cooled. The bomb contents, a red liquid or slush, are transferred to a beaker and the bomb rinsed out with no more than 5 ml of methanol. With stirring at room temperature, ethyl acetate is slowly added to turbidity; about 15 ml are needed. The mixture is let stand 1 h (Note 3) and the yellow-orange precipitate is removed by filtration, mp 225–228°C. This product can be recrystallized from methanol (15 ml/4 g of solid) in 73–92% recovery to give a 37% average yield of pale yellow salt having an mp of 226–228°C (lit.,[219,220] 226–227°C) (Note 4).

After removal of the crude product, upon standing the ethyl acetate filtrate continues to deposit a dark yellow solid. This is not a second crop of the desired 1,2,3-trimethyl-3-phenylindoleninium iodide; it is, according to mp, UV, and NMR data and the literature,[220] the isomeric 1,3,3-trimethyl-2-phenyl salt, mp 195–199°C, raised to 198–201°C after recrystallization from methanol (lit.[220]: 196°C, 202–203°C, 203°C). Moreover, treatment with a base gives 1,3,3-trimethyl-2-phenyl-2-hydroxyindoline, but not 3-phenylFischer's base, since its IR spectrum lacks the two sharp absorptions near 1615 and 1650 cm^{-1} that are characteristic of the 2-methylene group. About 4.0 g are obtained. This material is fluorescent, whereas the 3-phenyl compound is not. This 2-phenyl salt is heated at 200°C under nitrogen for 5 min and recrystallized from methanol to give on average an additional 3 g (30%) of the 3-phenyl salt (Notes 5 and 6).

The 3-phenyl salt is treated with 10% aqueous NaOH and the resultant oil is taken up in toluene, washed with water, dried over sodium sulfate, the solvent removed by vacuum rotary evaporation (foaming!), and the residue subjected to rapid pot-to-pot distillation under nitrogen to give 75–85% recovery of 1,3-dimethyl-2-methylene-3-phenylindoline, bp 130–140°C.1–2 mm (lit.[219] 130°C/0.08 mm) (Note 7).

Concentration of the filtrates gives some starting 2-phenylindole (mp and IR comparisons), and the IR and NMR spectra of the concentrated filtrates and washings combined from several runs suggest the presence of small or very small amounts of the other seven indoles and three other indolenines possible from (partial) methylations and rearrangements occurring during this reaction.

Note 1. A high-quality material having a mp of 187°C or better is used.

Note 2. There is no great difference between reactions heated for 8 and for 16h. Yields of crude product averaged 4.5 g (45.6% of 9.87 g theo.); once an 8-h run gave 5.2 g.

Note 3. In one run in which the reaction mixture stood overnight before filtering, the first solid product showed an mp of 195–198°C and was almost entirely the 2-phenyl salt. Apparently the 3-phenyl salt equilibrates in the solution to the 2-isomer, which is more stable because the phenyl group is now conjugated with the indolenine nucleus. The confusion in the early literature undoubtedly arose from not appreciating that the identity of the product depends upon the duration of the crystallization time.

Note 4. Russian workers[219] report a 27% yield when using a 3.27:1 mole ratio of MeI:phenylindole at 120°C for 3 h. The present author obtained mostly starting material and little product under those conditions and the more vigorous conditions described here were necessary.

Note 5. The 2-phenyl salt had previously[220] been isomerized in an unspecified yield by heating 0.5 g in 6 ml methanol in a sealed tube at 120–150°C for 3 h and then at 180°C for 0.5 h.

Note 6. This preparation has been scaled up 20-fold in a 2-liter autoclave.

Note 7. The Russian authors[219] prepared this compound in 45% yield by a Fischer synthesis between 3-phenyl-2-butanone and 1-methyl-1-phenylhydrazine. The first substance is not easily available, and the second reactant is expensive. The ketone and phenylhydrazine give the expected 2,3-dimethyl-3-phenylindolenine, but methylation of this substance gave the rearranged product, 1,3,3-trimethyl-2-phenylindoleninium iodide, mp 203°C.[221]

1.5.3. 5-Formylsalicylaldehyde

CAUTION: Perform this preparation in a good hood because of the possible formation of bis(chloromethyl)ether, as well as the pungent odors of salicylaldehyde, concentrated hydrochloric acid and acetic acid.

A mixture of 45 g of paraformaldehyde and 750 ml of reagent-grade concd. hydrochloric acid in a 2-liter Erlenmeyer flask is cooled in an ice-bath to 5–10°C and 155 g of ice-cold salicylaldehyde (Note 1) are added with swirling by hand (Note 2). After 4 h in the ice bath with occasional swirling, during which time a pale yellow oil precipitates, the flask is removed from the bath and allowed to stand at room temperature (20–27°C) for 36–40 h. During this time the oil slowly becomes a slush of pale orange or pink crystals (Note 3) of crude 5-chloromethylsalicylaldehyde.

Before filtering and washing this highly reactive chloromethyl compound, first a mixture of 625 ml of water (Note 4) and 625 ml of acetic acid in a 4-liter Erlenmeyer flask on a stirring hotplate is brought to 80–85°C (Note 5).

The slurry of chloromethylsalicylaldehyde is filtered on a *chilled* fritted funnel, sucked as well as practical in a minimum time (< 1 min, tamped down with a glass or plastic utensil, *not* a metal spatula), and washed as rapidly as possible two or three times with small amounts of *ice-cold* water (do not let solid ice enter the funnel) (Note 6). The literature[222] reports a 43% yield of dried, recrystallized chloromethyl compound.

To the stirred, hot aqueous acetic acid solution are added first 225 g of hexamethylenetetramine and then the damp filter cake of chloromethylsalicylaldehyde. The stirred mixture is brought just to boiling and refluxed for 1.5 hr (Note 7), and then 550 ml of concd. hydrochloric acid are added and the mixture is boiled (Note 7) for 7 min (*no longer*!), during which time the solution changes color from dark orange-brown to light orange. The hot solution is divided among three 4-liter Erlenmeyer flasks or beakers (ca. 650 ml each vessel) set in ice baths, and diluted with a total of 6 liters of cold water (ca. 2 liters each vessel). The solutions are let stand in the ice baths for at least 4 hr and the precipitate is collected by filtration, washed with a small amount of ice-cold water (in which it is slightly soluble), and air dried. The pale yellow or off-white product weighs 70–80 g (37–42% yield overall from salicylaldehyde; reported, 63% from isolated chloromethyl compound, or 27% overall) and has a mp of 105–106°C (lit.[222], 108–109°C). This material is sufficiently pure for most purposes, including formation of spiropyrans. Recrystallization from aqueous ethanol containing ca. 0.1% of 1 N HCl (Note 8) gives colorless crystals having an mp of 108–109°C with a recovery of 75–80% (Note 9).

Note 1. The quality of the salicylaldehyde is crucial to the success of this preparation. A “technical” grade is totally unsatisfactory, giving deep red dyes and resins (probably from phenolic impurities). Aldrich 98% is satisfactory if used from a freshly opened, newly purchased bottle; opened and unopened bottles approximately 9 months old were both unsatisfactory. Fluka 99% puriss. and products packaged under argon are satisfactory. Fischer "reagent, purified via bisulfite compound" directly gave practically colorless crystalline chloromethyl compound, but is a very expensive item.

Note 2. In this lab-scale preparation, continuous mechanical stirring does not improve the yield or purity of the chloromethylsalicylaldehyde, and lessens the convenience.

Note 3. Temperature control is critical during the initial reaction in the ice bath and in the standing afterward. The purity of the crude product is drastically reduced if the reaction mixture ever reaches temperatures above ca. 35°C; deep red gums are formed. The color is no doubt due to condensation of the chloromethyl compound with salicylaldehyde acting as a phenol to give aurin–like triarylmethyl dyestuffs; see Note 1.

Note 4. The water must be distilled or deionized, since traces of iron will form highly colored chelates that will contaminate the final product. Using a metal spatula to press the strongly acid filter cake of the chloromethyl compound may also color the material.

Note 5. The temperature is kept below boiling even though there is no significant heat of reaction in the next step, because the added solids act as boiling chips.

Note 6. The ice must be made from metal-free water; see Note 4. The washing is to remove the concentrated acid mother liquor. If the pH is too low during the next step, the hexamine will merely hydrolize more rapidly than it will be quaternized by the chloromethyl compound. The mechanism of the Sommelet reaction has been reviewed.[223]

Note 7. The flask is covered with a watch glass and the temperature adjusted so that the upper part of the flask acts as an air condenser. The solution can be refluxed with negligible escape of vapor.

Note 8. In the total absence of acid, some hemiacetal formation occurs at the 5-formyl group. The higher C=O frequency of this group in the IR spectrum will show a decreased intensity relative to the lower (H-bonded) C=O frequency of the 1-formyl group, and the NMR spectrum also will exhibit evidence of the change of Ar-C*H*=O to Ar-C*H*(OH) (OEt). Normally, the crude product, unless very thoroughly dried, will retain sufficient acid to serve the purpose. Too much acid gives the characteristic oxygen-bridged eight-membered ring "anhydro dimer" of the salicylaldehyde.

Note 9. This procedure modifies the reported[221] one in that instead of anhydrous hydrogen chloride and aqueous formaldehyde as the chloromethylating reagent, the more convenient combination of aqueous hydrogen chloride and anhydrous (para)-formaldehyde is used. In a run using the cyclic trimer trioxane as the formaldehyde source, the overall yield was only 20%. The further modification of bubbling HCl gas through the reaction mixture of the present procedure was not examined because of the probability of forming unacceptable amounts of bis(chloromethyl)ether. Because of the necessity of working as rapidly as possible with the cold chloromethyl intermediate, and the large volumes involved, it is not practical in the lab to scale up this preparation further, but with a sufficient supply of large vessels and ice baths, multiple runs can be overlapped conveniently. Note that only 8–9 g of product are obtained per liter of solution. Attempts to run the final hydrolysis in more concentrated solution led to lower yields of less pure product. The alternative route of chloromethylating 4-hydroxybenzaldehyde, followed by a Sommelet reaction, gave only a 30% yield in the latter step.[222] The Duff reaction on 4-hydroxybenzaldehyde, even the modification in which trifluoroacetic acid is used as solvent, gave very low yields of the desired product.[7]

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2

Spirooxazines

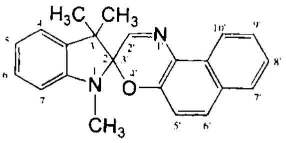
SHUICHI MAEDA

2.1. INTRODUCTION

Photochromic spirooxazine compounds are molecules containing a condensed ring- substituted 2*H*-[1,4]oxazine in which the number 2 carbon of the oxazine ring is involved in a spiro linkage. Photochromism of spirooxazines implies the heterolytic or homolytic cleavage and reformation of the carbon–oxygen single bond of the oxazine ring, as seen in Figure 2.1.

The first photochromic spirooxazine compounds synthesized (1970) belonged to the spiroindolinonaphthoxazine ring system. Generally, they were colorless in dilute organic solvents and polymer matrices and became blue upon exposure to UV light.

Both Ono and Osada[1] and Arnold and Vollmer[2] disclosed indolinospironaphthoxazines derived from 1-nitroso-2-naphthol. The synthesis of 1,3,3-trimethylspiro[indoline-2,3'-[3 *H*]naphth[2,1*b*][1,4]oxazine] (compounds **1**: abbreviation NISO) is mentioned later.



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In liquid or solid solution, the parent indolinospironaphthoxazine (NISO) turns blue upon irradiation with UV light and rapidly fades back to colorless when the

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Shuichi Maeda • Mitsubishi Chemical Corporation, Imaging Materials Laboratory, 1000 Kamoshidacho Aobaku Yokohamashi Japan

Organic Photochromic and Thermochromic Compounds, Vol. 1, edited by John C. Crano and Robert Guglielmetti, Plenum Press, New York, 1999.

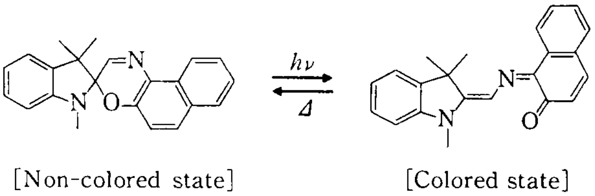


Figure 2.1. Spirooxazines as photochromic compounds.

activating radiation is removed. Only UV-A light (315–380 nm) is required for activation. It is generally recognized that the blue color is caused by the formation of the ring-opened merocyanine structure, which absorbs in the region of 600 nm.

There was essentially no activity in this area between the disclosure of Ono and Osada[1] or Arnold and Vollmer[2] and the U.S. patent issued to Hovey *et al.*[3] During the 1980s there was a rapid acceleration of research and publications on spirooxazines. The vast majority of the publications available at this time are patents and patent applications.

Spirooxazines have excellent resistance to light-induced degradation. This property, also called fatigue resistance, is considered to be due to photochemical stability of the oxazine molecule framework in the ring-closed form as well as in the open-ring form. The fatigue resistance of the spirooxazines has led to their successful use in various applications, for example, eyewear.

2.2. STRUCTURE, SYNTHESIS, AND PHOTOCHROMIC PROPERTIES

2.2.1. Substitution on the Naphthoxazine Ring Moiety

Hovey *et al.*[3] reported an enhancement in photochromic response by the addition of a methoxy group in the 9'-position or a bromine in the 8'-position, as shown in Table 2.1. Although dramatically improving the photochromic response, these substituents had little effect on the position of the visible absorption band.

A more interesting result arises from attaching an amino group on the 6'-position of NISO. The addition of an alicyclic amino group in the 6'-position (see

Table 2.1. Photochromic Response of Substituted NISO in Cellulose Acetobutyrate

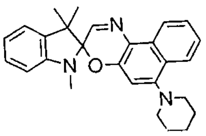
Substituent	Photochromic response (ΔOD)
None	0.9
9'-Methoxy	1.4
9'-Ethoxy	1.4
8'-Bromo	1.2

OD: optical density.

compound **2**) causes a 30–40 nm hypsochromic shift in the visible absorption band of the activated form. Whereas NISO gives a blue color upon UV irradiation in a poly(methyl methacrylate) matrix, 6'-piperidino-NISO yields a violet or purple color.

Quantum yields of the photochromism of spirooxazines are markedly dependent on the presence of electron-donating substituents in the 6'-position on the oxazine ring and on the nature of the solvent. Nonpolar and less viscous solvents give the highest yields, reaching 0.74 in the case of compound **2** in toluene. Replacing the methyl group on the nitrogen in the indoline part of the molecule with an isobutyl group has no effect on the quantum yield in either toluene or in a polyurethane matrix.[4]

The presence of a methoxy group in the 5'-position (compound **3**) causes a shift in the thermal equilibrium between the uncolored and colored species toward the colored species.



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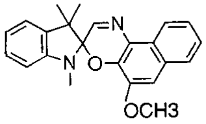

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2.2.2. Substitution on the Indoline Ring Moiety

The photochromic response of spirooxazines was shown to be somewhat affected by the substituent on the indolino nitrogen[5] (Table 2.2). For various 1-alkyl-5,6-dimethyl-9'-methoxy NISOs in cellulose acetobutyrate, photochromic activity increased in the order 1-methyl < 1-ethyl < 1- *n*-propyl < 1-*n*-butyl. However, the effect was not straightforward.

Hovey *et al.*[3] reported an increased photochromic response with the addition of electron-donating groups to the 4- through 7-positions of the indolino ring system. Placement of a methyl or methoxy group on the 4- through 7-positions of NISO generally improved the activity, but the degree of the effect was dependent on the substituted position (Table 2.3).

Table 2.2. Photochromic Response of 1-alkyl-5,6-(or 4-)-dimethyl-9'-methoxy-NISO in Cellulose Acetobutyrate

1-Alkyl group	Photochromic response (ΔOD)
Methyl	0.84
Ethyl	0.92
n-Propyl	1.35
Isopropyl	0.98
n-Butyl	1.45
n-Octyl	1.09

OD: optical density.

Table 2.3. Photochromic Response of Substituted NISO in Cellulose Acetobutyrate

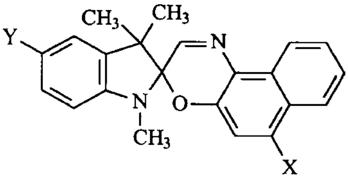
Substituent	Photochromic response (Δ*OD*)
None	0.9
5-Methyl	1.4
6-Methyl	1.1
7-Methyl	0.8
4(or 6),5-Dimethyl	1.1
4,7-Dimethyl	1.3
5-Methoxy	2.7
4,7-Dimethoxy	1.2

OD: optical density.

Chu[6] claimed that the addition of a trifluoromethyl group to the 4- or 6-position of indolinospironaphthoxazine resulted in a similar hypsochromic shift.

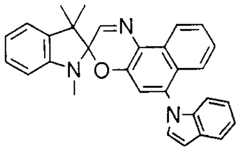
Rickwood *et al.*[7] also reported that absorbance shifts can be achieved by the use of electronegative groups attached to the spiroindolino moiety. Chloro- and trifluoromethyl substituents on the 5-position of the spiroindolino moiety effected hypsochromic shifts on the order of 10 and 18 nm, respectively, as shown in Table 2.4. A much larger shift of 38 nm was achieved through the use of a nitrogen at the 7-position (compound **4**), while an additional nitrogen center at the 4-position (compound **5**) caused a further shift of 14 nm. Further still, an NISO incorporating two electronegative centers on the indolino moiety plus a methoxy on the 5' position, the 4,6-bis-trifluoromethyl derivative **6,** showed a hypsochromic shift of 64 nm relative to compound **1** (see Table 2.5).

Table 2.4. Effects of Substituents Attached to the Naphthoxazine Moiety



	X	Y	λ max in Polyurethane (nm)
a	Indolino	H	606
b	Piperidino	H	578
c	Piperidino	Cl	568
d	Piperidino	CF_3	560
e	Morpholino	H	580
f	Aziridino	H	574
g	Diethylamino	H	574
h	Perhydroindolino	H	576
i	Methoxy	H	574
j	Tetramethylguanidino	H	568

The synthesis of 6'-indolino-1,3,3'-trimethylspiro[indolino-2,3'-[3*H*]naphth-[2,1-*b*][1,4]oxazine] (compound **7**) is given later.



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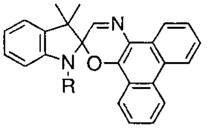
2.2.3. Other Indolinospirooxazines

Benzannellation of the naphthoxazine moiety has been accomplished to yield compounds **8, 9,** and **10.** The visible absorption band of the anthracene derivative **10**



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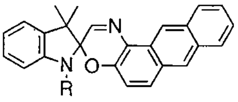

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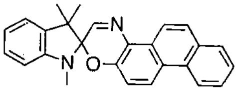

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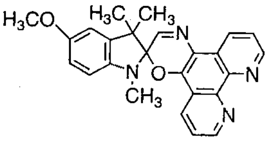

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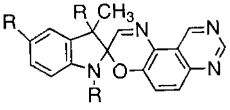

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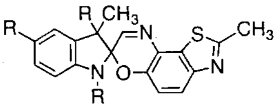

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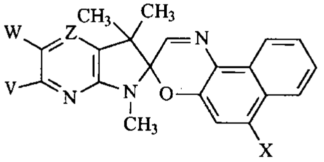
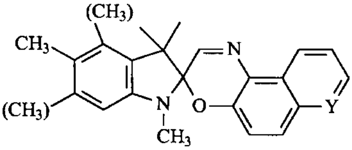
Table 2.5. Effect of Electronegative Groups Attached to the Indolino Moiety



Compound	X	Z	W	V	λ_{max} in Polyurethane (nm)
4	Piperidino	CH	H	H	540
5	Piperidino	N	H	H	526
	Tetramethylguanidino	N	H	H	516
	Tetramethylguanidino	CH	CF_3	H	520
	Methoxy	CH	CF_3	H	522
	Methoxy	N	H	H	524
6	Methoxy	CCF_3	H	CF_3	510

Table 2.6. Comparison of Spironaphthoxazine and Spiropyridobenzoxazine (compound **11**) in Polymer Matrix Prepared from CR- 39® Monomer



	Sensitivity (OD/min)	Equilibrium response (OD)	Fade $T_{1/2}$ (s)	Fatigue $T_{1/2}$ (h)	λ_{max} activated (nm)
Y=CH	0.44	0.22	58	410	615
Y=N (compound **11**)	0.56	0.42	122	280	609

has the same wavelength as that of the naphthalene derivative when UV activated. Examples **12, 13,** and **14,** spirooxazines with heteroaromatic rings, are also shown.

Kwak and Hurditch[8] patented the family of indolino spirooxazines derived from 5-nitroso-6-hydroxyquinoline. This family, the spiropyridobenzoxazines, in general possesses greater sensitivities (that is, rates of activation) and equilibrium responses (Table 2.6). For example, spiropyridobenzoxazine **11** has a sensitivity of 0.56 (ΔOD/min) and an equilibrium response of 0.42 (ΔOD) versus a sensitivity of 0.44 and an equilibrium response of 0.22 for the corresponding spironaphthoxazine.

Compound **12,** incorporating two heterocyclic nuclei, is very polarizable and shows a large solvatochromic behavior.[9] A polar solvent shifts the equilibrium toward the opened form as shown in Table 2.7. Nuclear magnetic resonance (NMR) experiments (400 MHz $1H$) showed that the open forms of “merocyanines” are transoid toward the azomethine bridge. The delocalized electronic structure tends to become more quinoidal with decreasing polarity of the medium.[9]

Table 2.7. Variation of the Spectrokinetic Parameters (k_Δ, λ_{max}, ΔA_0) of Compound **12** with the Solvent[a]

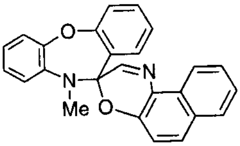
Solvent	k_Δ s^{-1}	ΔA_0	λ_{max} (nm)	Shoulder (nm)
Cyclohexane	0.24	0.14	584	545
Toluene	0.21	0.49	595	555
Dioxane	0.50	0.47	597	555
Acetonitrile	0.22	0.56	601	557
Dimethyl sulfoxide	0.27	0.37	610	571
Ethanol	0.16	0.81	605	566
Methanol	0.22	0.86	609	567

[a] $A_0 = A_0 - A_i$ with A_0 = absorbance immediately after the flash and A_i = absorbance of the original solution (Ref. 9).

Guglielmetti *et al.*[10] reported compounds **13** and **14** having the heteroatoms in the oxazine moiety. These series of the spiropyrimidobenzoxazines and spirothiazolobenzoxazines extended the available range of photochromic properties.

2.2.4. Miscellaneous Spirooxazines

Compound **15** exhibited photochromic properties only at low temperatures in the range –20 to –40°C.[11] Furthermore, as reported in Table 2.8 compound **15** showed interesting properties in various solvents; the λ_{max} of the aza-merocyanine form is red shifted when the solvent polarity is increased and the activation temperature is strongly affected by the nature of the solvent.



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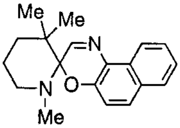
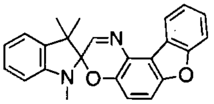
Kawauchi *et al.* reported replacing the indoline group of the spirooxazines with piperidine.[12] In contrast to a blue-activated form (λ_{max} = 610 nm) of the parent NISO, the activated form of the piperidino compound **16** was pink (λ_{max} = 562 nm) in methyl alcohol (Figure 2.2). The relative light fatigue resistance of compound **16** was compared with typical photochromic compounds using an Xe-Cl excimer laser (308 nm, 60 mJ/pulse) as the exciting light source and a 450-W Xe lamp as the bleaching light source. Compound **16** exhibited excellent resistance to light-induced degradation, as was the case with the parent NISO. The synthesis of 1',3',3'-trimethylspiro[3*H*-naphth[2,1-*b*][1,4]oxazine-3,2'-piperidine] (compound **16**) is given later in this chapter.



16

The spirooxazines derived from hydroxynitrosodibenzofurans have been disclosed by Yamamoto and Taniguchi.[13] These photochromic compounds are interesting because their colored forms have two absorption bands in the visible range. For instance, compound **17** had absorption bands at 460 and 632 nm in methyl alcohol after UV irradiation.

The bis-spirooxazine compound **18** was prepared by Kureha Chem. Ind.[14] using 1,5-dinitroso-2,6-dihydroxynaphthalene. The formation of the bis-oxazine structure caused a bathochromic shift, both in the unactivated compound



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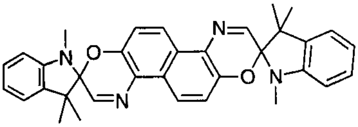

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Table 2.8. Coloration and Fading Temperature and Absorption Maxima in Various Solvents of Compound **15**

Solvent	Activation temp. (°C)[a]	Open form λ_{max} (nm)	Fading temp. (°C)[b]
Iso-PrOH	60–65	590	60±2
$ClCH_2CH_2Cl$	70–75	576	70±2
MeCN	80–85	570	80±2
PhMe	90–95	572	90±2

[a] Temperature range at which the colored form is detectable.
[b] Temperature at which the colored form is not detectable.

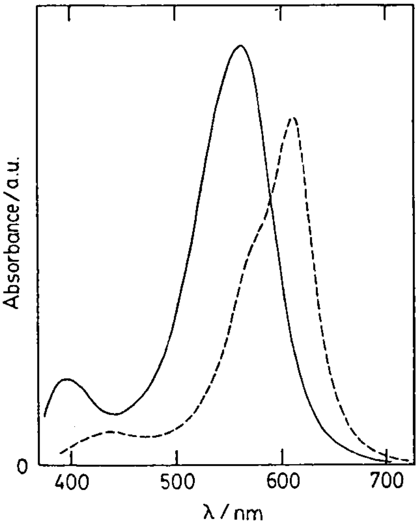
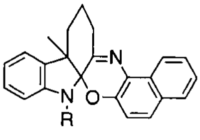


Figure 2.2. Visible absorption spectra of compound **16** (—) and the parent NISO (– – –) in methanol at 25°C after ultraviolet irradiation.

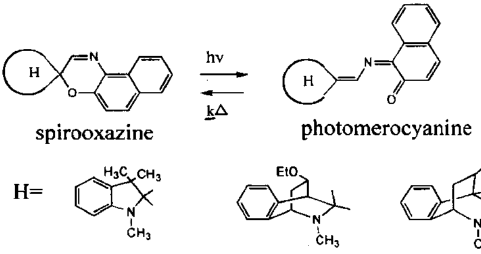
(λ_{max} = 380 nm) and in the colored form [λ_{max} = 630 nm in poly(methyl methacrylate)].

In the case of compound **19,** the indoline and naphthoxazine moieties are linked by a bridged chain; the configuration is relatively rigid even after cleavage of the C–O in the oxazine ring. The ring-opened species can be observed in acetonitrile, but not in cyclohexane.[15] The synthesis of compound **19** is given later.



19

Guglielmetti *et al.* [16] synthesized new spiro- azabicycloalkanenaphthoxazines such as compounds **20** and **21.** It is interesting to note that owing to the steric hindrance within these compounds, the C–O bond lengths of the compounds are longer than normal and photochromic colorability is enhanced.



Compound 1 20 21

2.2.5. Chelation of Spirooxazine Derivatives

Tamaki *et al.*[17] reported that chelation of the colored forms of spirooxazines with divalent metals induced considerable shifts of the absorption spectra and significant retardation of decoloration in the dark.

Oda[18] investigated photostabilization by amphoteric counterions such as zinc salts of 1-hydroxy-2-naphthoic acid and its derivatives. They were very effective in stabilizing the colored forms of spirooxazines (see Figure 2.3).

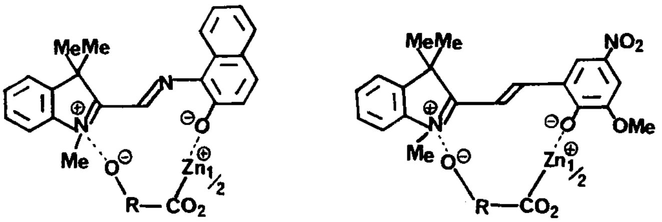
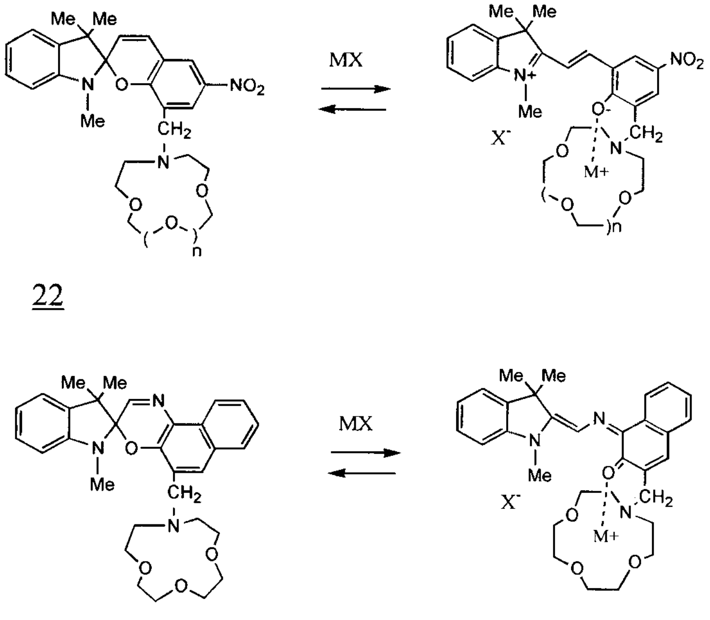


Figure 2.3. Chelation of spirooxazine derivatives.

2.2.6. Crowned Spirooxazines

A spironaphthoxazine derivative incorporating a monoaza-12-crown-4 entity at the 5'-position has been prepared by Kimura *et al.*[19] It is a light-resistant, cation-complexable photochromic compound.

Complexation of alkali metal ions by the crowned spironaphthoxazine allowed the spironaphthoxazine skeleton to isomerize to its corresponding open colored form, even under dark conditions. Specifically, lithium cation complexation stabilized the open form owing to the intramolecular interaction between its oxo group and the crown-complexed cation (Scheme 1).



22

23

Scheme 1

The reversibility in the ionic-conductivity switching of the spirooxazine system lasted even after 30 cycles, whereas the corresponding spiropyran system declined gradually in switching magnitude and ionic conductivity, as shown in Figure 2.4. The excellent durability of the spirooxazine system is due to the much better light resistance of the spironaphthoxazine skeleton than that of the spirobenzopyran one.

2.2.7. Electropolymerization of Spironaphthoxazine – Thiophene Derivatives

Guglielmetti[20] reported the synthesis of spironaphthoxazines (compound **24**) containing one thiophene entity which are precursors for the preparation of new molecular materials by electrochemical polymerization or copolymerization.

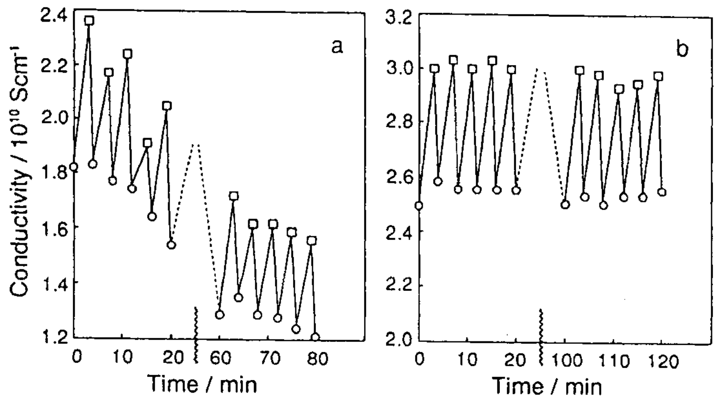
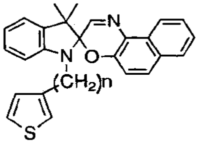


Figure 2.4. Photoinduced ionic-conductivity switching in ion- conducting composite films containing **22** (a) or **23** (b). Visible- and UV-light irradiation started at the points of (□) and (○), respectively.



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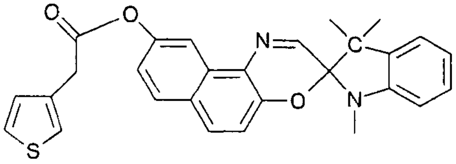
Guglielmetti *et al.*[21] also reported the synthesis of a series of thiophenes (e.g., **25**) and terthiophenes (e.g., **26**) substituted with spironaphthoxazine photochromic groups. It has been shown that electropolymerization of the thiophene group in **25** that occurs at 1.7 V [vs. saturated calomel electrode (SCE)] is blocked by the



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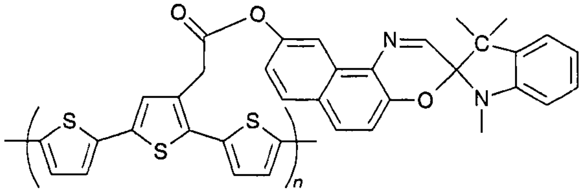

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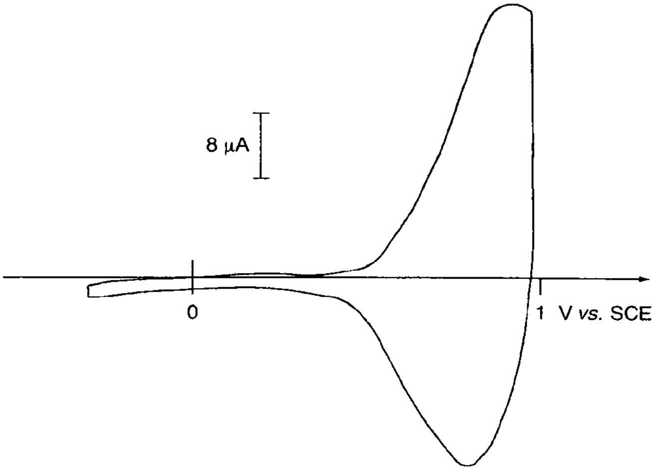


Figure 2.5. Cyclic voltammogram of poly(terthienyl- spironaphthoxazine) in 0.1 mol dm^{-3} NBu_4ClO_4-MeCN (scan rate 100 m Vs^{-1}).

oxidation of the spironaphthoxazine group occurring at 1.1 V. This was overcome by the use of a spironaphthoxazine–terthiophene compound (**26**) as the monomer in which the electropolymerization potential of the terthiophene moiety lies at 0.95 V, which is lower than that of spironaphthoxazine, thus allowing the electropolymerization to take place. A set of reversible cyclic voltammograms of poly(terthiophene) films with spironaphthoxazine showed a distinct, nearly symmetrical wave with an oxidation potential at 0.9 V and a reduction peak at 0.8 V, as shown in Figure 2.5.

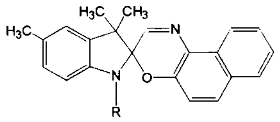
2.3. MOLECULAR STRUCTURE AND MECHANISM OF THE PHOTOCHROMIC REACTIONS

2.3.1. Nature of the Closed Form

Direct evidence for the structure of the closed form has been obtained by X-ray crystallographic structure determination of several spirooxazines.[22] The results have shown that the spiro carbon-to-oxygen bonds of the closed forms of the photochromic compounds are 0.01–0.05 Å longer than in a number of other oxazines.[23–25] This is in agreement with the rationale for the photochromic reaction being due to the rupture of the spiro carbon-to-oxygen bond by UV light absorption. Two types of the crystal structure of the closed forms are shown in Figure 2.6.

2.3.2. Nature of the Colored Form

Except for a few cases in which they were exceptionally stable,[26] the open-form structures have not yet been determined. Guglielmetti *et al.*[26] synthesized the first permanent opened forms of the spiroindolinooxazine compound **27**. NMR spectro-



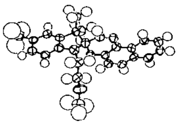
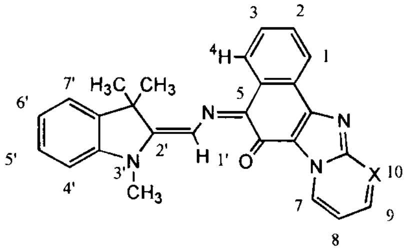
	–R		Molecular Structure
(1)	–CH3	TYPE-I	
(2)	–C2H4OCH3	TYPE-III	

Figure 2.6. Crystal structure of closed form obtained by X-ray analysis.



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scopic, dipole-moment, and X-ray crystallographic investigations showed that the stable open form was present in a quinoid electronic distribution and a trans-trans-cis geometry (TTC).

Molecular orbital calculations can provide the optimized structure and indicate the thermodynamic relative stabilities. Nakamura *et al.*[27] reported the results of an *ab initio* calculation of spironaphthoxazine, focusing on the determination of the most stable structure of the colored form. Figure 2.7 shows the optimized structure of the four open forms by using the *ab initio* molecular orbital method (HF 6-31G**/3-21G).

The calculation[27] indicated that: (1) all isomers converged to the planar form; (2) the most stable isomer is TTC; (3) the electrostatic interaction between the central hydrogen and the oxygen of the carbonyl group contributed to the stability; and (4) hydrogen–hydrogen repulsion was the reason for the destabilization of the open form.

The important bond angles and distances for these open-form isomers are shown in Table 2.9. All C=N bond show a double-bond character, whereas the other

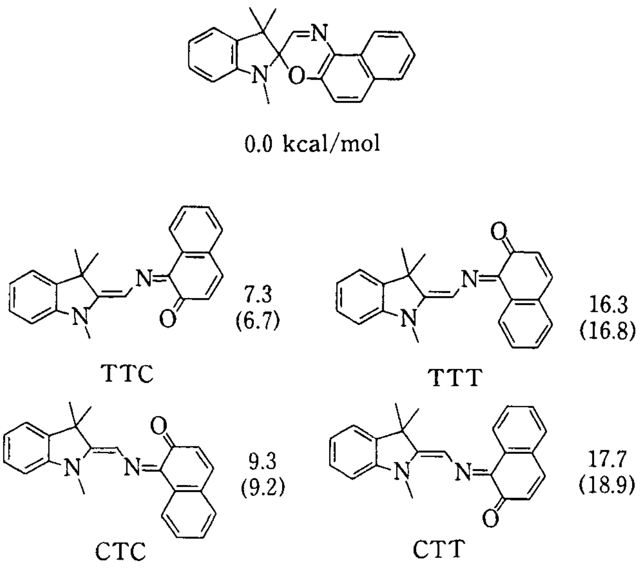


Figure 2.7. Thermodynamic relative stabilities calculated at the RHF level with the 6-31G** basis set and at the MP2 level with the 3-21G basis set (in parentheses) on the geometries optimized at the RHF level with the 3-21G basis set.

Table 2.9. Optimized Structure of the Four Isomers (in Å and deg.)

	TTC	CTC	TTT	CTT
Bonds				
Cspiro–C(CH_3)$_2$	1.534	1.540	1.536	1.539
Cspiro=C	1.350	1.351	1.356	1.358
Cspiro–N	1.371	1.366	1.365	1.358
C(H)–N	1.376	1.374	1.359	1.357
C=N	1.281	1.283	1.271	1.274
C(N)–C(O)	1.491	1.490	1.507	1.506
C=O	1.227	1.227	1.221	1.221
Angles				
Cspiro–C–N	119.6	122.6	117.3	120.4
C(H)–N–C	128.6	128.1	139.9	139.2

bonds in the azomethine bridge appear to have an intermediate character. In the trans-trans-trans (TTT) and cis-trans-trans (CTT) isomers, the H–H repulsion and resulting large bond angle of C(H)–N–C are clearly shown to be responsible for the destabilization.

From the standpoint of application, it is important whether the electronic structure is ketonelike or zwitterioniclike. The calculation results indicate that the C=O bond distance is in the region of the normal carbonyl length of 1.22 Å; consequently, the electronic ground state is ketonelike.

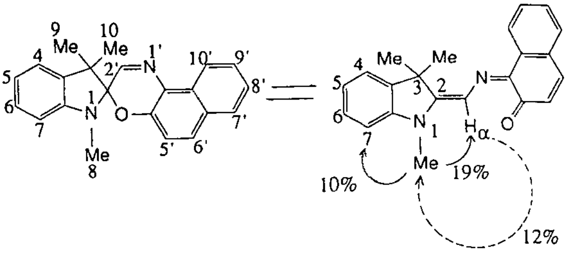


Figure 2.8. ^{1}H NMR NOE difference spectrum of the colored open form obtained upon irradiation of the olefinic proton H α.

Irie *et al.*[28] obtained experimental evidence for the most stable conformation of the open form by using ^{1}H NMR nuclear Overhauser effect (NOE) measurements. Irradiation of the protons in the NCH_3 moiety (3.79 ppm) produced positive NOEs of 10% at the H7 aromatic proton (7.49 ppm) and 19% at the H α olefinic proton. Irradiation of this α hydrogen produced a 12% enhancement of the NCH_3 proton, as illustrated in Figure 2.8. These observations indicated that the geometrical structure of the colored open form of spirooxazine is the TTC form.

2.3.3. Mechanism of the Photochromic Reactions

A recent study by laser flash photolysis showed that a triplet state is not involved in the coloration mechanism of spirooxazines when in solution. A similar conclusion was reported, noting that the photocoloration occurs only in the excited singlet state because of the independence of the reaction to the presence of oxygen.[29]

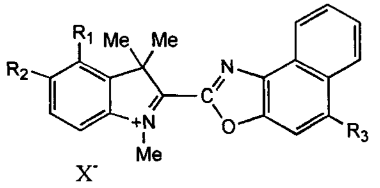
Aramaki *et al.*[30] examined the photochromic reactions of spirooxazines by picosecond time-resolved Raman spectroscopy. Vibrational resonance Raman spectra of the merocyanine isomer(s) recorded over a 50-ps–1.5-ns interval did not change. This indicated that the open ring opening to form a stable merocyanine isomer or the distribution of isomers[31] was complete within 50 ps and that the isomer(s) distribution remained unchanged for at least 1.5 ns.

Schneider[32] investigated the primary processes in the ring-opening reaction by picosecond time-resolved absorption and emission spectroscopy. The heterolytic bond cleavage between the spiro-carbon and the neighboring oxygen is commonly accepted as the primary photochemical step after exciting indolinospirooxazines with UV photons. The nonplanar intermediate "X" generated in this way is said to relax very rapidly to a distribution of open forms that are similar in structure to merocyanines. The existence of an intermediate "X" is proven for various derivatives of spirooxazines. The buildup time for these "X" forms is generally shorter than 2 ps, and the following reaction to the planar forms takes 2 to 12 ps, depending on the nature of the solvent as well as the kind of substituent added to the parent molecule.

Resonance-enhanced coherent anti-Stokes Raman spectroscopy (CARS) has proven to be a useful technique for investigating the molecular structures of transient species.[33] In nonpolar and polar solvents, CARS spectra of spirooxazine derivatives indicated the existence of two similar isomeric species.

Wilkinson[34] reported that the photochemical formation of the open merocyanine forms of several spirooxazines in different solvents has been studied using both picosecond transient absorption (PTA) and picosecond time-resolved resonance Raman (PTR^3) methods. The initially formed S_1 states relax to the ground state with lifetimes that range from 1 to 13 ps, depending on the solvent. Evolution through various geomeric isomers, which typically takes several hundreds of picoseconds, results in the formation of the equilibrium isomeric distribution. Resonance–Raman measurements clearly showed that for at least one of the compounds in butane-1-ol, several conformations made major contributions to the equilibrium mixture. In cyclohexane, however, the situation appeared simpler, with one conformation (TTC) dominating the distribution.

Malatesta[35] proposed the key intermediate product (compound **28**) of the oxidative degradation of photochromic spirooxazines. These species may result from the photochromic irreversible degradation of the spirooxazines even under conditions of partial or total absence of oxidation as, for example, in polymers coated with thin films of barrier agents such as SiO_2, SiO_xC_y, Al_2O_3, and MgO.

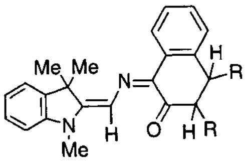


$R_1=R_2=CH_3$

$R_3=H$

28

Malatesta *et al.*[36] disclosed that spirooxazines react easily in their open merocyanine (MC) forms with free radicals to give deeply colored, reduced, free-radical adducts (FRA) that are devoid of photochromic activity. The radicals attack the $C_5'=C_6'$ double bond of MC and yield stable, deeply colored, free-radical adducts (compound **29**) that can no longer close back to the corresponding spiro form. The adducts absorb in the 510–560-nm region and are characterized by high molar absorptivities.



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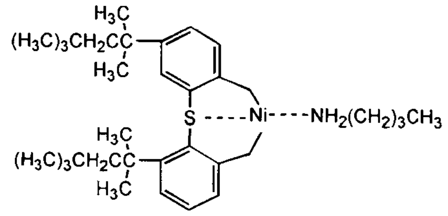
2.4. APPLICATIONS

2.4.1. Stabilization of Spirooxazines

Indolinospirooxazines are inherently more fatigue resistant than the spiropyrans. As measured by the quantum yield for photodegradation, the spironaphthoxazines are two or three orders of magnitude more photostable than the spirobenzopyrans.[37] From the point of view of industrial applications, spirooxazines are reported to be stabilized even further by various protective methods.

Chu[38] reported that the addition of the organonickel complex, Cyasorb® 1084 (compound **30** from American Cyanamid) to cellulose acetobutyrate polymer containing the spironaphthoxazine increased the photostability of the photochromic compound considerably. Chu[39] also demonstrated that the addition of a hindered amine light stabilizer (HALS, Tinuvin® 770 compound **31** from Ciba-Geigy), to polymer films containing the spirooxazine improved fatigue resistance.



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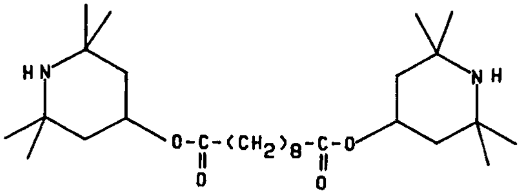

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Kawasaki *et al.*[40] disclosed the use of hindered phenols such as 2,6-di(*tert*-butyl)phenol as stabilizers for spirooxazines in poly(vinyl butyral). The hindered phenols not only improved photochromic durability but also photochromic response, besides accelerating the thermal recovery rate.

Tateoka *et al.*[41] reported that nitroxyl free radicals such as those shown in Figure 2.9 were quite useful as stabilizers for spirooxazines.

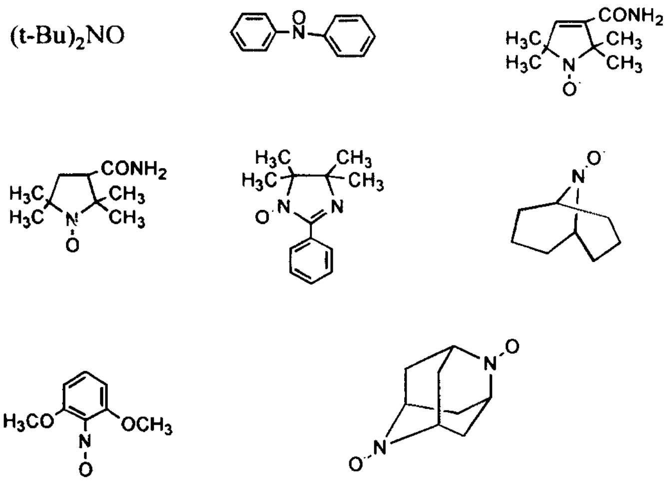

Figure 2.9. Light stabilizers of spirooxazines.

The thermal fading of spirooxazines has been shown to be dependent on the matrix. Tateoka *et al.*[42] reported that the fading rate for the colored form could be increased by adding a plasticizer, for example, dibutyl phthalate to poly(vinyl butyral).

Malatesta[43] investigated the photochromism and thermochromism of spirooxazines in cationic (CTAB, hexadecyltrimethylammonium bromide) and nonionic (TX-100) micellar solutions, and in sodium bis-2-ethylhexylsulfosuccinate (AOT) toluene–water inverted micelles. The thermo- and photocolorability increased in TX-100 and CTAB micelles and decreased in inverted micelles.

J.-P. Boilot[44] reported the photochromism of spirooxazine-doped gels. In organic–inorganic hybrid matrices, a competition was observed between normal and reverse photochromism because of the presence of two chemical environments for the dye molecules in $CH_2{=}CHSi(OC_2H_5)_3$ (VTEOS) and $Si(OC_2H_5)_4$ (TEOS) mixtures. When the spirooxazine molecules were surrounded by vinyl groups, the photochromism was normal with a stable closed form and a metastable merocyanine with a quinoid structure. For reverse photochromism, the molecules were surrounded by hydroxyl groups. In this case, the photochromism was reversed with a stable open zwitterionic form.

2.4.2. Commercial Plastic Photochromic Lenses

Spirooxazines (NISO) have UV activation properties and thermal bleaching properties that are convenient for eyewear applications. A plastic photochromic lens must have several features, such as (1) ultraviolet energy protection, (2) comfortably lightweight, and (3) tint from a fashionably light tint to a functionally darker tinted sun lens.[45]

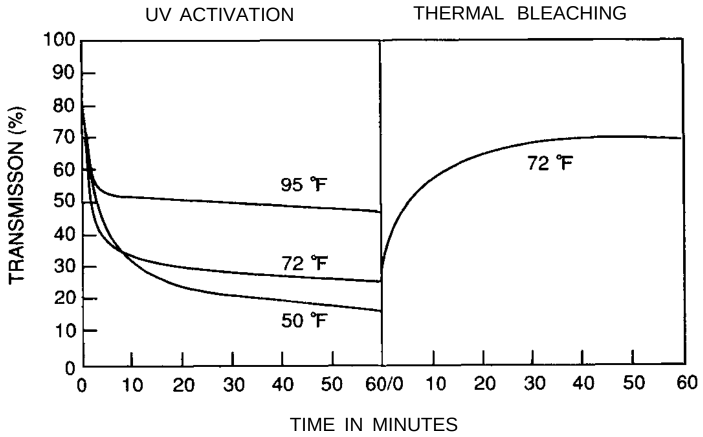

Figure 2.10. Photochromic performance of a Transitions® lens. (Reprinted from Ref. 45 with permission of copyright owner: Chapman & Hall Ltd.)

In the early 1980s, American Optical (AO) commercialized a NISO photochromic lens. However, the lens was unsuccessful in the market because of its hue when activated and poor response.

At present, some U.S. and Japanese manufacturers are producing and commercially marketing plastic photochromic lenses. Rodenstock has been marketing the Colormatic® lenses. Transitions Optical, Inc. has been selling a number of Transitions® photochromic lenses in various markets since 1991. The first-generation Transitions lens contained a light-brownish tint with a bleached transmittance of 80%. The equilibrium saturation density of the lens was dependent upon the temperature, as shown in Figure 2.10. On a typical summer day, the activated transmittance varied from approximately 48% at 95°F to 14% at 50°F. The activated spectrum at 72°F showed relatively broad-band absorption in the visible range, as shown in Figure 2.11. The next generations of Transitions lenses included such improvements as higher bleached transmittance, faster photochromic responses, and less temperature dependence.

2.4.3. Microencapsulated Photochromic Ink

Mitsubishi Chemical Corp. developed a water-based ink composed of photochromic-containing capsules and an aqueous polymer binder.[46] The average particle size of the capsules containing photochromic spirooxazine and antioxidant was 20 μm. By using this ink composition, cotton clothes could be screen printed. The printed part showed coloration within 10 s when exposed to sunlight and exhibited good fatigue resistance. Furthermore, it bleached within 15 s in the dark, and this process was observed repeatedly.

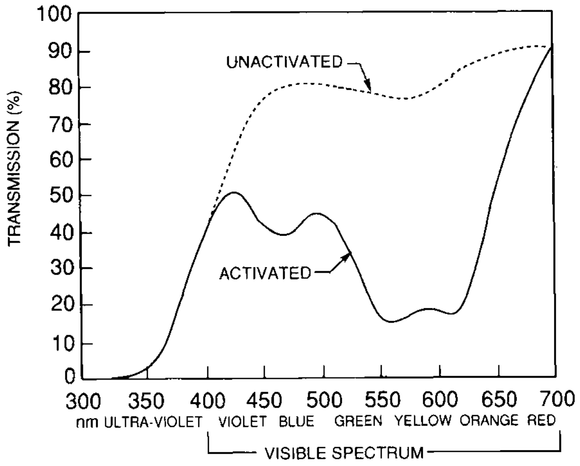

Figure 2.11. Visible spectra of a Transitions® lens before and after UV irradiation (activation). (Reprinted from Ref. 45 with permission of copyright owner: Chapman & Hall Ltd.)

2.4.4. Photochromic Lamiglass

Nissan Motor and Mitsubishi Chemical Corp. investigated photochromic lamiglass consisting of a photochromic layer, an intermediate poly(vinyl butyral) film, and glass plates. The photochromic intermediate film was sandwiched between two clear glass plates as shown in Figure 2.12. The absorption spectra in the dark are shown in Figure 2.13. The clear glass filters the shorter wavelengths. The lamiglass is activated by solar light of approximately 350 nm.

This feature proved to be useful when used in automobile windshields. It controlled light transmittance in proportion to solar intensity. This material provided a comfortable driving atmosphere because of its high glare protection. Under low light intensity, the lamiglass exhibited a high transmission of 80%. On the other hand, when exposed to sunlight, the transmittance gradually decreased and the glass showed a blue color. The maximum wavelength was 630 nm.

This lamiglass exhibited a high optical density in the saturation state. The coloration reached 50% of its saturated value in 20 s. The decoloration speed is slower, as shown in Figure 2.14. Furthermore, it had excellent resistance to visible

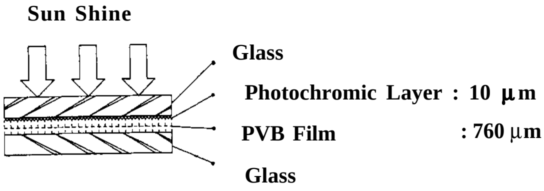

Figure 2.12. Composition of photochromic lamiglass.

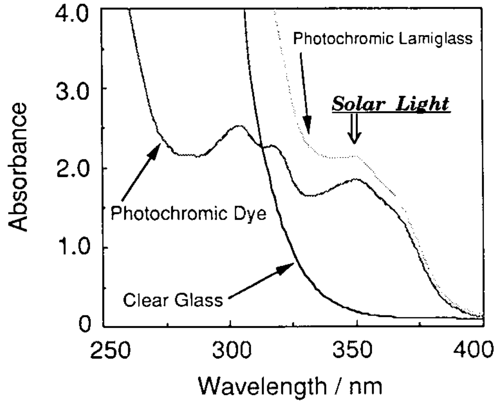

Figure 2.13. Absorption spectra before irradiation.

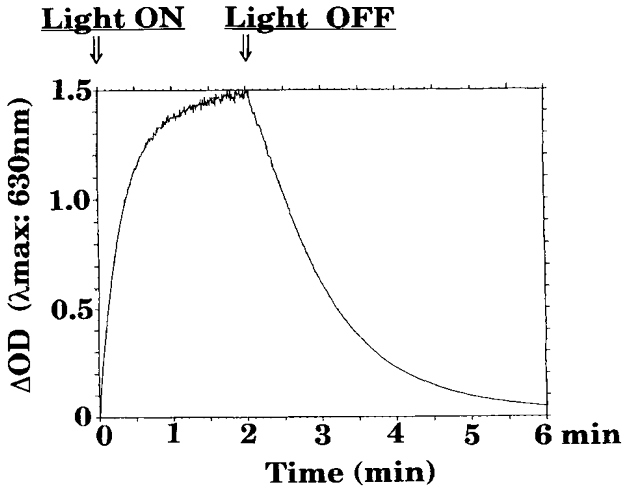

Figure 2.14. Photoinduced absorbance change.

and UV sunlight. Photochromic activity changed little after exposure for over 3000 h with a xenon fademeter.

2.5. SYNTHESIS EXAMPLES

2.5.1. Synthesis of 1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphth[2,1 *b*][1,4]oxazine] (compound 1)

Compound **1** was prepared by reacting 1-nitroso-2-naphthol (18 g) in MeOH (200 ml) under reflux with solution of 1,3,3-trimethyl-2-methyleneindoline (17 g) in

MeOH (50 ml) which was added over a period of 10 min. After refluxing for 1 h, the reaction mixture was cooled. A brown solid precipitated, which was filtered and washed with plenty of methanol and which yielded 15 g of product. The product was purified by repeated charcoal treatment and recrystallization from acetone, mp 124– 125°C.

IR (KBr): 3054, 2961, 1619, 1605, 1589, 1506, 1484, 1452, 1438, 1421, 1381, 1358, 1297, 1271, 1242, 1073, 1028, 1000, 962, 813, 751, 740 cm^{-1}.

2.5.2. Synthesis of 6'-Indolino-1,3,3-trimethylspiro[indolino- 2,3'-[3*H*]naphth[2,1-*b*][1,4] oxazine] (compound 7)

Method A. A solution of 86.5 g (0.5 mol) of 1-nitroso-2- naphthol in 650 ml of methanol was heated to reflux and treated in one portion with a solution of 173 g (1.0 mol) of 1,3,3-trimethyl-2-methyleneindoline in 100 ml of methanol. The resulting solution was heated under reflux for 10 min and then treated over the course of 1 min with a solution of 86.5 g (0.50 mol) of 1-nitroso-2-naphthol in 250 ml of methanol. The resulting dark solution was refluxed for another hour, concentrated, and the residue washed with acetone to obtain compound 7 as a yellow solid; mp 253–255°C; yield 9%.

Method B. A solution of 5.80 g (0.020 mol) of 4-indolino-1-nitroso-2-naphthol and 3.46 g (0.020 mol) of 1,3,3-trimethyl-2-methylene indoline in 100 ml of 1,4-dioxane was heated under reflux for 21 h. The resulting purple solution was evaporated to dryness and the residue purified by flash chromatography over silica with diethyl ether–hexane (1 : 7 = v : v) to give 5.56 g as a green gum or solid, which was further treated by washing with acetone to give compound **7** as a yellow solid; mp 255–257°C; yield 58%.

^{1}H NMR (CDCl3): δ = 8.59 (d, 1H, H- 10'), 7.95 (d, 1H, H-7'), 7.69 (s, 1H, H-2'), 7.62–6.29 (m, 10 H, aromatic), 6.93 (s, 1H, H-5’), 3.17 (m, 2H, CH_2Ar), 2.77 (s, 3H NCH_3) 1.36 (s, 6H, 2X-CH_3).

2.5.3. Synthesis of 1',3',3'- trimethylspiro[3*H*-naphth[2,1- *b*][1,4]-oxazine-3,2'-piperidine] (compound 16)

1-Nitroso-2-naphthol (6.93 g) was added to ethanol (70 ml) and the mixture heated under reflux to completely dissolve the 1-nitroso-2-naphthol under a nitrogen atmosphere. A slurry of 1,2,3,3-tetramethyl-3,4,5,6- tetrahydropuridinium iodide was added to the solution and refluxed for 2 h. The reaction mixture was allowed to stand for a few days and the brown precipitate was obtained by filtration. The precipitate was recrystallized from ethanol or methanol to give pale yellow needles of compound **16** (yield, ~ 10%), mp 104–106°C.

^{1}H NMR ($CDCl_3$): δ = 0. 96 and 1.26 (6H, s, 3'-Me), 2.26 1.29– (3H, s, N-ME), 1.29–2.94 (6H, m, 4'-,5'- ,6'-H), 7.05–8.52 (7H, m, aromatic H),^{13} C NMR ($CDCl_3$): δ = 20.9 (5'-C), 22.0 and 26.4 (3'-Me), 32.8 (4'-C), 39.5 (N-Me), 39.9 (3'-C), 48.2

(6'-C), 92.6 (spiro-C), 116.6 (5-C), 121.4 (10-C), 122.3 (10b-C), 123.6 (9-C), 127.6 (7-C), 128.9 (6a-C,) 129.8 (6-C), 131.1 (10a-C), 145.6 (4a-C), 153.0 (2-C).

2.5.4. Synthesis of Compound 19

4a-Methyl-2,3,4,4a-*tetra*hydro-1*H*-carbazole was prepared from 2-methylcyclohexanone and phenylhydrazine. The carbazole obtained was transformed into the corresponding carbazolium iodide by treating with iodomethane. The carbazolium iodide, triethylamine, 1-nitroso-2-naphthol were dissolved in absolute ethanol and refluxed for 3 h under a nitrogen atmosphere. After the solvent was removed, the residue was chromatographed on a silica gel column [eluent dichloromethane–cyclohexane (v : v = 2 : 1)]. Orange-red crystals were obtained after recrystallization (acetone), mp 218–220°C.

IR (cm^{-1}): 2966, 1620, 1609, 1593 and 1482. ^1H NMR ($CDCl_3$): δ=1.51 (s, 3H, 12b-CH_3), 1.8 (m, 4H, 13-CH_2– and 14-CH_2–), 2.54 (s, 3H, N- CH_3), 2.9 (m, 2H, 15-CH_2–) and 6.50–8.65 (m, Ar-H).

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3

Benzo and Naphthopyrans (Chromenes)

BARRY VAN GEMERT

3.1. INTRODUCTION

3.1.1. Definition

The benzo and naphthopyrans that are the subject of this chapter have the general structures (**1, 2, 3, 4**) shown in Figure 3.1 in which R^3 and R^4 are *not* combined to form a spiro heterocyclic group. The benzo or naphtho portions of **1, 2, 3,** and **4** often contain additional substituents, while on the other hand, R^1 and R^2 are usually hydrogen (see Section 3.2.2.1). Compounds in which R^3 and R^4 are combined into a spiro heterocycle are commonly referred to as spiropyrans. Although structurally related, the spiropyrans represent a completely different class of photochromics, based on their photochemistry, and are reviewed in Chapter 1 of this book. Until the past decade, the photochromism of benzo and naphthopyrans had gone largely unstudied, although their chemistries, including preparations, properties, and reactions, have been thoroughly explored.[1,2] Bertelson[3] and Laarhoven[4] briefly reviewed the photochromism of benzo and naphthopyrans as a part of their more comprehensive reports, respectively, on spiropyrans and related compounds and 4n+2 systems: molecules derived from Z-hexa-1,3,5-triene/cyclohexa-1,3-diene.

3.1.2. Historical Perspective

The lack of interest until recently in the photochromism of benzo and naphthopyrans is due in part to the limited, and in some cases, misinformation found in the early literature. A case in point are the early publications dealing with

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Barry Van Gemert • PPG Industries, Monroeville, PA 15146 USA

Organic Photochromic and Thermochromic Compounds, Vol. 1, edited by John C. Crano and Robert Guglielmetti, Plenum Press, New York, 1999.

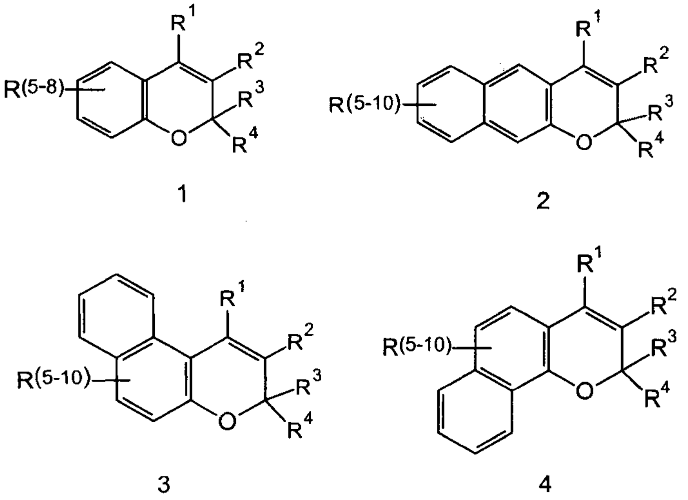
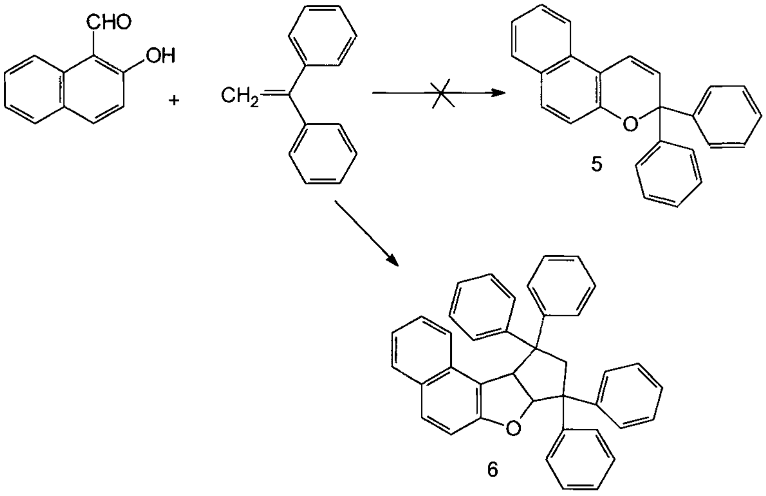


Figure 3.1. General structures of benzo and naphthopyrans.

3,3-diphenyl-3 *H*-naphtho[2,1-*b*]pyran (**5**). In 1940 Wizinger and Wenning[5] reported the first preparation of this compound (Scheme 1) which, unknown to them, yielded a two-to-one adduct (**6**) of diphenylethylene and 2-hydroxy-1-naphthaldehyde. This mistake was corrected by Livingston *et al.*[6] in 1960 when the adduct was correctly identified, but not before Hirshberg and Fischer[7] reported that the Wizinger product, which he believed to be **5,** was not photochromic.

In 1966, Becker and Michl[8] reported for the first time on the photochromism of 2*H*-1-benzopyrans. Becker investigated more than 25 compounds and found that "in



Scheme 1

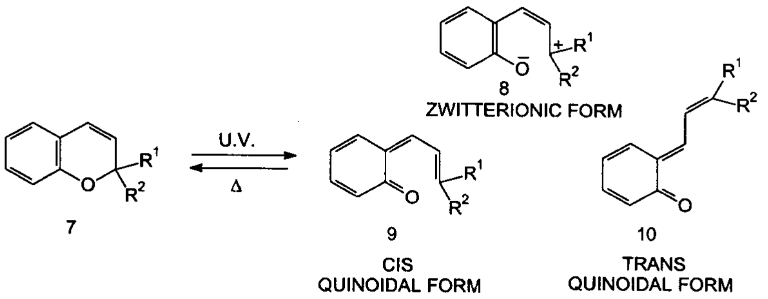
some cases, colorless to colored conversion can be accomplished at room temperature." Some general relationships were described, for example, "benzo annellation in positions 5,6 or 7,8 increases the stability of the colored form; benzo annellation in 6,7 decreases it," but detailed photochromic properties of specific compounds were not presented. In a 1971 U.S. patent,[9] Becker described the photochromism of **5** in example (o) as "changes to orange with ultraviolet irradiation below about –40°C then bleaches to colorless at room temperature." A room temperature laser flash study on **5** reported by Lenoble and Becker[10] in 1986 correctly reports the color of the open form as being yellow (absorbance maximum at 430 nm), but fails to shed light on the lifetime of the colored form at room temperature, saying only that it is "stable to above 400 microseconds."

3.1.3. Current Review

Recent interest in the photochromism of benzo and naphthopyrans has been sparked by commercialization of photochromic plastic ophthalmic eyeware in the early 1990s. The research and development oganizations of several companies [PPG Industries and Essilor International (joint partners in Transitions Optical), Pilkington PLC, Tokuyama Soda, and Rodenstock to name a few] have studied benzo and naphthopyrans for their potential in offering complementary colors (yellow to orange) to the better-known (blue) indolinospironaphthoxazines. This work has led to a large number of patents that have been issued or published in the past five or so years. This review chapter (covering information through early 1996) attempts to put all this recent work in perspective by including practical information, when it is available, on equilibrium response in solution and/or plastic substrates, absorption maxima of the open and closed forms, methods of incorporation, fatigue rates, stabilization, and synthetic methodology. To highlight the emphasis in this book on synthesis, detailed preparation schemes are given for a few key examples. This is the first comprehensive review on the photochromism of benzo and naphthopyrans, and should prove to be a useful resource to those working in this area. A note of caution: Although the amount of information that has been published over the past five or so years has been large, most of it is contained in the patent literature, where broad claims are occasionally made (especially in the area of lifetime or "fatigue") that are frequently unsubstantiated in the accompanying experimental details. In addition, most of the data from the patent literature tend to be qualitative in nature.

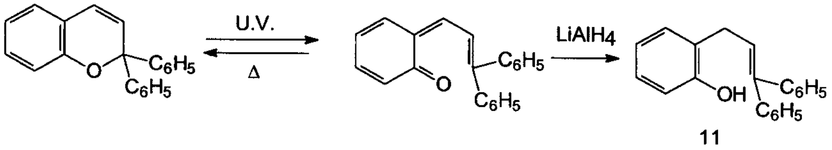
3.1.4. Photochromic Mechanism

By analogy to the spiropyrans, the photochromism of benzo and naphthopyrans is believed to involve the breaking of the oxygen–carbon bond of the pyran, as shown in Scheme 2. Kolc and Becker[11] showed that this is indeed the case by reducing the open form of a benzopyran at low temperature with lithium aluminium hydride (Scheme 3). The resulting phenol (**11**) was identified by spectroscopic techniques (IR and NMR). A more difficult question relating to the photochromism of benzo and naphthopyrans is which electronic and/or geometric configuration best



Scheme 2

describes the open form, i.e., zwitterionic (**8**), cis quinoidal (**9**), or trans quinoidal (**10**)? The limited solvatochromism observed for the open form of the majority of benzo and naphthopyrans would lend support to an uncharged quinoidal species vs. the charged zwitterionic state. On the other hand, it is likely that certain substituents at what could be termed "special positions" (see Sections 3.2.2.5 and 3.2.2.6) stabilize and therefore increase the proportion of zwitterionic character of the open form. Crano *et al.*[12] reported, without providing details, that low-temperature NMR studies of the open form of 3,3-diphenyl-3*H*-naphthol[2,1-*b*]pyran supports a structure best represented by a quinoidal species. As will be discussed in detail in later sections, the predominance of a cis vs. trans quinoidal species will depend on substituents, and in the case of the naphthopyrans **3** and **4**, the parent structure.



Scheme 3

3.1.5. Performance Testing

For testing performance, photochromic compounds should be placed in an environment (i.e., substrate or matrix) that relates to their proposed end use. For example, benzo and naphthopyrans being considered for use in ophthalmic eyeware should be incorporated into an optical plastic. Photochromic optical plastics can be prepared by an imbition process[13] or the compounds can be mixed with a monomer and cast by methods described for oxazines.[14] In the latter process, the photochromic compounds must withstand the casting process, that is, exposure to free radical initiators. Samples being compared should have identical levels of photochromic compounds present. Photochromic properties can be conveniently measured[15] at room temperature on an apparatus (Figure 3.2) employing a triangular optical bench equipped with a 300-W xenon arc lamp (components available from Ealing Electro-

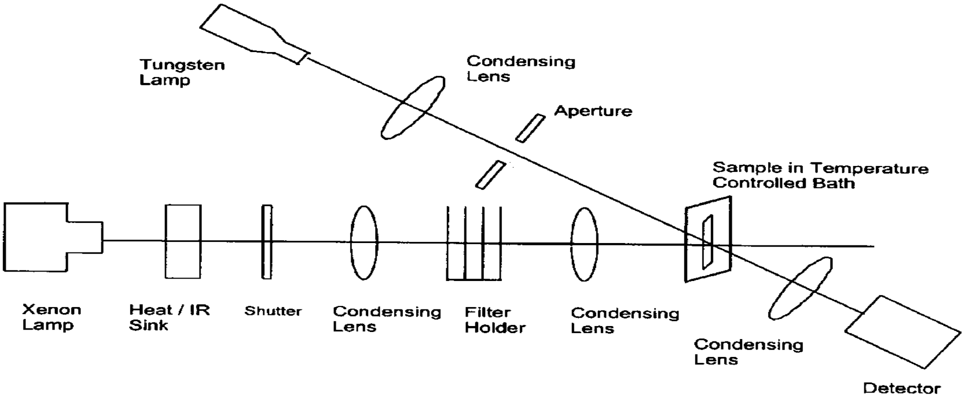
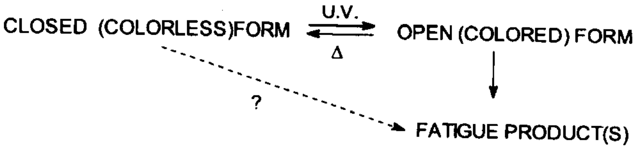


Figure 3.2. Triangular optical bench.

Optics Inc., Holliston, MA). Light from the lamp is passed through a copper sulfate solution to remove infrared, a neutral density glass filter to regulate irradiance, a shutter assembly, and the sample. The optical density of the sample is determined using a tungsten lamp, a bandpass filter, and a silicon detector mounted on a separate optical bench positioned at an angle to the first bench. The photochromic response of the sample is defined as the change in optical density (ΔOD) upon exposure to the light from the xenon lamp as measured through the bandpass filter. The change in optical density is determined as a function of time of exposure, and both an initial rate of change, calculated from a 30-s reading, and a 10 to 20-min equilibrium or steady-state response are determined for each sample. After achieving the steady-state condition, exposure to the activating radiation is discontinued and the rate of fade is measured. The fade rate is normally expressed as $t_{1/2}$, which is defined as the time in seconds required for the sample to return to a ΔOD of one-half the equilibrium value.

3.1.6. Fatigue Testing

The loss of response in a photochromic system (i.e., the irreversible formation of nonphotochromic products) is commonly referred to as “fatigue” (Scheme 4). Although the open form is most commonly implicated, both the closed and open forms of a photochromic molecule may be capable of undergoing such nondesirable thermal or photochemical reactions. Much like dyes, organic photochromic compounds are more fatigue prone than those based on inorganic chemistry. Fatigue has therefore limited the utility of organic photochromes in applications involving prolonged exposure to intense heat or ultraviolet light.

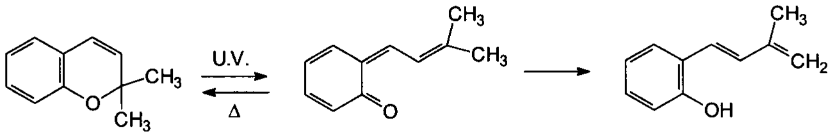


Scheme 4

Samples should be prepared for fatigue tests using the same considerations that have applied to the performance test samples. Although in most applications of photochromics, activation is brought about by solar exposure, it is usually not convenient to fatigue test articles in the sun. The intensity of sunlight will vary from day to day, depending on weather conditions and the time of the year (angle of the sun). The total amount and spectral composition of the UV will also depend on the angle and direction of exposure. A more constant source of light in a controlled environment is therefore routinely used in place of solar exposure. An example of a frequently used instrument is the Q.U.V. Accelerated Weathering Tester sold by the Q-Panel Co., Cleveland, OH. Various manufacturers also sell solar simulators based on xenon light sources. Regardless of the artificial light source used, a relationship has to be developed to extrapolate results from these accelerated tests to solar exposure (assuming the photochromic article will be used outside). After a sample is exposed in the test device for a period of time, it is routinely performance tested to determine the loss in response brought about by the simulated use. This loss can be proportional to the destruction of photochromic molecules within the sample or it could appear much greater than the actual loss if decomposed photochromic molecules form a UV screen, preventing activation of molecules lying beneath it. Regardless of how photochromism is lost, fatigue is routinely expressed as a half-life, i.e., $t_{1/2}$. The $t_{1/2}$ is the time required for half of the equilibrium or steady-state response to be lost.

3.1.7. Fatigue Specific to Pyrans

Early studies by Padwa *et al.*[16] showed that the irradiation of 2,2-dimethylbenzopyran in acetone yielded 2-methyl-4-(2-hydroxyphenyl)-1,3-butadiene as the exclusive photoproduct. The reaction was rationalized as proceeding through a quinoidal ring-opened intermediate (**12**), followed by a 1,7-sigmatropic hydrogen shift to yield (**13**) (Scheme 5). As a result of this problem with pyrans having a C–H grouping on the carbon adjacent to the pyran oxygen, efforts to find more fatigue-resistant compounds within this class of photochromics have focused on molecules with an alternative substitution.



12 13

Scheme 5

3.1.8. Stability and Stabilization

It is difficult to specifically state the expected lifetime of a class of photochromic molecules because lifetime can be dramatically affected by such factors as concentration, environment (i.e., matrix), stabilizers, strength and spectral profile of impinging light, as well as substituents. On the other hand, it is fair to say that some of the more stable naphthopyrans approach the photostability of the indolinospironaphthoxazines, a class of photochromic molecules generally recognized as possessing exceptional stability.[17] This statement is based on the high level of research in this area that has led to the inclusion of pyrans in commercial products by all of the major plastic photochromic lens manufacturers[18] (Transitions Optical, Hoya, Seiko, Rodenstock, and INDO).

Stabilizing molecules that have been claimed[19] as having a beneficial effect on photochromes fall into three general classes: hindered amine light stabilizers (HALS), UV absorbers, and antioxidants. Occasionally combinations of these materials have been found to have an enhanced effect when compared with the stabilization brought about by the individual components of a mixture.[20] Contact with water, oxygen, and free radicals has been reported to exacerbate fatigue problems.[21] Often a number of undefined factors will influence the effectiveness (or lack thereof) of any stabilization additive. As a result, the Edisonian approach (trial and error) is generally relied upon in developing a stabilizer package. This is especially true when dealing with mixtures of photochromic compounds.

3.2. 3*H*-NAPHTHO[2,1-*b*]PYRANS

3.2.1. Nomenclature

The very early literature refers to 3*H*-naphtho[2,1-*b*]pyrans as 5,6-benzo-2*H*-1-benzopyrans. The common term *chromene* is frequently used in place of the more

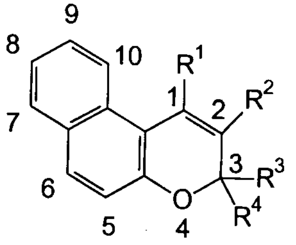


Figure 3.3. Numbering system for 3*H*-naphtho[2,1-*b*]pyrans.

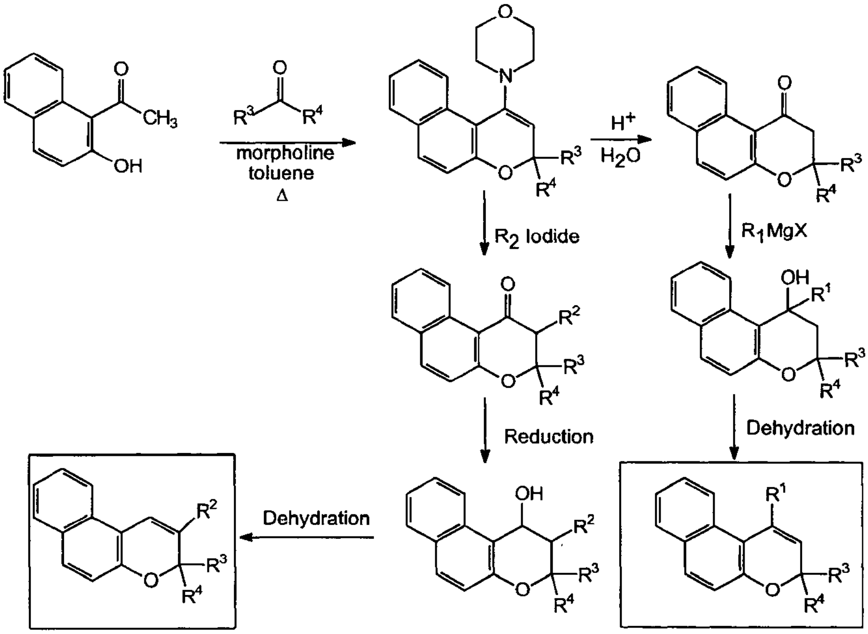
correct *2H-1-benzopyran.* As a result, the naphthopyrans have been called *benzochromenes* or very incorrectly simply *chromenes.* The structure and numbering system for the 3*H*-naphtho[2,1- *b*]pyrans is shown in Figure 3.3.

3.2.2. Structure–Photochromic Activity Relationships

3.2.2.1. Substitution at the 1- and 2-Positions

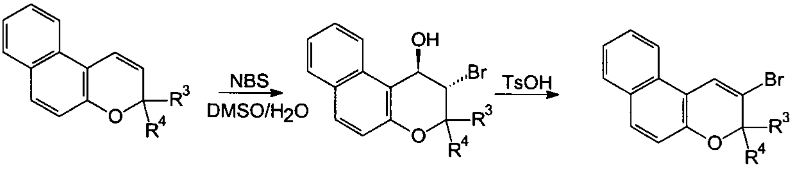
The great majority of patents require hydrogens at the 1- and 2-positions, leading one to believe that alternative substitution leads to greatly diminished photochromism. This would most likely not be a result of inhibition of the photochemical ring opening (or bond breaking) but rather a result of steric inhibition of bond rotation or isomerization, allowing the reactive centers to become remote from each other. Nevertheless, compounds containing substituents such as methyl at these positions have been claimed in the photochromic patent literature.[22]

Compounds substituted in the 1- and 2-positions are best prepared by the series of reactions outlined in Scheme 6.[22] The first step in the sequence (condensation of a hydroxyacetonaphthone with a ketone or aldehyde) gives good yields only in cases where R_3 and/or R_4 are not aryl.[23] Condensation with a diaryl ketone (i.e., a benzophenone) can be accomplished in low yield with sodium *t*-butoxide in



Scheme 6

refluxing benzene.[24] Kelly and Vanderplas[25] have reported on an improved version of the Kabbe condensation that is useful with base-sensitive substrates. Gabbutt *et al.*[26] have reported that benzopyrans (and 3*H*-naphtho[2,1-*b*]pyrans) can be substituted with bromine in the 2-position using the sequence shown in Scheme 7.



Scheme 7

3.2.2.2. Substitution at the 3-Position

A reasonable level of room-temperature photochromism in polymer matrix requires that the pyran be substituted at the 3-position with conjugative substituents such as phenyl. This enhanced photochromism of aryl-substituted pyrans was noted early on by Becker and Michl.[8] Pyrans containing aryl groups at the 3-position also have improved fatigue resistance compared with compounds substituted at the 3-position with groups containing α-hydrogens (see Section 3.1.7). The photochromic properties of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran and related compounds are shown in Table 3.1.[15] The rapid fade and low steady-state optical density at room temperature for the compounds described in Table 3.1 are believed to be caused by steric destabilization of the trans quinoidal form (Figure 3.4). Note the juxtaposition of the two highlighted hydrogens in **14.** The destabilization of this open form would mean that once ring opening occurs, conversion from the cis-quinoidal to the trans-quinoidal species would be unlikely and that the molecule would be positioned to undergo a rapid ring reclosure to the colorless ground state. This would be visually observed as a very rapid fade or perhaps in extreme cases, as a lack of photochromism at room temperature.

The visible and UV spectra for 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran are shown in Figures 3.5 and 3.6. From the UV spectrum it can be seen that 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran has a reasonable absorption in the UVA region (320–400 nm). As a result, this compound (and its analogs) activate (color) in normal unfiltered sunlight. The visible spectrum, which is typical of 3*H*-

Table 3.1. Photochromic Properties of (Substituted) 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran Imbibed into Polymerizates of Diethyleneglycol bis(allyl carbonate)

Phenyl substituents	λ_{max} (visible) (nm)	Δ*OD* Steady-state	*FadeT*$_{1/2}$ (s)
None	432	0.36	45
p-MeO	468	0.25	35
p-MeO, *p*'-MeO	480	0.15	40

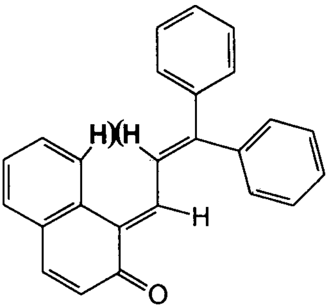


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Figure 3.4. Steric destabilization of the trans quinoidal open form of 3,3-diphenyl-3*H* -naphtho[2,1-*b*]pyran.

naphtho[2,1-*b*]pyrans, is broad with a bandwidth at half peak height of approximately 80 nm. These spectral properties make this class of compounds useful in a variety of applications. The data in Table 3.1 can be used as a guide for estimating performance in other carriers, for example, solvents. A general rule of thumb for solvents vs. polymers is that one would expect the activation and fade rates to be considerably faster and the resulting intensity much lower in the former. The opposite would be true (slower activation and fade with higher optical density) in polymers that are more rigid than polymerizates of diethyleneglycol bis(allyl carbonate).

Substituents on the phenyl groups of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran can have substantial effects on color, intensity, and fade. Electron-donating groups in the para position(s) result in a bathochromic shift in the visible spectrum, a lower equilibrium intensity, and a somewhat more rapid fade (Table 3.1). An additional

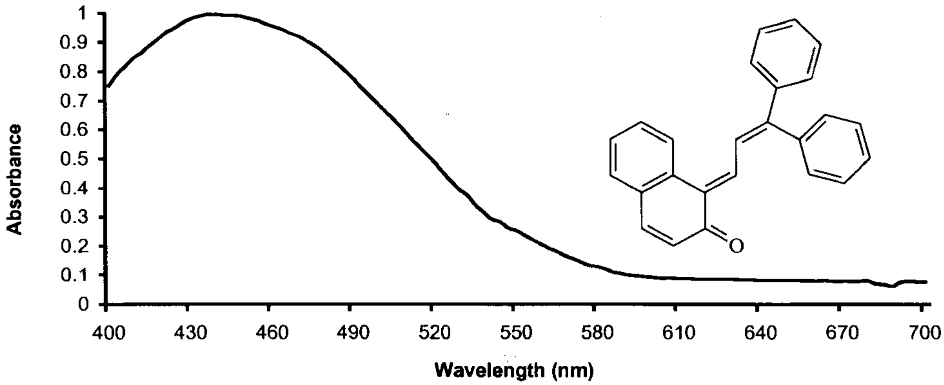


Figure 3.5. Visible spectrum of open form of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.

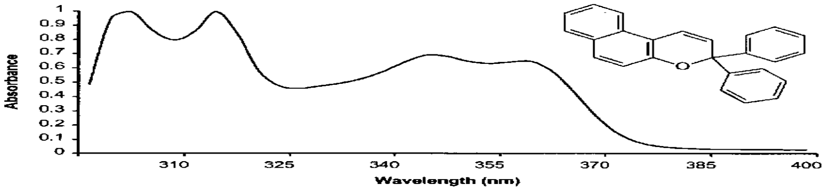


Figure 3.6 UV spectrum of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.

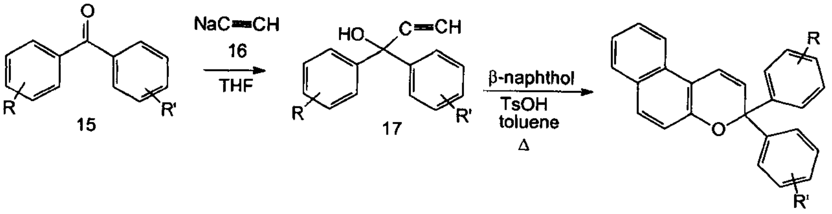
color shift can be obtained by incorporating the electron-donating substituent (such as oxygen) located at the para position into a fused five- or six-membered ring.[27] The additional bathochromic shift can be attributed to a better overlap of a nonbonding electron pair on oxygen (or nitrogen) with the π-orbitals of the benzene ring. Not unexpectedly, substitution at the meta position of the aryl group(s) (a position that cannot participate by resonance with any charge developed in the open form) has a limited effect on the properties of the colored species. Ortho substitution,[28] which might be expected to have effects similar to para substitution, unexpectedly dramatically enhances optical density and slows the rate of fade. Data that demonstrate the effect of ortho substitution can be found in Table 3.2. The increase in optical density can for the most part be attributed to a slowing of the fade rate. The fade rate order for 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran having an ortho substituent on one of the aryl groups appears to have an inverse correlation to the size of that substituent (H>> F > $OCH_3 \approx CH_3$). Any difference in methyl and methoxy may be due largely to electronic effects (i.e., donating groups at conjugative positions increasing fade) superimposed upon the steric effect of these groups.

The synthesis of 3*H*-naphtho[2,1-*b*]pyrans substituted in the 3-position with aryl groups is most easily accomplished by the two-step process outlined in Scheme

Table 3.2. Photochromic Properties of Ortho-Substituted 3,3-Diaryl-3*H*-naphtho[2,1-*b*] pyrans Imbibed into Polymerizates of Diethyleneglycol bis(allyl carbonate)

Aryl substituents	λ_{max} (visible) (nm)	Δ*OD* Steady-state	Fade $T_{1/2}$ (s)
o-F, *p*'-MeO	456	1.00	170
o-F, m',*p*'-diMeO	472	1.05	203
o-Me, *p,p*'-diMeO	475	1.36	510
o-Me, *p*'-MeO	469	2.40	> 600
o,p- diMeO	455	1.42	510
o,o-diF, *p*'- MeO	450	2.23	> 1800

8. In this sequence[29,30] a (substituted or unsubstituted) benzophenone (**15**) is reacted with sodium acetylide (**16**) in an ether solvent at room temperature to yield a 1,1-diaryl-2- propyn-1-ol (**17**). This intermediate can be condensed with a β-naphthol in the presence of an acid catalyst at 30 to 50°C to yield the pyran.

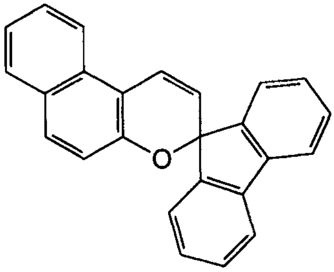


Scheme 8

Photochromic 3*H*-naphtho[2,1*b*]pyrans containing a 3-aryl grouping (substituted or unsubstituted phenyl or naphthyl) and a 3-heteroaromatic group (thienyl, furanyl, and the like) have been patented.[31] Although these compounds offer the disadvantage of a more involved synthesis using more expensive starting materials, they are reported to have a greater Δ luminous transmission than 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.

Yet another variation on the same theme links the two aryl groups together [32–34] to form spirofluorenylidene (**18**) spirosuberenylidene (**19**) and the like (Figure 3.7). The photochromic properties of these compounds (intense and slow to fade) are best explained if one considers them di-ortho-substituted 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans.

The synthesis of photochromic compounds from a diarylpropargyl alcohol and a di-β-hydroxynaphthalene (2,3- or 2,6- or 2,7-) yields a dipyran.[35] Scheme 9 shows the preparation of a dipyran (**21**) from 2,6-dihydroxynaphthalene (**20**). The photochromic properties of these compounds are quite similar to those of a 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran with an oxy-containing heterocycle fused to the naphtho



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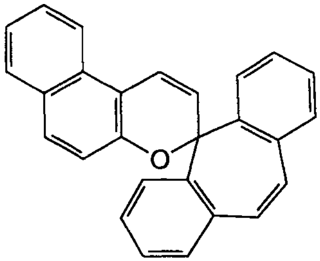

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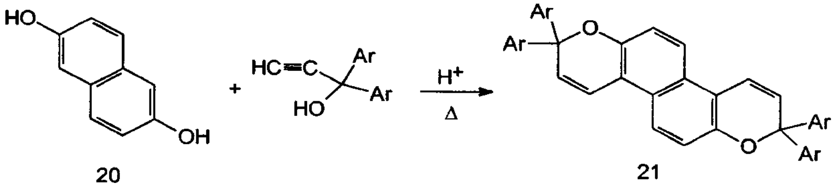
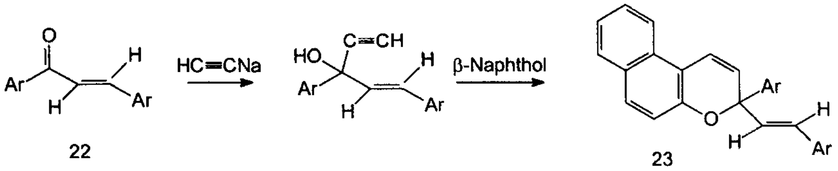
Figure 3.7. Spiro (3*H*-naphtho[2,1- *b*]pyran-3,9'-fluorene) and spiro (3*H*-naphtho[2,1-*b*]pyran-3,5'-dibenzosuberene).

portion of the molecule. That is, it appears unlikely that more than one pyran ring opens on exposure to UV at any given time in any single molecule.



Scheme 9

3,3-Diaryl-3 *H*-naphtho[2,1- *b*]pyrans with a double bond inserted between one of the aryl groups and the pyran (**23**) have been prepared[36] by substituting a chalcone (**22**) (benzylideneacetophenone) in place of a benzophenone in the standard propargyl alcohol synthesis (Scheme 10). The added double bond results in the colored (open) form absorbing at longer wavelengths than a similarly substituted 3,3-diaryl-3*H*-naphtho[2,1- *b*]pyran.



Scheme 10

3.2.2.3. Pyran Substitution via Heteroaromatic Annellation

Irie has studied a series of 3*H*-naphtho[2,1-*b*]pyrans containing aromatic and heteroaromatic groups annellated at the 2- and 3-positions.[37–39] When a heteroaromatic group is fused in one orientation, a reverse photochromic system is produced (Figure 3.8) in which the naphthopyran (**24**) is the colored form (yellow). On

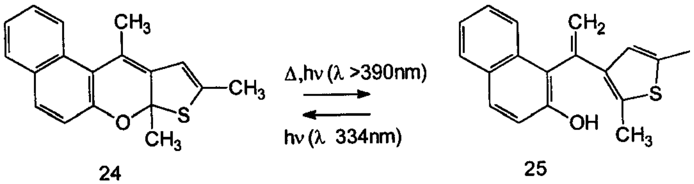


Figure 3.8. A reverse photochromic system.

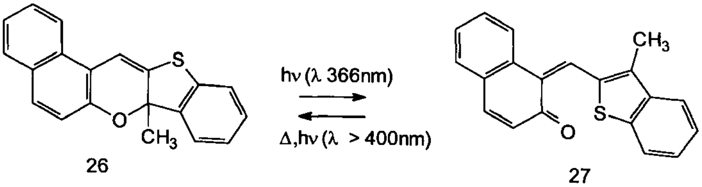


Figure 3.9. Photochromic heteroaromatic annellated 3*H*-naphtho[2,1-*b*]pyran.

exposure to visible light or strong heating, the pyran converts to a (colorless) vinyl naphthol (**25**). Exposure to UV reverts the naphthol to the pyran. When the heteroaromatic group has the opposite orientation (**26**) (Figure 3.9) and the methyl at the 1-position is removed, a much more normal photochromic system is produced. Replacement of benzthieno in **26** with naphtho[40,41] yields a yellow quinoidal open form analogous to **27** that undergoes further photochemistry.

3.2.2.4. Substitution at the 5-Position

Oxy substituents (methoxy, acetoxy) result in a hypsochromic shift of approximately 36 nm in the UV spectrum of the closed form. This hypsochromic shift in the UV would be expected to negatively affect the solar response of these compounds. While a 5-methoxy has no influence on the color of the open form, a 5-acetoxy (and several related groups) [42,43] results in a bathochromic shift (in the case of acetoxy) of 25 nm. This lengthening of the chromophore of the colored species (**28**) can be attributed to participation of the 5-substituent as shown in Figure 3.10.[15]

3.2.2.5. Substitution at the 6-Position

Electron-donating substituents (alkoxy[44] and amino[45,46] result in a bathochromic shift and an increase of the extinction coefficient of the long wavelength

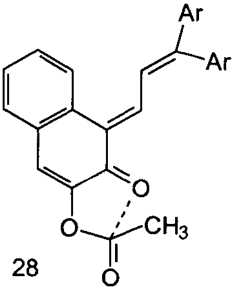
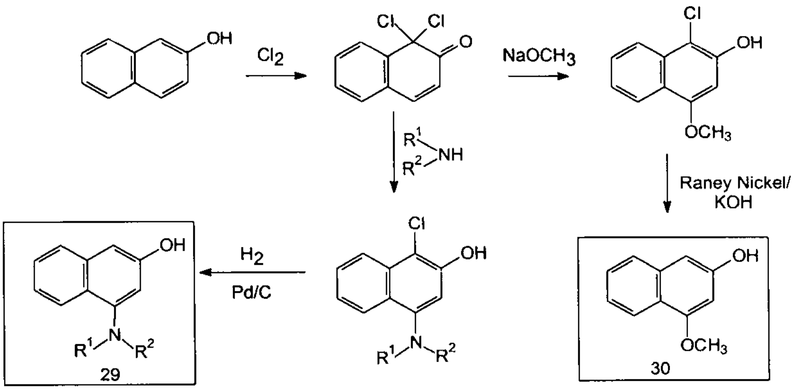


Figure 3.10. Participation of a 5-acetoxy group in the chromophore of the open form.

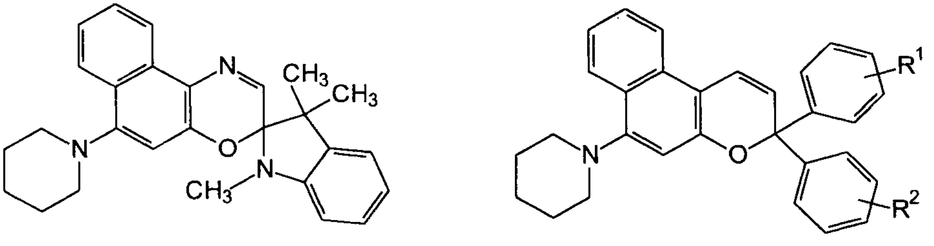
absorbance in the UV spectrum of the closed form. The color of the open form is shifted hypsochromically and the saturation optical density is increased. New chemistry has been developed (Scheme 11) for the preparation of the relatively unknown 1-alkoxy and 1-amino-3-hydroxynaphthalenes required for the synthesis of these derivatives. Comparative photochromic properties for representative 6-alkoxy and 6-amino-3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans are shown in Table 3.3. In many ways the effects on the photochromic properties brought about by a 6-substituent in the 3*H*-naphtho[2,1-*b*]pyrans is similar to those seen in the 6'-amino naphthoxazines.[47] Structural comparisons for these two classes (**31**), (**32**) of photochromic molecules are shown in Figure 3.11. The term *hyperchromism* has been used to describe[48] substitution at this position and its effects on photochromic response. An additional zwitterionic open form (**33**) can be drawn for 6-amino- (or alkoxy-)3*H*-naphtho[2,1-*b*]pyrans (Figure 3.12). This may be invoked to explain the unusual properties of the colored species of this series of compounds.



Scheme 11

Table 3.3. Photochromic Properties of 6-Alkoxy and 6-Amino-3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans Internally Cast in Polyurethane

Substituents		Transmission (%)		
3,3-Phenyl	6-Position	Bleached	Activated	λ_{max} (nm)
4-MeO,4'-MeO	1-Piperidino	86	58	452
4-MeO,4'-MeO	1-Morpholino	87	58	452
4-MeO,4'-CF3	1-Morpholino	90	75	432
4-MeO,4'-MeO	Methoxy	81	59	455
4-MeO,4'-MeO	H	91	84	490
2,4-MeO,4'-MeO	H	90	58	488



6'-piperidinonaphthoxazine (31) 6-piperidino-3H-naphtho[2,1-b]pyran (32)

Figure 3.11. Structural comparison of photochromic 6'-piperidinonaphthoxazines and 6-piperidino-3*H*-naphtho[2,1-*b*]pyrans.

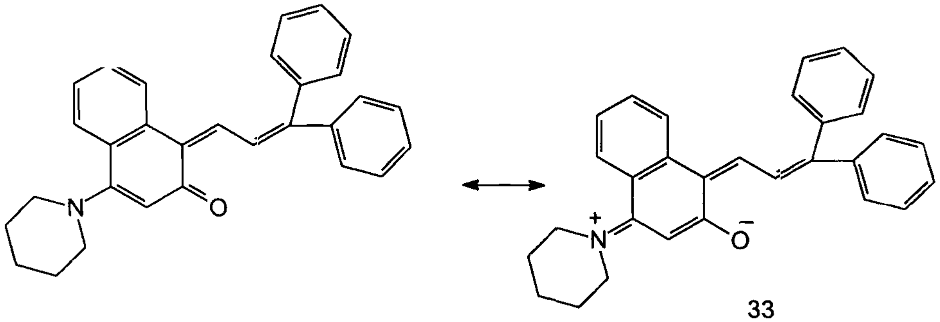


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Figure 3.12. Resonance contributors to the open form of 6-piperidino-3*H*-naphtho[2, 1-*b*]pyran.

3.2.2.6. Substitution at the 8-Position

Electron-donating substituents (alkoxy[49,50] and fused five- and six-membered rings containing oxygen and nitrogen[51]) at the 8-position of a 3*H*-naphtho[2,1-*b*]pyran result in a bathochromic shift in both the UV of the closed form and the visible spectrum of the open form. The fade rate of the open form is slowed, with a resulting enhancement of the steady-state optical density. In Table 3.4 the photochromic properties of 8-methoxy-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran are compared with isomeric compounds with methoxy at other positions on the naphtho portion of the molecule. As is the case with alkoxy and amino substituents in the 6-position, an additional zwitterionic form (**34**) can again be drawn for the open form of 8-alkoxy (or amino) 3*H*-naphtho[2,1-*b*]pyrans (Figure 3.13). A notable difference when comparing zwitterionic resonance forms (**33**) and (**34**) is that in **34,** the aromaticity is destroyed in both of the rings within the naphtho portion of the molecule, whereas in **33,** aromaticity is lost in only one. The net result should be that **34** is a higher energy species and less of a contributor to the hybrid than would be expected for **33.**

Table 3.4. Substitution of Methoxy on the Naphtho Portion of 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran: Effect on Photochromic Properties of Compounds Imbibed into Polymerizates of Diethyleneglycol bis(allyl carbonate)

Substituent	λ_{max} (visible) (nm)	λ_{max} (UV)(nm)	Sensitivity (ΔOD/min)	ΔOD (sat.)
5-MeO	432	323	0.49	0.46
7-MeO	432	365	0.92	0.39
8-MeO	473	376	1.25	0.73
9-MeO	426	329	0.62	0.31

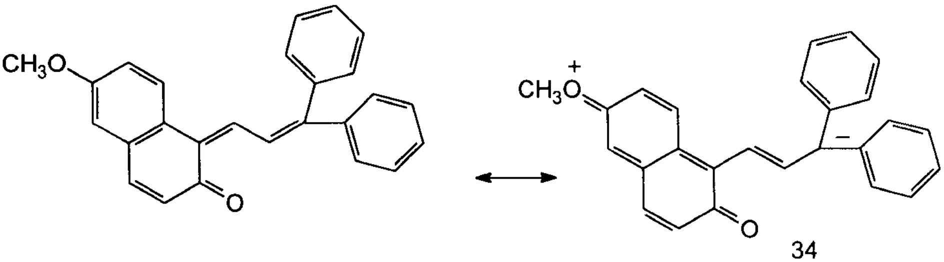

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Figure 3.13. Resonance contributors to the open form of 8-methoxy-3*H*-naphtho[2,1-*b*]pyran.

3.2.2.7. Substitution at the 7-, 9-, and 10-Positions

Electron-donating groups such as methoxy have little effect at the 7- and 9-positions (Table 3.4) or have not been reported (10-position) owing to the unavailability of starting material. Flanking an 8-alkoxy group with a 7-alkyl or 9-carboxy group[52] enhances the photochromic effect under solar conditions, primarily as a result of further shifting UV absorptions closer to the threshold of the visible.

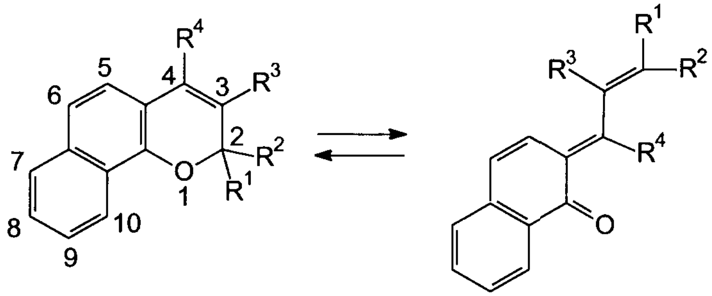
3.2.2.8. General Note

Several patents dealing with 2*H*-naphthol[1,2-*b*]pyrans also claim the 3*H*-naphtho[1,2-*b*]pyrans and 2*H*-1-benzopyrans as a matter of course. In cases where the 3*H*-naphtho[2,1-*b*]pyrans are of little utility due to low steady-state optical density at room temperature, the references will be discussed under the following section dealing with the 2*H*-naphtho[1,2-*b*]pyrans.

3.3. 2*H*-NAPHTHO[1,2-*b*]PYRANS

3.3.1. Nomenclature

The structure and numbering system for 2*H*-naphtho[1,2-*b*] pyrans (**35**) are shown in Figure 3.14. The color of the open form of 2*H*- naphtho[1,2-*b*]pyrans (**36**),



35 **36**

Figure 3.14. 2*H*-Naphtho[1,2-*b*] pyrans, closed and trans quinoidal open forms.

Table 3.5. Comparative Photochromic Properties of 2,2-Diphenyl-2*H*-naphtho[1,2-*b*]pyran (A) and 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran (B) Imbibed into Polymerizates of Diethyleneglycol bis(allyl carbonate)

Compound	$\lambda_{\max}$ (visible) (nm)	$\lambda_{\max}$ (UV) (nm)	Fade $t_{1/2}$ (s)	ΔOD (sat.)
A	476	355	> 1800	1.37
B	432	359	45	0.36

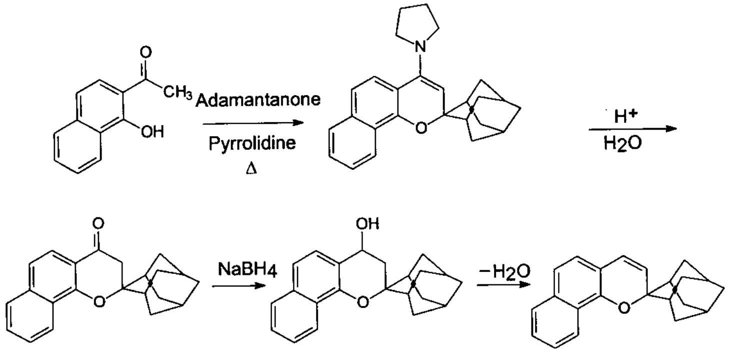
relative to similarly substituted 3*H*-naphtho[1,2-*b*]pyrans, is bathochromically shifted, more intense, and slower to fade (Table 3.5). These properties are believed to be due in part to the stability (lack of steric interactions) of the trans quinoidal open form **(36)** shown in Figure 3.14. Compare this with (**14**) in Figure 3.4.

3.3.2. Substituent Effects

3.3.2.1. Substitution at the 2-Position

The first 2*H*-naphtho[1,2-*b*]pyran patented[30] that is described as having acceptable properties (intensity, fade, fatigue) for use in plastic photochromic ophthalmic lenses contains the spiro adamantylidene group at the 2-position (compound **37,** Scheme 12). The bulky adamantylidene group is reported to enhance the quantum efficiency of ring opening by weakening the C–O bond in the pyran. At the same time, fatigue via a 1,7-hydrogen shift would result in a violation of Bredt's rule (the disallowance of bridgehead double bonds). In polymerizates of diethyleneglycol bis(allyl carbonate), **37** is yellow ($\lambda_{\max}$ 449 nm) in the activated state with a fade $t_{1/2}$ equal to 225 s. Complete conversion from the colored to colorless form has been found to require a substantial amount of time. For example, plastic substrates containing this compound that are activated and then placed in the dark are observed to retain some coloration for a day or more. At present, this phenomenon is not fully understood.

Following up on this work, additional patents have issued covering related compounds incorporating at the 2-position, spiro bicyclo[3,3,1]9-nonylidene[53] as well as spiro 2-norbornanylidene and the like.[54] These compounds are best prepared via the Kabbe[23] synthesis as outlined in Scheme 12.



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Scheme 12

2*H*-Naphtho[1,2- *b*]pyrans have been patented[55] that are purple in the activated state. These contain, in addition to a methyl at the 2-position, a phenyl containing ortho and/or para amino functionality. While these compounds have intensely colored open forms, they appear to be of little use due to fatigue problems associated with the previously discussed potential of the colored species undergoing an irreversible sigmatropic 1,7-hydrogen shift.

2*H*-Naphtho[1,2- *b*]pyrans containing 2-cyclopropyl-2-aryl (and heteroaryl) substitution[56] as well as 2,2-dicyclopropyl substitution[57] have been patented. The cyclopropyl groups with their partial double-bond character tend to lengthen the chromophore compared with 2-alkyl-substituted 2*H*-naphtho[1,2-*b*]pyrans, resulting in bathochromically shifted open forms.

Substitution of two aryl groups at the 2-position results in an extremely intense orange photochromic compound that is very slow to fade in solution and polymers[15] (Table 3.5). It has been reported that the fade rate in solution can be promoted by the addition of minor amounts of acids and bases.[58] It is not known if this principle can be applied to plastic substrates.

3.3.2.2. Substitution at the 5-Position

A better method of promoting fade in 2,2-diaryl (and other) 2*H*-naphtho[1,2-*b*]pyrans is to introduce a substituent at the 5-position. Such substitution produces steric crowding in the trans quinoidal open form (see Figure 3.14). The steric crowding will result in a destabilization of the colored species and a more rapid conversion (fading) to the colorless ground state. Methyl has been introduced in the 5-position for this purpose.[59] The synthesis of the starting material for these 5,6-

Table 3.6. Photochromic Properties for a Series of 2,2-Diaryl-5-Substituted 2*H*-naphtho[1,2-*b*]pyrans Internally Cast in Polymethacrylate

Phenyl substituent	5-Substituent	6-Substituent	Δ*OD* (sat.)	Fade $t_{1/2}$ (s)	λ_{max}(nm)
(None)	H	H	1.37	> 1800	476
4,4'-diMeO	$COOCH_3$	MeO	0.48	305	510
(None)	$COOCH_3$	CH_3CH_2COO	0.19	257	470
4,4'-diMeO	$COOCH_3$	CH_3	0.42	217	505
(None)	CH_3	H	1.29	640	482

dimethyl-2*H*-naphtho[1,2-*b*]pyrans (3,4-dimethyl-1-naphthol) is not disclosed and may be difficult. Alkoxycarbonyl (and related functionality) at the 5-position has also been reported[60] to promote fade. A comparison of photochromic properties for a series of 2,2-diaryl-5-substituted-2*H*-naphtho[1,2-*b*]pyrans is shown in Table 3.6.

The color, rate of fade, and intensity of 2,2-diphenyl-5-alkoxycarbonyl-2*H*-naphtho[l,2-*b*]pyran will be further affected by additional substituents on the molecule. As can be seen in Table 3.6, para methoxy(s) on the phenyls speeds the fade and bathochromically shifts the colored form. Electron-donating groups at the 6-position have a similar effect on the color but tend to slow the fade. The enhanced rate of fade brought about by the 5-carbomethoxy can be further promoted by a 6-propionyloxy (or related) group.

The 5- and 6-positions of a 2*H*-naphtho[1,2-*b*]pyran can be linked together with a fused indeno group[61] as shown in Figure 3.15. The resulting substituted or unsubstituted methylene bridge at the 5-position of this novel naphthopyran serves a dual purpose: It can be appropriately sized by varying its substitution to achieve a desirable fade and intensity for the photochromic compound. It also effectively holds the phenyl group at the 6-position in plane with the naphthropyran, thereby extending the chromophore. The net result is that when the indeno-fused 2*H*-naphtho[1,2-*b*]pyran is substituted at the 2-position with, for example *p*-methoxy phenyls, compounds that are blue in the activated state are produced.

3-Methoxycarbonyl-1-naphthols used to prepare 5-methoxycarbonyl (and related)-2*H*-naphtho[1,2-*b*]pyrans can be synthesized from 3-carboxy-1,4-dihydroxy-naphthalene (which is commercially available), or may be prepared by the sequence

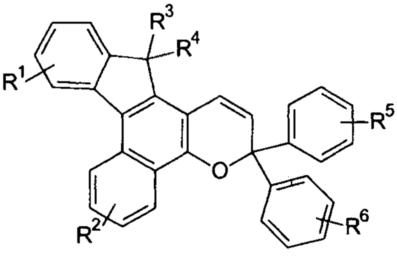
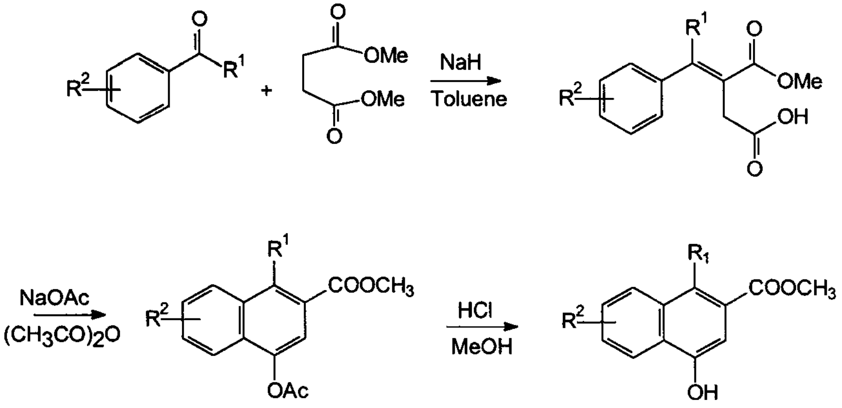
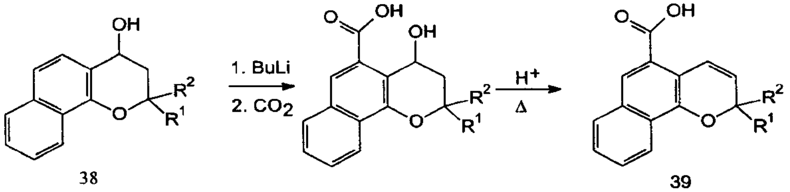


Figure 3.15. General structure of an indeno fused naphthopyran.

outlined in Scheme 13. An additional method of preparation of 5- substituted 2*H*-naphtho[1,2-*b*]pyrans (**39**) involves directed lithiation[62] of 4-hydroxy-2*H*-naphtho[1,2-*b*]pyran (**38**) (Scheme 14). This chemistry has also been demonstrated for 2*H*-1-benzopyrans.



Scheme 13



Scheme 14

3.4. 2*H*-NAPHTHO[2,3-*b*]PYRANS

The structure and numbering system for 2,2-disubstituted 2*H*-naphtho [2,3-*b*]pyrans is shown in Figure 3.16. Even when R^1 and R^2 in **40** are the conjugative substituents, phenyl, the compound is photochromic only at very low (dry ice– acetone) temperatures. This is most likely owing to the open (colored) form **(41)** being such a high-energy species (unstable) as a result of the loss of aromaticity of both of the rings in the naphthalene nucleus. Two different methods[63,64] that have been used to prepare compounds within this series are shown in Scheme 15.

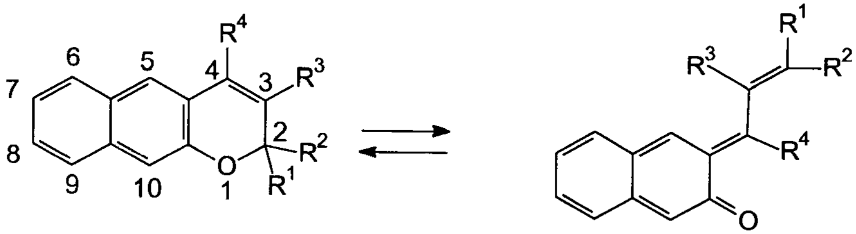


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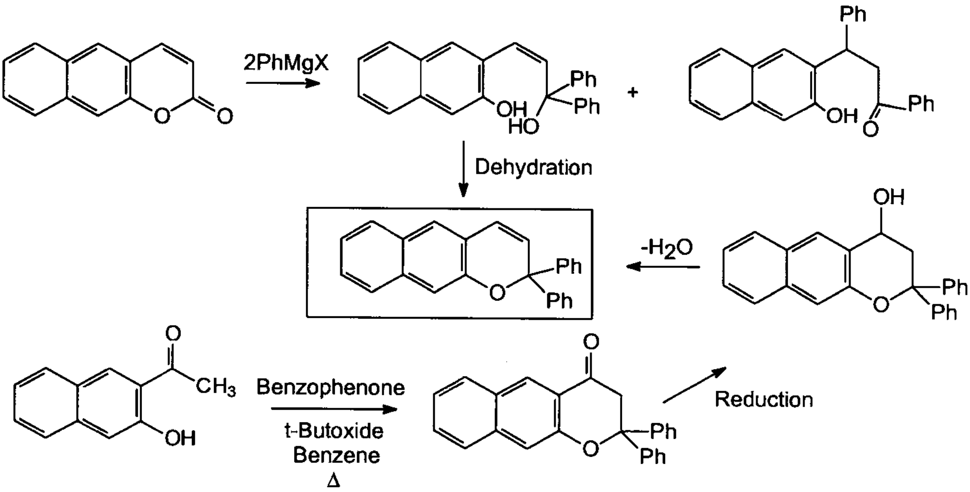
Figure 3.16. 2*H*-Naphtho[2,3-*b*]pyrans, closed and open forms.



Scheme 15

3.5. 2*H*-1-BENZOPYRANS (CHROMENES)

3.5.1. General

As mentioned earlier, 2*H*-1-benzopyrans are often referred to, especially in the older literature, by the common name *chromenes.* The more proper term *2H-1-benzopyran* is used in this chapter even though many of the references cited in this (and earlier) sections have used the chromene terminology. The structure and numbering system for 2*H*-1-benzopyrans is shown in Figure 3.17.

The photochromic properties of a number of naturally occurring 2*H*-1-benzopyrans were studied at low temperatures by Kolc and Becker.[65] A few examples of this structurally diverse class of compounds are shown in Figure 3.18.

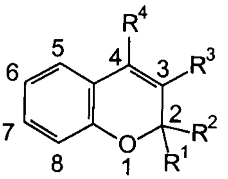
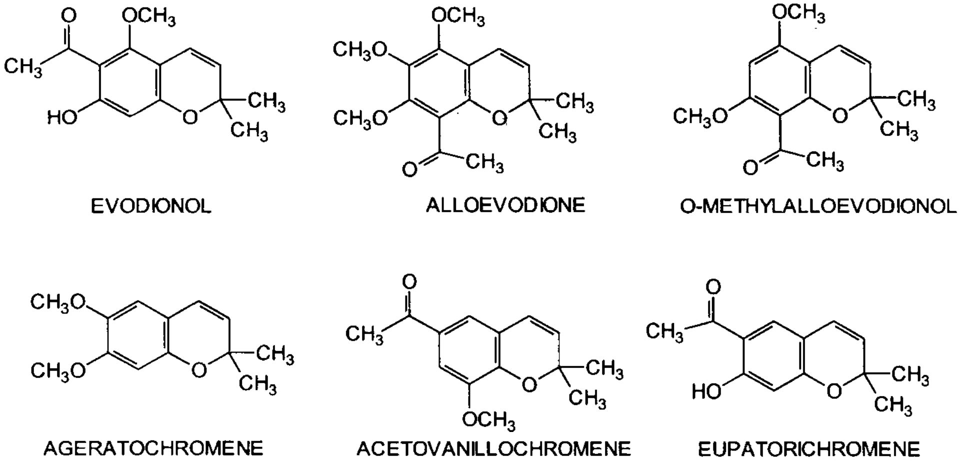


Figure 3.17. The structure and numbering system for 2*H*-1-benzopyrans.



EVODIONOL ALLOEVODIONE O-METHYLALLOEVODIONOL

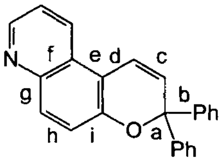
AGERATOCHROMENE ACETOVANILLOCHROMENE EUPATORICHROMENE

Figure 3.18. Naturally occurring 2*H*-1-benzopyrans.

2*H*-1-Benzopyrans are, as a group, less photochromic than 3*H*-naphtho[2,1-*b*]pyrans and 2*H*-naphtho[1,2-*b*]pyrans having the same substituents,[8] and they are more fatigue prone. An additional problem with the 2*H*-1-benzopyrans is that they are less responsive to solar radiation due to their UV absorptions being at lower wavelengths than the naphthopyrans. As a result of these problems, researchers have modified the parent compound in an attempt to provide molecules with commercial potential.

3.5.2. Substituent Effects

The most widely used modification to 2*H*-1-benzopyrans has been heteroaromatic annellation. Guglielmetti has prepared and patented[66] 2*H*-1-benzopyrans with heteroaromatic groups annellated on the (5,6) or f-face. Some representative compounds are shown in Figure 3.19 with **41** showing the lettering system used to designate the faces of 2*H*-1-benzopyran. When the heteroaromatic group is a six-member ring such as pyridine or pyrimidine, the photochromic properties tend to mimic the corresponding naphthopyrans. An X-ray crystal structure of a pyrido-fused 2,2-diphenyl-2*H*-1-benzopyran (**42**) has shown[67] the $(Ph)_2C$–O bond to be elongated compared with standard oxygen-containing heterocycles. This is believed



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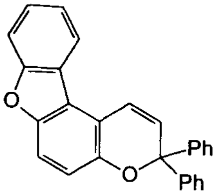

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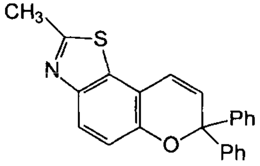
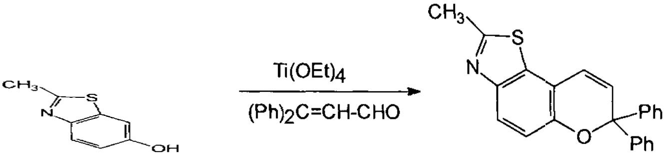


44

Figure 3.19. Representative examples of 2*H*-1- benzopyrans annellated with heteroaromatic groups on the f-face.

to be due in part to steric interactions between the two phenyl groups and probably explains, at least in part, the enhanced photochromism of benzo and naphthopyrans so substituted.

When the annellated heteroaromatic group is a five-member ring (**43, 44**), the properties are best described as intermediate between a naphtho and benzopyran. The standard method of synthesis for diaryl naphthopyrans (acid-catalyzed condensation between a diaryl propargyl alcohol and a naphthol, Scheme 8) is reported[68] not to work for heteroaromatic fused phenols. This is true especially in cases where the heteroaromatic phenol contains a (basic) nitrogen. Alternatively, these pyrans can be prepared by the method of Casiraghi[69] outlined in Scheme 16.



Scheme 16

Kumar[70] has prepared a series of 2*H*-1-benzopyrans with heteroaromatic groups annellated on the f, g, or h face. These compounds have enhanced optical density due to the phenyls at the 2-position being ortho substituted, an effect much like that observed in the 3,3-diaryl-3*H*- naphtho[2,1*b*]pyrans as shown in Section 2.2.2. It is interesting that the colored forms of many of these compounds have very broad, double-humped absorptions. An example of the visible spectrum of a representative compound is shown in Figure 3.20.

Additional modifications to heteroannellated 2-*H*-1-benzopyrans have involved substituting a spiro fluorene[71] for both phenyls at the 2-position (**45**) or substituting a benzothieno or benzofurano group[72] for one of the phenyls (**46**). A representative example of each type of compound is shown in Figure 3.21.

Recently, Stauffer *et al.*[73] have studied 6-hydroxy-substituted 2*H*-1-benzopyrans and combined electrochemistry with photochemistry in an approach to exerting control over the light-induced switching capability of these molecules (Scheme 17).

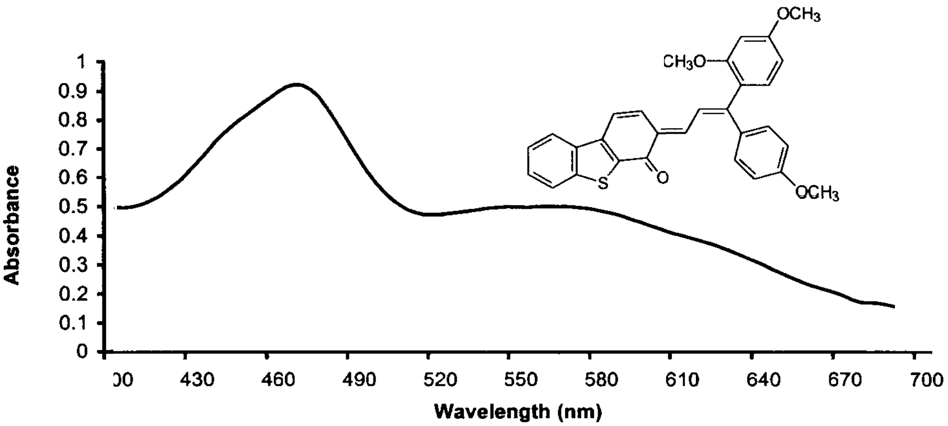


Figure 3.20. Visible spectrum of open form of 2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-2*H*-benzo(*b*)thieno[3,2-*h*]-1-benzopyran.

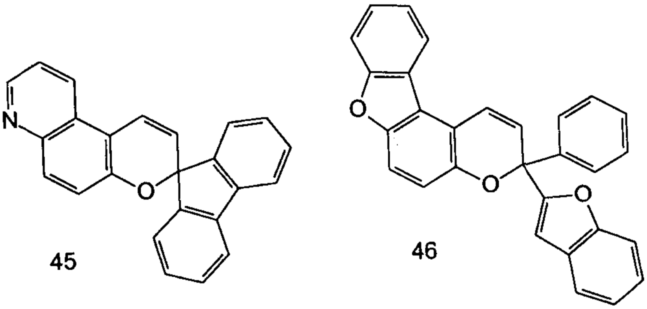


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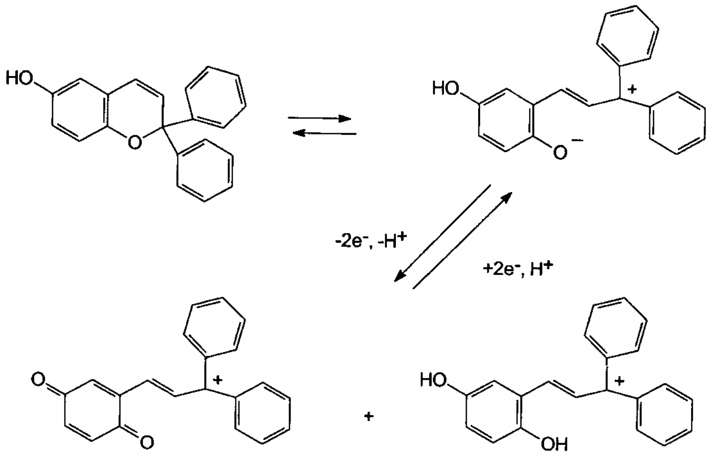
Figure 3.21. 2*H*-1-benzopyrans with novel substitution at the 2-position.



Scheme 17

3.6. SYNTHETIC METHODS

The following three preparations, adapted from the literature, demonstrate the primary methods of synthesis of benzo and naphthopyrans.

3.6.1. Preparation of 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran (5)[28]

To a 500-ml reaction flask were added, 1,1-diphenyl-2-propyn-1-ol (0.1 mol, 20.8 g, Farchan Laboratories), 2-naphthol (0.11 mol, 15 g) and 200 ml of toluene. The mixture was warmed to 55°C with stirring while dodecylbenzenesulfonic acid was added dropwise until a permanent dark red-black color was obtained. The temperature was maintained at 55°C until thin-layer chromatography (TLC) indicated the reaction was complete (approximately 1 h). Then the mixture was poured into an equal volume of 10% aqueous sodium hydroxide, shaken, and the organic fraction separated. The toluene solution was washed with water, phase separated, and the solvent removed on a rotary evaporator. The resulting light tan crystals were slurried with hexane, suction filtered, and dried to yield 18.4 g of product with a melting point range of 156–158°C.

3.6.2. Preparation of 2-Methyl-7,7-diphenyl-7*H*-pyrano[2,3-*g*]benzothiazole (44)[68]

Under an atmosphere of dry nitrogen, titanium tetraethoxide (2.4 g, 10.4 mmol) in 10 ml of dry toluene was added over 10 min to 2-methyl-6-hydroxybenzothiazole (1.72 g, 10.4 mmol) in 40 ml of dry toluene. When the addition was complete, the reaction mixture was boiled for 15 min and then slowly distilled to remove the ethanol. A total of 20 ml of solvent was collected. The reaction mixture was allowed to cool to room temperature and β-phenylcinnamaldehyde (2.17 g, 10.4 mmol) in 50 ml of dry toluene was added dropwise to it. When the addition was complete, the reaction mixture was refluxed for 2 to 5 h, allowed to cool, and poured onto 100 ml of dilute aqueous ammonium chloride solution. The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent removed on a rotary evaporator. The residue was chromatographed on silica using 40% diethyl ether in pentane as eluent. The photochromic fractions were combined, the solvent removed, and the crystalline residue recrystallized from a heptane–benzene mixture. The product (1.6 g, 44%) had a melting point of 215°C.

3.6.3. Preparation of 2,2'-Spiroadamantylidene-2*H*-naphtho[1,2-*b*]pyran (37)[30]

A solution was prepared by dissolving 1-hydroxy-2-acetonaphthone (10 g, 0.054 mol), adamantanone (10.0 g, 0.067 mol), and pyrrolidine (8 g, 0.113 mol) in 300 ml of toluene. The solution was boiled for 10 h and water was separated using a

Dean–Stark trap. During this period the yellow reaction mixture turned first crimson and then dark brown. Toluene was removed under reduced pressure and the residual enamine crystallized from acetone as discolored crystals (8 g). The enamine (10 g) was treated with concentrated HCl (1 ml) in methanol (200 ml). The crimson solution was evaporated and the residual dark oil crystallized from acetone, yielding the intermediate ketopyran (8.4 g, yellow needles from acetone). The crystals were added to methanol and an excess of sodium borohydride was gradually added to the solution, yielding on standard workup 7.47 g of the hydroxypyran. The crystalline hydroxy intermediate was well mixed with 4.5 g of anhydrous copper sulfate and heated to 150–160°C in a carbon dioxide current for 10 min. Upon cooling, the product was extracted into methylene chloride. Removal of the solvent under reduced pressure gave 6.3 g of discolored solid that was decolorized with carbon and recrystallized from acetone (melting point not reported).

3.7. CONCLUDING REMARKS

Intense research efforts by several groups interested in the commercialization of photochromic plastic ophthalmic lenses have, through structural modification, dramatically enhanced the photochromic properties of benzo and naphthopyrans. Publication of this information, primarily in the form of patents, has greatly increased the knowledge base for this class of compounds. As this information becomes more widespread through journal publications, chemists in academia as well as industrial development chemists working on other potential applications of organic photochromics will no doubt investigate these unique chemicals. The net results will be a greater basic understanding of these molecules and the discovery of additional applications beyond photochromic eyeware (and novelties such as T-shirts, toys, and dolls). In the process, enhancements will most likely to be made to these molecules, further improving their photochromic properties. How far and in what direction will this research lead? The reader, picking up this book some time in the future, will have those answers. The author, at this time, can only wonder.

Acknowledgment

The author is indebted to PPG Industries and Transitions Optical for providing the resources and the opportunity to write this chapter.

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4

Fulgide Family Compounds: Synthesis, Photochromism, and Applications

MEI-GONG FAN, LIANHE YU, AND WEIH ZHAO

4.1. INTRODUCTION

The fulgide family constitutes an important type of photochromic compounds and several reviews[1–3] have been published. Stobbe[4] first discovered the photochromism of some phenyl-substituted bismethylene succinic anhydrides in the solid state and named as fulgides. The general formula for fulgides is shown for compound **1.**

Fulgides are generally synthesized by a Stobbe condensation of aryl aldehyde or ketone with a substituted methylene succinate, followed by hydrolysis and dehydration processes as shown in Scheme 1.

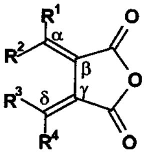
The Stobbe condensation was reviewed by Johnson and Daub in 1951.[5] They postulated the formation of a lactonic ester as an intermediate (see Scheme 2). The base-induced elimination of the lactonic ester led to the regiospecific formation of the half-ester, which is esterified to yield compound **2.**

At least one of the four substituent groups on the fulgide is an aromatic ring, for example, a phenyl group. The structure of the fulgide is skillfully constructed as a hexatriene unit that has two different isomers, a Z form (**3**) and an E form (**4**) based on the α,β-unsaturated double bond, R^3 and R^4 being the same.

If one considers the two double bonds α,β and γ,δ, substituted fulgides with four different groups, R^1, R^2, R^3 and R^4 in compound **1,** four geometrical isomers, e.g., (E,E), (E,Z), (Z,E), and (Z,Z) structures, can exist.

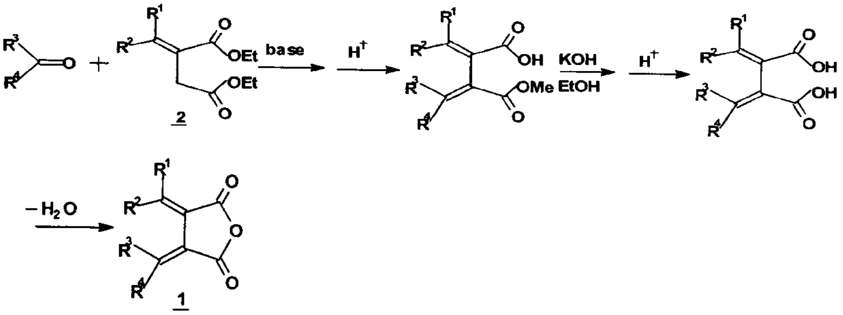
Mei-Gong Fan • Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101. P.R. China

Organic Photochromic and Thermochromic Compounds, Vol. 1, edited by John C. Crano and Robert Guglielmetti, Plenum Press, New York, 1999.

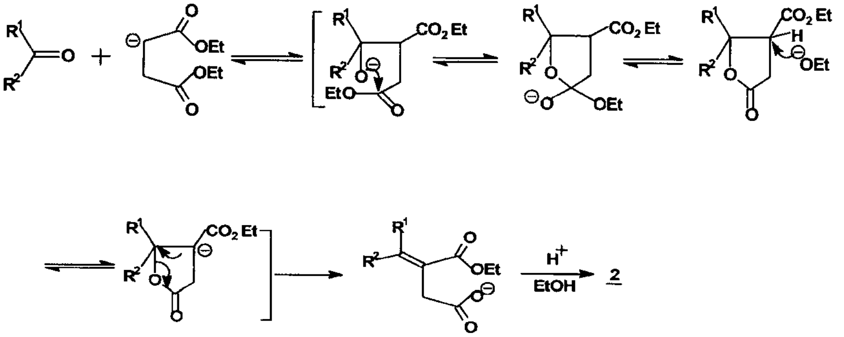


1

Molecular structure of compound 1.



Scheme 1. Preparation of fulgides via Stobbe condensation.



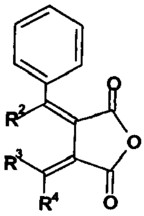
Scheme 2. Mechanism of Stobbe condensation.

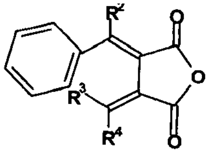
The first compound of the fulgide family developed by Heller *et al*.[3] was a succinimide which was called a fulgimide. The general formula is shown in compound **5.**

Isofulgimides were also introduced by Heller *et al.*[3] in 1993. An isofulgimide is a fulgide derivative in which one of the oxygens in the carbonyl group of the anhydride ring of the fulgide is replaced by a substituted imino, as shown in compounds **6** and **7.**

In the same year, Heller *et al.*[3] reported a new kind of photochromic compound – dicyanomethylene derivatives of fulgide. According to the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), they should be named as 5-dicyanomethylene-tetrahydrofuran-2-one derivatives, as shown in formula **8.**

Fulgenolide and fulgenate having the general formula found in structures **9–11** have also been published by Heller and Szewczyk[6] and Yokoyama *et al.*[7,8]


3 (Z isomer)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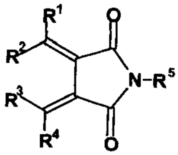
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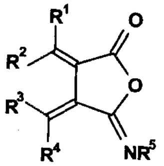
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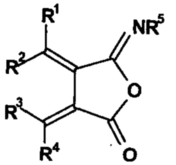
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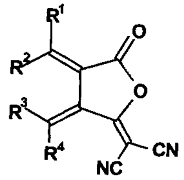
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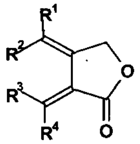
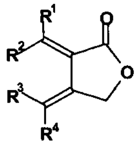
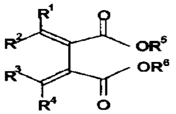

9 (L-fulgenolide)


10 (U-fulgenolide)


11 (Fulgenate)

A fulgenolide is a kind of lactone. When R^2 is an aromatic group, only the L isomer (**9**) has photochromic behavior. Fulgenates have excellent photochromic properties, but the absorption band is blue shifted compared with that of the corresponding fulgide.

Based on the five classes of fulgide family compounds, many realistic and potential applications have been developed and suggested; for example, actinometry, optical storage, optical data processing, and nonlinear optical materials, optical waveguides, optical switches, security and printing applications, eyewear and leisure products. Applications of the fulgide family of compounds are discussed at the end of this chapter.

The photochromic mechanism of fulgides is fairly complicated. Santiago and Becker[9] and Lenoble and Becker[10] reported that the photochromic reaction of a phenyl-substituted fulgide involved an excited singlet state from a π,π^* transition. Picosecond laser photolysis studies on a furyl fulgide[11–13] confirmed this statement. Zhao *et al.*[14] and Ming and Fan[15] studied the photochromic mechanism of a pyrryl-substituted fulgide. They not only found the excited singlet state but also showed that the excited triplet state was involved.

4.2. FULGIDES WITH AROMATIC RING SYSTEMS

4.2.1. Phenyl Fulgides

Fulgides are aromatic substituted bismethylene succinic anhydride derivatives, the photochromism of which was first discovered by Stobbe.[4] Early work was also carried out on aryl fulgide systems. The difficulties encountered with most applications of fulgides are related to the unwanted side reactions: (1) the photochemical E → Z isomerization, (2) the sigmatropic proton shifts, and (3) the thermally disrotatory opening reaction. However, the photochromic properties of fulgides can be modified by molecular design and tailoring. The general synthesis method is discussed in Section 4.1.

The overall yields, melting points, and spectroscopic properties of some aryl fulgides are listed in Table 4.1. The general structure is shown in Section 4.1 as model compound **1.**

Fulgide **1** with four different groups R^1–R^4, of which at least one group is aryl, can exist as four geometrical isomers. There are two conventions in use for

Table 4.1. Overall Yields, Melting Points, and UV Absorption Data for Phenyl Fulgides (**1**)

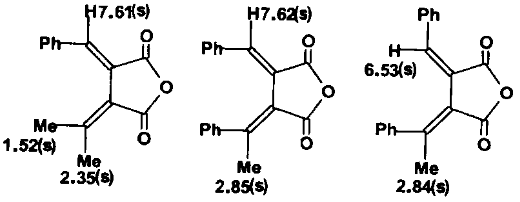
No.	R^1	R^2	R^3	R^4	Yield (%)	mp (°C)	$\lambda_{max/nm}$ (log ε, solvent)	Ref.
1a	H	Ph	Ph	H	31.3	202–203	—	17
1a	H	Ph	Ph	H	22	210–211	—	22
1b	H	Ph	Mesityl	H	—	136–137	—	17
1c	H	Ph	Ph	Me	34.6	148	344 (3.89, hexane)	16
1d	H	Ph	Me	Ph	51.7	120–121	341 (4.07, hexane)	16
1e	Me	Me	Mesityl	H	41.3	191–192	293 (4.25, ethanol)	18
1f	Me	Me	H	Mesityl	54.7	140–141	336 (3.79, ethanol)	18
1g	Me	Me	H	DCP	—	205–206	269 (3.44, ethanol)	18
1h	Me	Me	DMP	H	24.6	161–162	336 (3.92, benzene)	19
1i	Me	Me	Ph	Me	—	205–206	269 (3.44, ethanol)	16
1j	Me	Me	Me	Ph	26.3	112	297 (4.03, hexane)	16
1k	Me	Me	Ph	Ph	26.7	167–169	—	20
1l	Me	Me	TMOP	H	—	147–148	3.48 (4.10, toluene)	21
1m	Me	Me	TMOP	Me	—	139	341 (3.81, toluene)	21
1n	Me	Me	Me	TMOP	—	149	338 (4.01, toluene)	21
1o	Et	Me	DMP	H	—	165–166	347 (4.08, benzene)	19
1p	Et	Et	DMP	H	0.57	144–146	338 (4.12, benzene)	19
1q	Et	Et	Ph	H	—	144–146	330 (4.04, benzene)	19
1r	Et	Me	Ph	Ph	8.3	147–148	354 (3.96, benzene)	19
1s	Et	Et	Ph	Ph	—	178–179	355 (3.95, benzene)	19
1t	Me	Ph	Me	Ph	—	139	331 (3.99, chloroform)	6
1u	Ph	Me	Me	Ph	—	215–216	328 (4.14, chloroform)	6
1v	Me	Ph	Ph	Me	—	175–176	289 (4.13, chloroform)	6
1w	H	*p*-MOP	*p*-MOP	H	—	168–168.5	375 (4.18, acetonitrile)	23

Notes: The overall yield is based on the phenyl aldehyde or ketone. DMP = 2,4-dimethylphenyl; DCP = 2,4-dichlorophenyl; TMOP = 3,4,5-trimethoxyphenyl; *p*-MOP = *p* - methoxyphenyl.

describing the isomers: one treats the molecules as derivatives of butadiene, the other as cinnamic acid derivatives. The (Z,Z) isomer, as a virtually strain-free arrangement, is the most likely and is predicted to be the most stable. There is a strong steric repulsion between the aryl rings in the (E,E) isomer. The most convenient method of determining the stereochemistry of fulgides is proton nuclear magnetic resonance (NMR) spectroscopy. X-ray crystallography is another quite useful technique.

4.2.2. Nuclear Magnetic Resonance Spectroscopy

The most convenient method for determining the stereochemistry of fulgides was proton NMR spectroscopy, which was established by Hart and Heller in 1972.[24] The proton NMR characteristics of fulgides reflect the differences arising from the shielding or deshielding effect between the aromatic ring and the adjacent carbonyl group. Ilge and Schutz[25] published ^1H NMR data on a series of fulgides that confirmed these magnetic anisotropic effects, namely, any groups "cis" to the carbonyl groups were deshielded and the "trans" groups were shielded. They also found that steric effects altered the magnitude of these effects by twisting the bond angles. The result could be confirmed by changing solvents (from $CDCl_3$ to C_6D_6) and investigating the solvent shifts so induced. Thus in the E form, the olefinic hydrogen or methyl absorptions appeared as a rule at a lower field than for the compounds in the corresponding Z form. Some examples demonstrating these effects are given in Scheme 3.

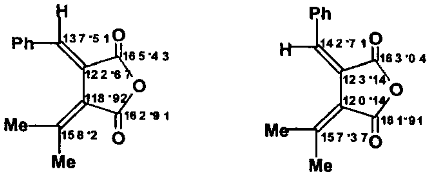


12 **13** **14**

Scheme 3. ^1H NMR data for selected fulgides [ppm, in $CDCl_3$].

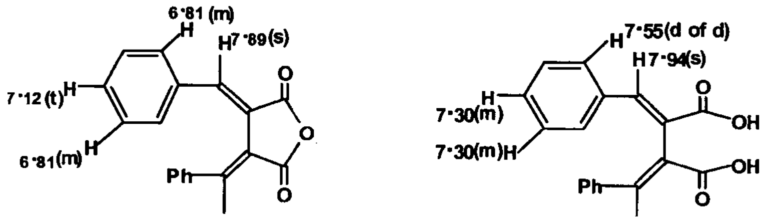
Ilge *et al.*[26] also reported the ^{13}C NMR chemical shifts of aryl fulgides. By means of the shift differences between suitably substituted compounds, results could be obtained on the relative variation of the rotation angles of the phenyl rings as well as the angle alterations between the exocyclic double bonds and the anhydride ring. The effects on α-bond polarization of 4-methoxy and 4-nitro substituents were also estimated. Typical ^{13}C NMR chemical shifts of the selected fulgides are listed in Scheme 4.

Scheme 5 lists chemical shift values of hydrogen atoms in compounds **13** and **16.** From these data, it is suggested that the slight deshielding of H(α) in compound **13** relative to **16** can be easily attributed to the effect of 2-cinnamic acid. In other



12 **15**

Scheme 4. Typical ^{13}C chemical shifts (ppm) of selected fulgides in $CDCl_3$.



13 **16**

Scheme 5. Chemical shift (ppm) of olefinic and aromatic hydrogen atoms in fulgide and fulgenic acid in $CDCl_3$.[19]

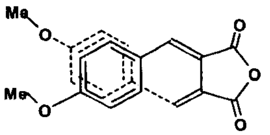
words, closing the diacid **16** into the anhydride **13** results in a significant shielding effect. In fulgide **13,** there are repulsive interactions between the two aromatic π-systems. As a result of this, aromatic hydrogen atoms of one ring are located in the shielding section of the magnetic fields induced by the other ring. The shielding effects decrease in the order of ortho > meta > para.[22]

Thus, careful use of these NMR effects together with characteristic splitting patterns for vicinal and allylic hydrogens allowed an unambiguous assignment of the stereochemistry to be made in most cases.

4.2.3. X-Ray Crystallography

For the bis-aryl fulgide **1** (R^1,R^4 = H, R^2,R^3 = aryl), there were arguments about the existence of the (E,E) structure; thus, an unambiguous assignment of the stereochemistry of fulgides was desirable.

1970, Cohen *et al.*[27] demonstrated by X-ray crystallography that (E,E) fulgide **17** did exist, with the aryl groups twisted by approximately 30° to the plane of the anhydride ring in the same sense. The benzene rings were not parallel, having an angle of 18.8° between the vectors normal to the planes of the two rings. This was confirmed by Boeyens *et al.*[23] in 1988. Deep yellow crystalline (E,E)-bis-(*p*-



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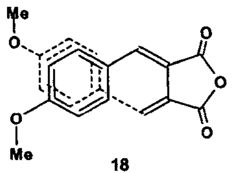

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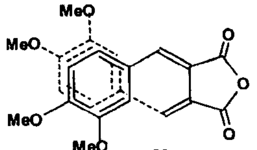

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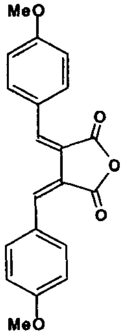

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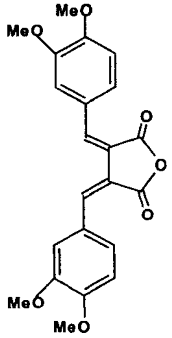

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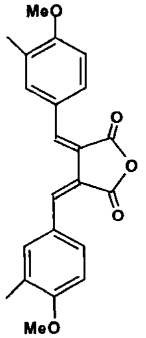

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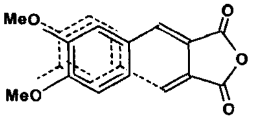

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methoxybenzylidene) succinic anhydride had the two methoxy groups oriented in the same way as shown in structure **17** (mp 168–168.5°C), but on heating **17** in acetone, compound **18** with the two methoxy groups oriented in the opposite way was obtained (mp 176–176.5°C). Both rotamers **17** and **18** in solution showed rapid interconversion to give identical UV absorption and NMR spectra. However, in the crystalline state, the close proximity of the two aromatic rings in these structures led to a sufficiently high energy barrier to restrict rotation of the methoxy groups. Irradiation of **17** in acetone with 366-nm UV light gave (Z,Z) anhydride **19** as red needles (mp 166–168°C) with the essential planar structure.[21]

In the case of bis-(3,4-dimethoxybenzylidene)succinic anhydride, the (E,E) rotamer obtained in the crystalline state was found to have the conformation shown in **20.** The aryl rings in **20** were not parallel, having their plane normals inclined at an angle of 50°. X-ray diffraction analysis of the (Z,Z) isomer **21** gave its structure and showed that planes of carbonyl and adjacent aromatic rings were nearly parallel.[28]

The crystallographic analysis of (E,E)-bis-[(3-methyl-4-methoxy)-benzylidene]succinic anhydride **22** showed that the two aryl rings were not parallel, with an angle of 15.5° between their planes. These rings were rotated by almost the same amount from the plane of the anhydride ring with the dihedral angles 32.3° and 29.3°. In the (Z,Z) isomer **23,** there was no steric overcrowding and so it was unexpected to find that the phenyl rings were almost coplanar, the dihedral angle being only 1.3°.[29]

X-ray crystallography studies on (E,E)-bis-(benzylidene)succinic anhydride confirmed that the two aryl rings were not parallel and neither of them were coplanar with the anhydride ring.[22]

Thus, X-ray crystallography has been used to establish the geometry of the fulgide isomers and to demonstrate the strain in the molecular structure which results in restricted rotation about the single bond and extended bond angles.

4.2.4. UV-Visible Spectroscopy

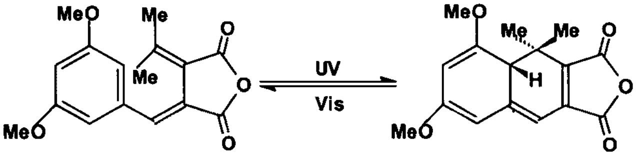
Since a fulgide, its E, Z isomers, and photocyclized form exhibit different absorption spectra, electronic absorption spectra are often used to investigate the photoreaction of fulgides. The UV absorption spectra data of some aryl fulgides are listed in Table 4.1.

In 1984, Ilge *et al.*[30] made a careful investigation of the UV spectroscopy of a large number of fulgides and found that the changes in electronic absorption spectra resulted from changes in substituents and structural isomerizations.

An increase of the number of phenyl rings as well as substituents of the phenyl rings causes correlatable bathochromic spectral shifts. An increase in the volume of the aryl rings could also cause this effect. Replacement of a α-hydrogen cis to the carbonyl group by an α-methyl group resulted in a hypsochromic shift of the absorption maximum wavelength of the fulgide (see Table 4.1).

Becker *et al.*[9] found that the absorption spectra of phenyl fulgides at – 196°C showed no characteristic difference from those at room temperature. The temperature independence of aryl fulgides was also reported by Ilge[31] in 1986.

When photochromic fulgides were irradiated by UV light, they photocyclized to give 1,8a-dihydronaphthalene derivatives (1,8a-DHNs), which exhibited much longer absorption maxima than that of the E or Z conformations of the corresponding fulgides (see Scheme 6). A marked solvatochromic effect was observed in the closed form (1,8a-DHN, **25**), whereas the original fulgide was little affected by solvent polarity (see Table 4.2). This effect was also observed in heteroaromatic fulgides (see Section 4.3).



24 25

Scheme 6. Photochromism of compounds **24** and **25.**

Table 4.2. Absorption Data for Fulgide **24** and the Cyclized Form **25** (1,8a-DHN) in Various Solvents

	λ_{max} (nm) (log∈)			
Compound	Methylcyclohexane	CCl_4	Toluene	*o*-Dichlorobenzene
Fulgide **24**	329 (4.18)	332 (4.07)	336 (3.92)	336 (4.11)
1,8a-DHN **25**	520	525	540	560

Source: Based on P. J. Darcy, R. J. Hart, and H. G. Heller, overcrowded molecules. Part 14. Photochromic systems involving (Z)-1-methylpropylidene (diphenylmethylene)-succinic and (E)-3,5-dimethoxybenzylidene (alkyl- substituted methylene) succinic anhydrides, *J. Chem. Soc., Perkin Trans. 1,* 1978, 571–576.

4.2.5. Photochromic Reaction, Substituent Effects, and Fatigue Resistance of Phenyl Fulgides

Photochromism in some phenyl fulgides was observed in crystals, solutions, polymers, and glassy matrices over a range of temperatures and conditions. Photochromic aryl fulgides photocyclized to form the 1,8a-dihydronaphthalene derivatives, resulting in a yellow to orange, red or blue color change on irradiation with UV light. The change could be reversed by irradiation with visible light.

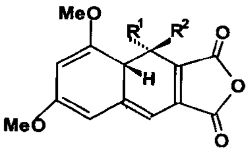
The 1,8a-DHNs undergo irreversible side reactions that include thermal disrotatory ring opening, a thermal 1,5-hydrogen shift to yield 1,2-dihydronaphthalene derivatives (1,2-DHNs), and in some cases, oxidation to the fully aromatic compound.

The rate constants for the thermal disrotatory ring opening and 1,5-H shift reactions of some 1,8a-DHNs (compounds **26** and **27**) are listed in Tables 4.3 and 4.4, respectively.

From the relationships between temperature and rate constants, the activation energy for the 1,5-*H* shift process in compound **27** has been calculated to be 33 kJ mol^{-1}.[21]

The electronic and steric characteristics of substituents affected the photochromic properties. This effect can be clearly seen in methoxyphenyl fulgides, which have been extensively studied, as shown in Table 4.5. It has been shown that in fulgide **28,** when (1) there is no alkoxy group in the ortho or para position of the aromatic ring and R^1 is hydrogen, or (2) when there is an alkoxy group in the ortho or para position and R^1 is an alkyl or phenyl group, fulgide **28** has marked photochromic properties. But if R^1 is hydrogen and the aryl ring contains ortho or para alkoxyl substituents, fulgides are not photochromic or only weakly photochromic.[21]

The side reactions of 1,8a-DHNs were due to the 8a-hydrogen. Replacement of the 8a-hydrogen by a methyl group can eliminate the *H*-shift reactions and prevent the thermal disrotatory ring opening reaction. However, the photocyclization and photo-opening reaction are little affected, based on their conrotatory reaction



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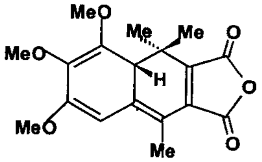

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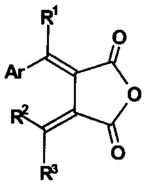

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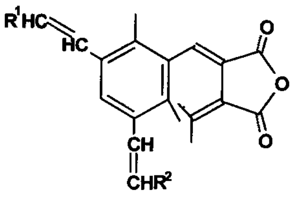

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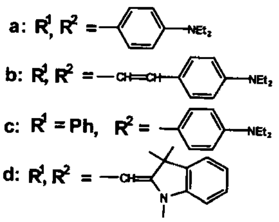


Table 4.3. Rate Constants for Disrotatory Ring Opening of the 1,8a-DHNs **26** Measured in Toluene

	R^1,R^2 = Me		R^1,R^2 = Et		R^1 = Et, R^2 = Me	
T (°C)	$k \times 10^5$ (s^{-1})	$t_{1/2}$ (h)	$k \times 10^5$ (s^{-1})	$t_{1/2}$ (h)	$k \times 10^5$ (s^{-1})	$t_{1/2}$ (h)
19	—	—	0.413	46.6	0.79	24.1
28	2.37	8.1	0.909	21.1	1.19	16.2
31	3.01	6.4	1.44	13.1	2.60	7.4
37	4.54	4.2	2.66	7.2	—	—
38	—	—	3.08	6.3	4.47	4.3
49	14.7	1.7	7.79	2.5	1.48	1.3

Source: Based on P. J. Darcy, R. J. Hart, and H. G. Heller, Overcrowded molecules. Part 14. Photochromic systems involving (Z)-1-methylpropylidene (diphenylmethylene)-succinic and (E)-3,5-dimethoxybenzylidene (alkyl-substituted methylene) succinic anhydrides, *J. Chem. Soc., Perkin Trans. 1,* 1978, 571–576.

Table 4.4. Rate Constants for 1,5-*H* Shift in the 1,8a-DHN **27**

T (°C)	$k \times 10^6$ (s^{-1})
16	36.72
21.5	47.26
26.3	58.43
30.3	66.87
35	84.54
39	98.92

Source: Based on P. J. Darcy, H. G. Heller, S. Patharakorn, R. D. Piggot, and J. Whittall, Photochromic systems. Part 1. Photochemical studies on (E)-2-isopropylidene-3-[1-(3,4,5-trimethoxyphenyl)-ethylidene] succinic anhydride and related compounds, *J. Chem. Soc., Perkin Trans. 1,* 1986, 315–319.

Table 4.5. Substituent Effect on Photochromism of Phenyl Fulgides **28**[9,21]

Ar	R^1	R^2	R^3	Photochromism
Ph	H	Ph	H	(+)
Ph	H	Ph	Ph	(+)
o-MOP	H	Me	Me	(−)
p-MOP	H	Me	Me	(−)
p-MOP	H	*p*-MOP	H	(−)
3,4-DMOP	H	3,4-DMOP	H	(−)
3,4,5-TMOP	H	3,4,5-TMOP	H	(−)
2,5-DMOP	H	Me	Me	(−)
2,5-DMOP	Me	Ph	H	(+)
2,5-DMOP	H	Me	Me	(+)
3,5-DMOP	H	Me	Me	(+)
3,5-DMOP	Me	Me	Me	(+)
3,5-DMOP	Me	*p*-MOP	H	(+)
2,3,4-TMOP	H	Me	Me	(−)
2,3,4-TMOP	Me	Me	Me	(+)
2,4,5-TMOP	Me	Me	Me	(+)

Notes: MOP = methoxyphenyl; DMOP = dimethoxyphenyl; TMOP = trimethoxyphenyl; (–) nonphotochromic and (+) photochromic.

manner.[18] The methoxy substituent influences the absorption characteristics of fulgide and 1,8a-DHN by donation of the nonbonded p-electrons of the oxygen into the conjugated system. When the methoxy group is in conjugation with the main chromophore, this effect is most remarkable. Thus methoxy groups in the 3- and/or 5-position of the phenyl ring have little effect on the absorption band of a fulgide, but cause a major bathochromic shift on the longest absorption band of 1,8a-DHN. Methoxy substituents in the 2-, 4-, and/or 6-position of the phenyl ring have little effect on the 1,8a-DHN, but cause a slight bathochromic shift of the

Table 4.6. Overall Yield, Melting Point λ_{max} (nm), and Fatigue Resistance of Compound **29** (in Toluene)

Compound **29**	Structure	Yield (%)	mp (°C)		λ_{max} (nm)		
				E[a]	C[a]	Cycle[b]	PF[c] (%)
a	Z[a]	20	211–213	366	633	500	0.09
b	Z	13	137–139	382	618	500	0.10
c	Z	14	193–194	361	610	300	0.22
d	Z	14	164–169	368	678	100	0.67

[a] E → E-isomer of fulgide; Z → Z-isomer of fulgide; C-colored form of fulgide.

[b] Photocoloring and bleaching cycles.

[c] PF is a normalized decrease in absorbance at the absorption maximum wavelength after repeated photocoloring and bleaching cycles.

absorption band of the fulgide. This is because in 1,8a-DHN, the planar structure allows the effective conjugation of the π-electrons with the anhydride chromophore. The methoxy group in the 3- and/or 5-positions also increases the sensitivity to the coloring reaction.[1]

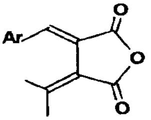
Most of the phenyl fulgides were not suitable for applications because of their low fatigue resistance (stability). Recently, two electron-donating substituents were introduced into the aryl ring of the fulgide molecule **29,**[32] which was prepared as the Z form but can undergo the Z → E → C photochromic reaction on irradiation with UV light. The overall yield of the preparation, spectroscopic properties, and fatigue resistance are given in Table 4.6.

Two electron-donating substituents in the 3,5-positions of phenyl fulgide caused a significant bathochromic shift of the absorption band of 1,8a-DHN with a large molecular extinction coefficient. Furthermore, they caused a remarkable increase in the coloration rate, while at the same time maintaining the bleaching rate. For example, for compound **29a,** the quantum yield for the photocoloring reaction was 0.65 (366-nm light irradiation) and the bleaching quantum yield was 0.052 (independent of bleaching light at 556–634 nm). The two electron-donating groups also improved the fatigue resistance of the fulgides.[32]

4.2.6. Miscellaneous Aryl Aromatic Fulgides

Apart from the phenyl fulgides, other carbon[34] aryl fulgides such as naphthyl fulgides **30** and **31,**[17,33] fluorenylidene fulgides **32,**[1,29] bisanthrylidene fulgide **33,**[35] and ferrocenyl fulgide **34**[36] were reported.

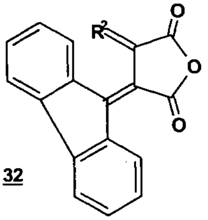
Naphthyl fulgides **30** showed photochromic properties similar to phenyl fulgides. On irradiation with UV light in toluene, it cyclized to give the red 4,4a-dihydrophenanthrene derivatives (DHPs). On prolonged irradiation, E → Z isomerization occurred to give a mixture of E and Z at the photostationary state; no other product could be detected. In contrast, naphthyl fulgide **31** gave an orange-red



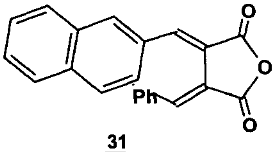
30

a Ar = α–Naphthyl

b Ar = β–Napthyl



32

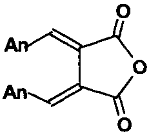


31

a R = Fluorenylidene

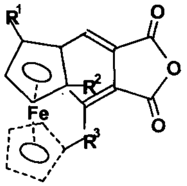
b R = diphenylmethylene

c R = 3,4,5–trimethoxyphenylethylidene



An= 9—Anthryl

33



34

a $R^1, R^2, R^3 = H$

b $R^1, R^2 = H, R^3 = OMe$

c $R^1, R^3 = H, R^2 = OMe$

d $R^2, R^3 = H, R^1 = OMe$

cyclized intermediate on irradiation with UV light in toluene, but on prolonged irradiation, a colorless product formed by a 1,5-*H* shift was obtained.[17]

Ferrocenyl fulgide **34** gave only E → Z isomerization without any photochromic cyclization reaction.[36] Fluorenylidene fulgide **32a** was prepared as black crystals, and **32b** as deep red crystals. Neither of them were photochromic. However, compound **32c,** which was a deep red crystal, was photochromic and gave a blue color when irradiated over a wide range of wavelengths.

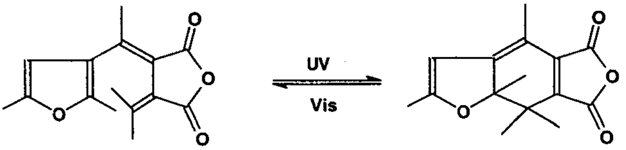
Unlike normal fulgides, the bis-(9-anthrylmethylene)succinic anhydride **33** underwent a facile intramolecular [4+4] cycloaddition reaction on exposure to white light to give a pale yellow adduct.[35]

4.3. FULGIDES WITH HETEROCYCLIC RING SYSTEMS

The investigation of molecular design and the preparation of heterocyclic fulgide derivatives have created wide interest owing to the potential importance of these compounds in optical recording. Recent studies have focused on the preparation of the fatigue-resistant photochromic fulgides using a variety of heterocyclic-substituted fulgides. This section discusses fulgides having different heterocyclic ring systems.

4.3.1. Furyl Fulgides

Replacement of the phenyl group by a 3-furyl group gives so-called furyl fulgides, which convert quantitatively to the colored form on irradiation with 366-nm light. The first example of this type of fulgide was (E)-α-2,5- dimethyl-3-furyl ethylidene (isopropylidene) succinic anhydride (**35**), which gives deep red 7,7a-dihydrobenzo-furan derivatives (**7,7a-DHBF, 36**) on irradiation with ultraviolet light, as shown in Scheme 7.



35 36

Scheme 7. Photochromism of compounds **35** and **36.**

Compound **35** is pale yellow (λ_{max} = 343 nm in toluene); **36** has an absorption minimum in the near-UV region and the absorption maximum wavelength (λ_{max}) is 494 nm in toluene. The UV/VIS absorption spectra of **35** and **36** have been reported in Ref. 37).

4.3.1.1. Substituent Effects on the Quantum Yield of Photochromic Reactions of Furyl Fulgides

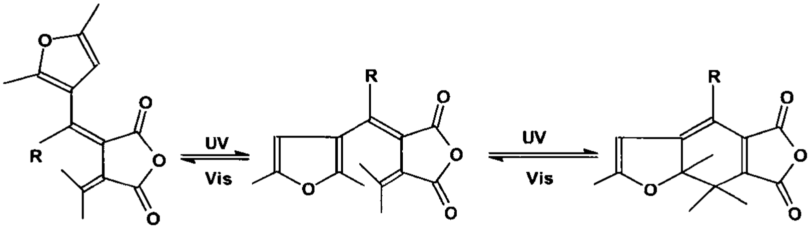
Heller and Langan[38] reported that the quantum yield for photocoloration ($\Phi_{E\rightarrow C}$) of fulgide **35** to the **7,7a-DHBF** (**36**) in toluene was 0.20, and the $\Phi_{E\rightarrow C}$ value appeared to be wavelength independent over the range 313–366 nm. Temperature (10–40°C) had little effect on the quantum yield for photocoloration. Furthermore, the cycles of photochromism of **35–36–35** did not affect the ($\Phi_{E\rightarrow C}$) value. These results showed that fulgide **35** is well suited for chemical actinometry in the near-UV and visible spectral region.

A highly efficient photochromic process is essential for organic photochromic compounds used as optical recording materials.[39,40] That means that the quantum yields for the photocoloring and bleaching reactions should be high, but the quantum yield for the side reactions should be as low as possible. In order to solve the problems mentioned earlier, extensive studies have been carried out, and some promising results have been obtained so far.

Structure modifications of fulgide molecules play an important role in increasing the values of quantum yields of the photochromic reactions. These modifications have included alternation of the substituents on the furan moiety and on the α-position.

4.3.1.2. α-Alkyl Substituent Effects on the Photochromism of Furyl Fulgides

Glaze *et al.* reported that fulgide **35** is a highly effective photochromic compound. But when the R is hydrogen atom **37a,** no photocyclization reaction occurs,[41] and only E → Z photoisomerization takes place when **37a** is irradiated by UV light, as shown in Scheme 8.



37Z **37E** **38**

a,R=H; **b,** R=Et; **c**,R=n-Pr; **d,** R=i-Pr; **e**,R=n-$C_{17}H_{35}$; **f,** R=t-Bu.

Scheme 8. Photochromic reaction of compounds **37** and **38.**

The effects of the substituent steric hindrance of the R group in fulgide **37b–37f** on the quantum yield for the photoreactions have been reported by Yokoyama *et al.*[42–44] and Kiji *et al.*[45] These authors demonstrated that steric hindrance has an important effect on the quantum yield of the photocyclization ($\Phi_{E\rightarrow C}$) and the E → Z isomerization ($\Phi_{E\rightarrow Z}$). The results are shown in Table 4.7.

With an increasing steric hindrance of R, the coloring quantum yields ($\Phi_{E\rightarrow C}$) of fulgide are greatly enhanced while the ($\Phi_{E\rightarrow Z}$) is simultaneously decreased. This

Table 4.7. Quantum Yields of Photoreactions of Compounds **37** (E,Z) and **38** (C) in Chloroform

Compound	R	$\Phi_{E\rightarrow C}$[a]	$\Phi_{E\rightarrow Z}$[a]	$\Phi_{Z\rightarrow E}$[a]	$\Phi_{C\rightarrow E}$[b]
b	Et	0.34	0.06	0.12	0.027
c	*n*-Pr	0.45	0.04	0.10	0.044
d	*i*-Pr	0.62	0.00	0.06	0.040
f	*t*-Bu	0.79	0.00	—	0.034[c]

[a] Irradiation at 366-nm light.
[b] Irradiation with 492-nm light.
[c] In toluene at room temperature.

observation could be explained by the fact that the bulky group R inhibited the E → Z isomerization of the α,β double bond and anchored the conformation of the furyl group in favor of the intramolecular photocyclization. Fulgide **37d** had a $\Phi_{E \rightarrow C}$ of 0.62 and $\Phi_{E \rightarrow Z}$ of zero. The elimination of the E → Z isomerization obviously has significance in many applications for fulgide molecules. However, the relatively small bleaching quantum yield of $\Phi_{C \rightarrow E}$ was not affected by the steric hindrance of R.

Fulgide **37e,** which has been synthesized by Hibino and Ando,[46] could be used to prepare Langmuir–Blodgett films having photochromic properties similar to those observed in organic solvents.

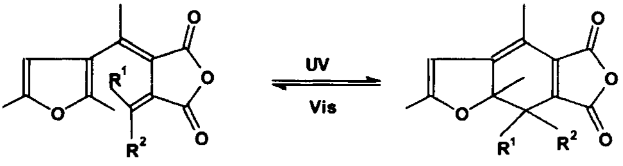
The R group had little effect on the absorption maximum (λ_{max}) and molar absorption coefficient (ϵ_{max}) of fulgides and **7,7a-DHBF** derivatives. The absoprtion maxima of E isomers were about 348 nm, which is about 10 nm shorter than those of Z isomers.

4.3.1.3. Steric Effects on the Photochromic Behavior of the Alkylidene Group of Furyl Fulgides

The substituents of the alkylidene groups in the fulgide molecules have been varied by Heller *et al.,*[3,47] Glaze *et al.,*[48] Tomada *et al.*[49] and Yokoyama's group[43,44] independently. The photochromic reactions are shown in Scheme 9.

Scheme 9 shows in fulgide **39,** replacement of the isopropylidene group (IPD) by a dicyclopropylidene group (DCP) caused a bathochromic shift in the absorption band of the **7,7a-DHBF,** owing to the partial double-bond character of the DCP group. It is obvious that the steric hindrance of R^1 and R^2 also affected the λ_{max} of the colored form. There was not a definite role for the substituent effect on the quantum yield of photoreactions. Table 4.8 shows the absorption spectroscopic data and quantum yields of photoreactions of fulgides with different R^1R^2 groups in toluene.

As seen from Table 4.8, the steric bulkiness of the norbornylidene (NBO) group **(39c)** did not work effectively to increase $\Phi_{E \rightarrow C}$, suggesting that only a huge alkylidene group such as adamantylidene (ADD) is necessary. Compound **39d**



39 **40**

a,$R^1 = R^2$ = Et; **b,**$R^1 = R^2$ = cyclopropyl; **c,**R^1R^2C= Norbornylidene(NBO); **d,** R^1R^2C= Adamantylidene (ADD).

Scheme 9. Photochromism of compounds **39** and **40.**

Table 4.8. Absorption Spectra Data and Quantum Yield of Furyl Fulgides **39** (E,Z) and its Colored Form (**40**) (C) with Bulky Alkylidene Substituents in Toluene

Compound	R¹ R²	E/ λ_{max} ($\in_{max}$)	Z/λ_{max} ($\in_{max}$)	C/λ_{max} ($\in_{max}$)	$\Phi_{E \to C}^{a}$	$\Phi_{E \to Z}^{a}$	$\Phi_{Z \to E}^{a}$	$\Phi_{C \to E}^{b}$
a	Et Et	344 (6300)	—	500(9900)	0.08	—	—	0.19
b	DCP[c]			500 (–)				
c	NBO[c]	348 (5140)	355 (8750)	514 (7340)	0.20	0.30	0.42	0.057
d	ADD[c]	344 (5090)	357 (9090)	519 (6880)	0.12	0.10	0.10	0.21

Note: λ_{max} (nm); $\in_{max}$ (mol^{-1} dm^3 cm^{-1}) .
[a] Irradiation at 366-nm light.
[b] Irradiation at 492-nm light.
[c] R¹R²C = DCP, NBO, and ADD, respectively.

contains a rigid inflexible spiroadamantylidene group, which resulted in a fourfold increase in the quantum efficiency for bleaching compared with the analogous compound **35** (R¹ = R² = Me).

4.3.1.4. Comprehensive Steric Effect on the Quantum Yield of the Photoreactions of Furyl Fulgides

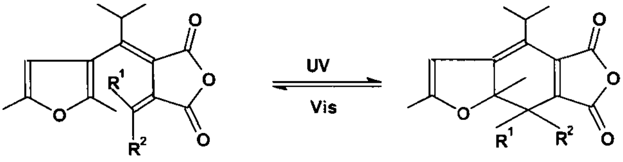
In order to obtain a photochromic fulgide having both large coloring and bleaching quantum yields, Heller[50] and Yokoyama *et al.*[43,44] have independently made efforts to this end. Yokoyama *et al.* reported that replacement of the IPD group in fulgide **37** by the NBO or ADD group, and at the same time with R replaced by an isopropyl group, gave fulgide **41.** Spectroscopic data for fulgide **41** and its colored form (**42**) are shown in Table 4.9. The photochromic reactions are shown in Scheme 10.

As seen in Table 4.9, fulgide **41,** having both an isopropyl group at the α-position and an adamantylidene group at the δ-position, exhibited a coloring quantum yield $\Phi_{E \to C}$ of 0.51. It was nearly threefold larger than that of fulgide **35.** The bleaching quantum yield $\Phi_{C \to E}$ was 0.26, which was fivefold larger than that of **36.** However, it should be noted that for fulgide **41b** (adamantylidene derivatives), the bleaching quantum yields ($\Phi_{C \to E}$) of UV irradiation were not negligible, i.e., the bulky ADD group also enhanced the bleaching quantum yield

Table 4.9. Absorption Spectra Data and Quantum Yields of Photoreactions of Fulgides **41** (E,Z) and its Colored Form (**42**) (C) with Bulky Substituents in Toluene

Compound	R¹R²C	E/λ_{max} (nm)	Z/λ_{max} (nm)	C/λ_{max} (nm)	$\Phi_{E \to C}^{a}$	$\Phi_{E \to Z}^{a}$	$\Phi_{Z \to E}^{a}$	$\Phi_{C \to E}^{a}$	$\Phi_{C \to E}^{b}$
a	NBO	343	—	515	0.56	0.01	0.01	0.00	0.049
b	ADD	337	355	520	0.51	0.02	0.05	0.28	0.26

[a] 366-nm light irradiation.
[b] 492-nm light irradiation at room temperature.



41 42

a, R^1R^2C= NBO; b, R^1R^2C= ADD.

Scheme 10. Photochromism of compounds **41** and **42.**

during UV irradiation. One of the possible reasons for the large bleaching quantum yield is that the sterically congested ADD group destabilized the rigid colored form. This destabilization caused a partial deactivation to the opened form from the excited state of the colored form. This was supported by the molecular orbital calculations.[44] Another interpretation is that a bulky and rigid group, such as ADD, weakened the σ-bond owing to the steric repulsion between the bulky 1-substituent and 7a-methyl group, which led to a ring-opening reaction.

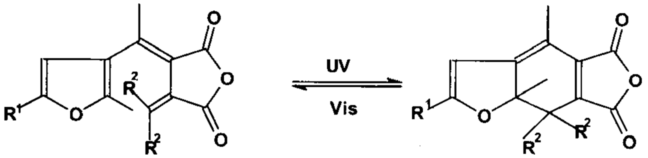
The fulgide **41b** had a high quantum yield for coloring (0.50 for 366-nm irradiation in toluene), while the corresponding **7,7a-DHBF** (**42b**) had a high quantum yield ($\Phi_{C\rightarrow E}$ = 0.26) for bleaching irradiation (546 nm at 26°C in toluene), which is in agreement with Yokoyama's results.

These results demonstrated that it is possible to design fulgide systems that have high quantum yields for both coloring and bleaching reactions and so far fulgide **41b** is the best one for such aims.

From Tables 4.8 and 4.9 we should note that with the increasing size of the alkylidene group from IPD→ NBO → ADD, the absorption maxima of **7,7a-DHBF** exhibited slight bathochromic shifts.

Whitall[2] reported that the 2-methyl group in the furyl moiety is essential to prevent fatigue reactions, but 2,4-dialkyl-3-acetyl-furans are too sterically hindered to undergo the Stobbe condensation and only substituents on the 5-position of the furan ring in the fulgide molecules can be varied easily. The substituent in the 5-position is in conjugation with the **7,7a-DHBF** chromophore. Heller[50] designed and synthesized a series of the 5-substituted furyl fulgides, as shown in Scheme 11.

The spectroscopic data for **43** and **44** are listed in Table 4.10. Fulgides **43a-43f** have similar photochromic properties in organic solvents. From Table 4.10 it can be seen that when the electron-donating substituents were introduced into the 5-position of the furyl ring, both fulgides and their colored form (**7,7a-DHBF**) exhibited bathochromic shifts corresponding to the behavior of compound **44f** (λ_{max} = 612 nm in toluene, a bathochromic shift of 100 nm by reference to **44a**). Tomoda et al.[49] reported that fulgide **45** containing an acetyl group in the 4-position of the furyl ring exhibited a low coloring quantum yield $\Phi_{E\rightarrow C}$ = 0.11 in toluene with irradiation with 311-nm light and a high bleaching quantum yield $\Phi_{C\rightarrow E}$ = 0.39 when irradiated with 477-nm light. The colored form **7,7a-DHBF** derivative (**46**) had a λ_{max} = 472 nm in toluene, as shown in Scheme 12.



Scheme 11. Photochromism of compounds **43** and **44**. **a,** R^1 =H; **b,** R^1 =Me; **c,** R^1 = Ph; **d,** R^1 = *p*-methoxyphenyl (*p*-MOP); **e,** R^1 =*p*- tetrahydropyrrylphenyl (*p*-TPP); **f,** R^1 =*p*-diethylaminophenyl (*p*-DAP). In compounds **43a–e,** R^2R^2C = IPD, **43f,** R^2R^2C = ADD.

Table 4. 10. Absorption Spectra Data for Compounds **43** and **44** in Toluene

Fulgide (**43**)

	43a	43b	43c	43d	43e	43f
λ_{max}	330	343	354	366	—	—
ϵ_{max}	6920	6780	6305	6000	—	—

7,7a-DHBF (**44**)

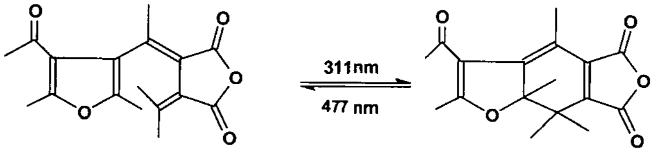
	44a	44b	44c	44d	44e	44f
λ_{max}	473	494	520	540	588	612
ϵ_{max}	6950	8200	15,750	18,200	26,250	18,500

Note: λ_{max} (nm); ϵ_{max} (dm^3 mol^{-1} cm^{-1}).

In fulgide **45,** the low $\Phi_{E\rightarrow C}$ and high $\Phi_{C\rightarrow E}$ values cannot be attributed to the steric hindrance effect of the acetyl group. They are due to the electronic effect, i.e., the electron-withdrawing ability of the 4-acetyl group. Therefore, not only the steric hindrance effect, but also the electronic effect of the substituents can influence the reactivity of both coloring and bleaching reactions.

4.3.1.5. Photochromism of Furyl Fulgides in Polymer Matrices

For practical applications, fulgides must retain their excellent photochromic properties in solvent and in a polymer matrix, because the ultimate photomemory media will certainly be provided as a plastic layer containing photochromic



45

46

Scheme 12. Photochromism of compounds **45** and **46.**

compounds. It is therefore important to study the photochemical reactions of fulgides in polymer matrices, and some interesting results have been reported.[51–55] Yokoyama *et al.*[53] described the photochromism of fulgide **35** in various polymer films. Table 4.11 shows the results of photochemical properties of fulgide **35** and **36** in polymer matrices.

In a polar polymer, i.e., cellulose acetate (CA) or nitrocellulose (NC) **35E, 35Z,** and **36** had a relatively longer absorption maximum wavelength than in less polar matrices. In NC the λ_{max} of **36** shifts to 528 nm, which is also longer than in organic solvents. The role of polymer films in the quantum yields of photoreactions is not clear. In a comparison of the photochemical properties of **35** in polymer films and in solvents, it was found that the $\Phi_{E \rightarrow C}$ in polymer matrices was substantially smaller than that in the corresponding solvent with similar polarity. However, the decoloration quantum yield $\Phi_{C \rightarrow E}$ in a polymer film was larger than that in solvents. In conclusion, the polymer matrix properties, such as polarity, viscosity, and glass transition temperature (T_g) are quite important for photochromic reactions and applications. The coloration, E → Z and Z → E isomerizations were suppressed in polymer matrices.

4.3.1.6. Crystal Structures of Furyl Fulgides

The X-ray structure of two isomers of fulgide **35** have been determined by Yoshioka *et al.*[56] In the E form, the succinic anhydride and the furyl ring were not coplanar and were considerably twisted relative to each other. This is due to the steric hindrance effect between the isopropylidene group and the 2-methyl group in the furyl moiety. The distance between the two reactive sites, which corresponds to the chemical bond formed during photocyclization, was 3.44 Å.

In the Z form, the succinic anhydride portion was also considerably twisted from the furyl ring moiety: the distance between the carbon-2 of the furyl ring and the tertiary carbon atom of the isopropylidene group was 5.34 Å, which was much

Table 4.11. Photochromic Properties of **35** (Z,E) and **36** (C) in Polymer Films

Property	PS[c]	PMMA[c]	PPMA[c]	CA[c]	NC[c]
$\Phi_{E \rightarrow C}$[a]	0.12	0.094	0.14	0.12	0.095
$\Phi_{E \rightarrow Z}$[a]	0.066	0.091	0.078	0.069	0.064
$\Phi_{Z \rightarrow E}$[a]	0.074	0.13	0.083	0.085	0.055
$\Phi_{C \rightarrow C}$[b]	0.10	0.059	0.049	0.028	0.07
λ_{max} (E) (nm)	346	343	344	349	352
λ_{max} (Z) (nm)	356	350	352	354	361
λ_{max} (C) (nm)	502	500	502	508	528
Dielectric const.	2.5–3.1	3.3–3.9	5–6	3.5–7.5	7.0–7.5

[a] Irradiated with 366-nm light.
[b] Irradiated with 502-nm light.
[c] PS = polystyrene, PMMA = poly(methyl methacrylate), PPMA = poly(propyl methacrylate), CA = cellulose acetate, NC = nitrocellulose.

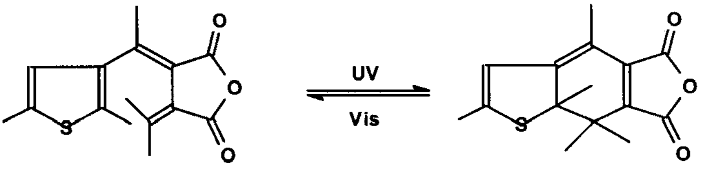
longer than that in the E isomer (3.44 Å). It seems that the direct cyclization reaction from the Z form to the colored form is impossible because of the long distance of the reaction sites. In other words, there is no all-cis hexatriene unit in the Z form, which is an essential component for the photocyclization of fulgides.

4.3.1.7. Helical Chirality of a Furyl Fulgide

Yokoyama *et al.*[57] reported that fulgide **35** was shown to be chiral, and its enantiotopomerization process was observed by variable-temperature ^1H NMR measurement. The enthalpy barrier (ΔH) for diastereotopomerization was observed and calculated.

4.3.2. Thienyl Fulgides

Replacement of the 3-furyl group by a 3-thienyl group led to the formation of thienyl-substituted fulgides,[58] which have photochromic properties similar to the furyl fulgides. Glaze *et al.*[58] reported that the main difference is a slight bathochromic shift of the absorption band of the colored form, 7,7a-dihydrobenzothiophene (**7,7a-DHBT, 48**). The photochemical reaction is shown in Scheme 13.

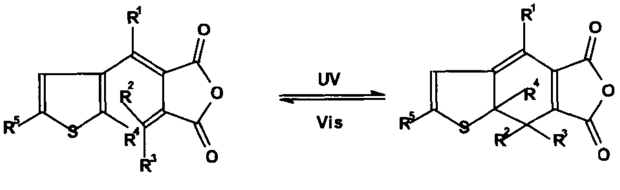


47 **48**

Scheme 13. Photochromism of compounds **47** and **48.**

The photochromism and kinetics of photochemical isomerization of thienyl fulgide (**47**) have been reported by Ulrich *et al.*[59] Either in liquid solution or in rigid polymer, fulgide **47** exhibited reversible photochromism to a high degree. The photoreactions took place in different media with different quantum yields. In methylene chloride, the decoloration processes of **48** took place very slowly to the quantum yield for bleaching was poor ($\Phi_{C\rightarrow E}$ = 0.01) – while in polystyrene (PS) matrix, the quantum yield was increased ($\Phi_{C\rightarrow E}$ = 0.3). However, the quantum yield for the coloring process (366 nm) turned out to be $\Phi_{E\rightarrow C}$ =0.15 for both methylene chloride solution and polystyrene matrix. The quantum yield of decoloration ($\Phi_{C\rightarrow E}$) in the case of methylene chloride solution was less than that in a PS matrix. This can be explained as follows: owing to the bulky benzene ring, the polymer matrix contains enough free volume to allow for reactions of the fulgide molecules, but in liquid solutions the radiation's deactivation process is competitive with the photoreaction and as a result the quantum yield for the photodecoloration reaction is decreased.

Thienyl fulgide (in PS) can be colored and bleached at all temperatures between 300 and 10 K. The coloring reaction does not require thermal activation, but for the bleaching process a small activation barrier (50 cm^{-1}) exists. Further studies on the photoreaction kinetics of thienyl fulgide derivatives (**49a–49c**) have been carried out by the same research group,[59] as shown in Scheme 14.



49 **50**

a, R^1 = i-Pr, R^2 =R^3=R^4=R^5= Me; **b,** R^1 = i-Pr, R^2R^3C=ADD, R^4=R^5=Me; **c,**R^1 = t-Bu, R^2 =R^3=R^4=R^5=Me; **d,** R^1=R^2=R^4=R^5=Me,R^3=n-C_6H_{13}; **e** ,R^1=R^2=R^4= R^5=Me,R^3=n-$C_{11}H_{23}$; **f,** R^1 = R^2 = R^3 =Me,R^4=R^5=n-C_6H_{13}. **g,** R^1=R^2=R^3=R^4=Me, R^5 = -CH=CH-C_6H_5; **h,**R^1=R^2=R^3=R^4=Me, R^5= CH=CH-C_6H_4-p-NEt_2.

Scheme 14. Photochromism of compounds **49** and **50.**

The same results for the quantum yield of the photoreactions of fulgides **49a–49c** have been obtained compared with those of the corresponding furyl fulgide, i.e., bulky substituents of R^1 can increase the $\Phi_{E\rightarrow C}$ and decrease the $\Phi_{E\rightarrow Z}$ and $\Phi_{Z\rightarrow E}$. For example, in toluene, $\Phi_{E\rightarrow C}$ =0.73, $\Phi_{C\rightarrow E}$ = 0.095 for **49c.**[41] Bulky substituents on the alkylidene group (**49b**) can enhance the $\Phi_{C\rightarrow E}$ by a factor of four compared with the ordinary thienyl fulgide (**47**).

The design and synthesis of substituted thienyl fulgides have been reported by several research groups.[58–61] Konishi *et al.*[61] have synthesized the long alkyl chain-substituted thienyl fulgides **49d–49f.** In toluene, **50d, 50e** possessed an absorption maximum at 522 nm while **50f** was at 537 nm. Tomoda *et al.*[62] reported that the introduction of an electron-donating group and conjugated chain into the 5-position of the thienyl ring can cause significant red shift of the absorption maximum of the colored form, **7,7a-DHBT.** The spectroscopic properties of several thienyl fulgides are summarized in Table 4.12.

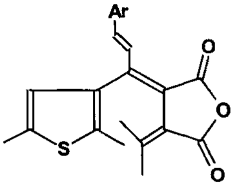
It should be pointed out that introduction of electron-donating substituents to the thienyl ring can lead to a red shift of λ_{max} and an increase of the molar absorption coefficient (ϵ_{max}) of the colored form. However, the quantum yield of bleaching is decreased, e.g., $\Phi_{C\rightarrow E}$ for **50h, 50g,** and **48** in toluene were 0.0043 (591), 0.0092 (556), and 0.14 (535), respectively (the values in parenthesis are the irradiation wavelength/nanometer for the bleaching process).

Table 4.12. Spectroscopic Properties of Thienyl Fulgide **49** (E,Z) and its Colored Forms (**50**) (C) in Toluene

Compound	R^1	R^2	R^3	R^4	R^5	E/λ_{max} (ϵ_{max})	Z/λ_{max} (ϵ_{max})	C/λ_{max} (ϵ_{max})
a	*i*-Pr	Me	Me	Me	Me	330 (2050)	330 (4000)	524 (8250)
b	*i*-Pr	ADD		Me	Me	340 (3580)	340 (2410)	546 (5970)
c	*t*-Bu	Me	Me	Me	Me	—	—	—
d	Me	Me	*n*-C_6H_{13}	Me	Me	—	—	522
e	Me	Me	*n*-$C_{11}H_{23}$	Me	Me	—	—	522
f	Me	Me	Me	C_6H_{13}	C_6H_{13}	—	—	537
g	Me	Me	Me	Me	SP[a]	334 (31,800)	—	557 (15,200)
h	Me	Me	Me	Me	*p*-DESP[b]	382 (41,400)	—	595 (30,500)

Note: λ_{max} (nm); ϵ_{max} ($dm^3\,mol^{-1}\,cm^{-1}$).
[a] SP = styrylphenyl.
[b] *p*-DESP = *p*-diethylamino styrylphenyl.

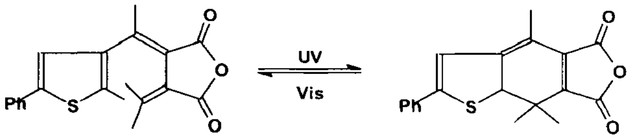
Effenberger and Wonner[63] have described the preparation and photochemistry of an anthrylvinyl thiophen fulgide (**51**).



51

Heller suggested that the colored form of fulgide **52**[58] can be used as a visible actinometer (430–600 nm), because **53** has a broader absorption band and a large molar extinction coefficient (ϵ = 12,000 $dm^3\,mol^{-1}\,cm^{-1}$ in toluene). The photochromic reaction is shown in Scheme 15.

X-ray analysis of **52** and **53** has also been reported by Kaftory.[64] The phenyl group is not coplanar with the thiophen ring in any of the compounds **52** and **53.**

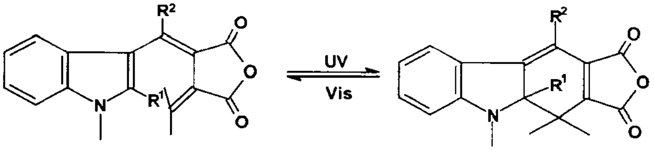


52 **53**

Scheme 15. Photochromism of compounds **52** and **53.**

4.3.3. Indolyl Fulgides

Indolyl-substituted heterocyclic fulgides have been studied by several research groups.[65–69] Wang *et al.*[70] and Fan *et al.*[71] reported the synthesis and crystal structures of azafulgide **54.** The structures and photochromic reactions are shown in Scheme 16.

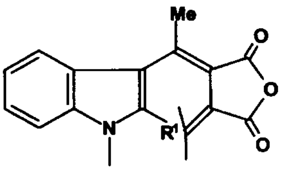


54 55

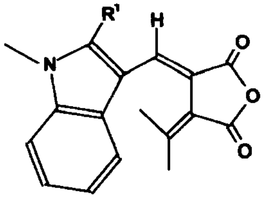
a, $R^1 = R^2$ =Me; **b,** R^1 = Ph, R^2 = H; **c,** R^1 = Me, R^2 = H.

Scheme 16. Photochromism of compounds **54** and **55.**

When R^2 is hydrogen, fulgides **54b** and **54c** are neither photochromic nor thermochromic. However, when R^2 was replaced by a methyl group, fulgide **54a** changed from pale yellow to blue or green on irradiation at 366-nm light either in the crystalline state, in solution, or in a rigid plastic matrix. The colored form, **55a,** was photobleached on exposure to visible light. X-ray crystal structures of fulgides **54a, 54b,** and **54c** were quite different. In fulgides **54b** and **54c,** X-ray analysis showed that an *S*-trans conformation is retained in their crystal structures, making it impossible for them to undergo conrotatory electrocyclic ring closure to yield a colored form. In fulgide **54a,** *S*-cis (cis-hexatriene conformation) was retained:



54a, R^1=Me

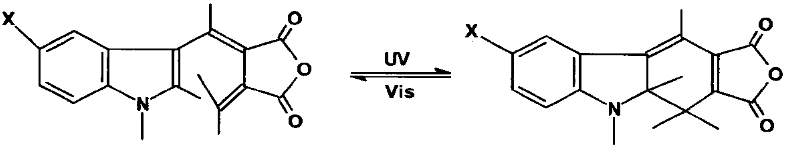


54b, R^1=Me **54c,** R^1=Ph

The distance between the two carbon atoms that form the new bond in photocyclization is very close (2.04 Å), which is favorable for cyclization.

Yokoyama and Kurita[72,73] demonstrated the design, synthesis, and photochromic behavior of 5-substituted indolyl fulgides (**56**). The molecular structure and photochromic reactions are shown as Scheme 17.

According to Pariser-Parr-Pople-Chemical Ionization (PPP-CI) calculations,[74] an electron-donating group introduced into the 5-position of the indole ring was suggested to cause a bathochromic shift of the absorption maximum of the colored form. The λ_{max} of **56** and **57** are summarized in Table 4.13. The quantum yields of



56 **57**

a, X = H; **b,** X = MeS-; **c,** X = MeO-; **d,** X = Me_2N-.

Scheme 17. Photochromism of compounds **56** and **57.**

the photocyclization reactions ($\Phi_{E\to C}$) decreased and the absorption maximum wavelength increased in the order H, MeS, MeO, and Me_2N. Compound **56d** was highly resistant toward the bleaching reaction, as shown in Table 4.13.

Substituent effects on the quantum yield of photoreactions of indolyl fulgide **58** have also been reported by Uchida *et al.*,[75] as shown in Table 4.14. The molecular structure and photochromic reactions are shown in Scheme 18.

Several conclusions can be drawn from the data in Table 4.14. When R^1 is propyl, $\Phi_{E\to Z}$, $\Phi_{Z\to E}$ are too small to be measured. In contrast, the coloring quantum yield ($\Phi_{E\to C}$) is larger than that of the methyl-substituted group. This is in good accord with the observation for furyl fulgides. The coloring quantum yield ($\Phi_{E\to C}$) of **58c,** with an *i*-Pr group, was five times as large as that of **58a.** A tendency for an increase in the bleaching quantum yield of the colored form under 403-nm light irradiation, along with an increase in the bulkiness of the R^1 group, was also observed. This is different from furyl fulgides; the reason is that the colored forms of indolyl fulgides have two absorption bands – one at about 380 nm and the other at about 580 nm. The UV absorption band of the colored form partially overlaps with the absorption band of the E form of indolyl fulgides. Irradiation with 403 nm light causes bleaching of the C form. When the IPD group is substituted by an ADD group, the bleaching quantum yield ($\Phi_{C\to E}$) of 608-nm irradiation is increased. In the discussion on the steric hindrance effects of R^1 and R^2 on the photochromism of furyl fulgides, a bulky R^1 worked to increase the coloring

Table 4.13. Absorption Spectra Data and Quantum Yields of Photoreactions of Indolyl Fulgide **56** (Z, E) and its Colored Form (**57**) (C) in Toluene

Compound	X	E/λ_{max} (ϵ_{max})	C/λ_{max} (ϵ_{max})	$\Phi_{E\to C}$ [a]	$\Phi_{C\to E}$ [a]	$\Phi_{C\to E}$ [b]	E/C
a	H	385 (8150)	584 (6810)	0.040	0.067	0.051	40/60
b	SMe	387 (8750)	600 (7090)	0.028	0.027	0.011	32/68
c	OMe	393 (9530)	625 (7060)	0.024	0.024	0.012	30/70
d	NMe_2	404 (8040)	673 (6200)	0.015	0.001	0.00004	3/97

Note: λ_{max} (nm); ϵ_{max} (mol^{-1} dm^3 cm^{-1}) .
[a] Irradiation with 403-nm light.
[b] Irradiation with 608-nm light.

Table 4.14. Effects of Substituents on Quantum Yield of Photoreactions and Spectroscopic Properties of Indolyl Fulgide **58** (Z,E) and its Colored Forms (**59**) (C) in Toluene

Compound	R^1	R^2R^2	R^3	R^4	$\Phi_{E\to C}$[a]	$\Phi_{C\to E}$[a]	$\Phi_{E\to Z}$[a]	$\Phi_{Z\to E}$[a]	$\Phi_{C\to E}$[b]	E/λ_{max} (ϵ_{max})	Z/λ_{max} (ϵ_{max})	C/λ_{max} (ϵ_{max})
a	Me	IPD	Me	Me	0.045	0.16	0.040	0.072	0.051	385 (8150)	397 (14,300)	584 (6810)
b	*n*-Pr	IPD	Me	Me	0.14	0.12	—	—	0.049	385 (7300)	—[c]	587 (7300)
c	*i*-Pr	IPD	Me	Me	0.23	0.31	0	—	0.054	385 (4790)	—[d]	574 (6180)
d	Me	ADD	Me	Me	0.037	0.52	0.11	0.063	0.42	384 (6980)	397 (13,900)	598 (5740)
e	*n*-Pr	ADD	Me	Me	0.054	0.22	—	—	0.33	386 (7150)	—[c]	600 (6240)
f	*i*-Pr	ADD	Me	Me	0.066	0.91	0	—	0.42	382 (4110)	—[d]	581 (5750)
g	Me	IPD	Et	Me	0.023	0.087	0.057	0.042	0.066	384 (8080)	395 (10,900)	616 (7460)
h	Me	IPD	Me	Et	0.095	0.23	0.048	0.059	0.049	384 (8080)	395 (17,400)	589 (7960)

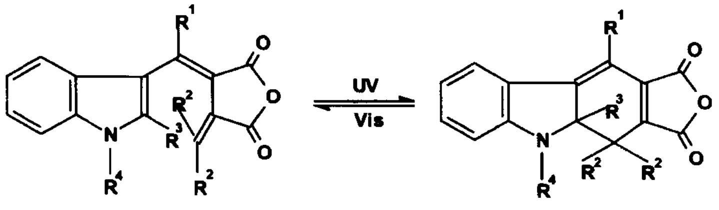
Note: λ_{max} (nm); ϵ_{max} (mol^{-1} dm^3 cm^{-1}).

[a] Irradiation with 403-nm light.

[b] Irradiation with 608-nm light.

[c] Impossible to calculate.

[d] The Z form was not detected during the photoreactions.



58 59

a, R^1= Me, R^2R^2C=IPD; **b,** R^1= n-Pr, R^2R^2C = IPD; **c,** R^1= i-Pr, R^2R^2C=IPD; **d,** R^1=Me, R^2R^2C= ADD; **e,** R^1=n-Pr, R^2R^2C=ADD; **f,** R^1=i-Pr, R^2R^2C=ADD (For 34a-f R^3=R^4=Me); **g,** R^1=R^4 =Me, R^2R^2C=IPD, R^3=Et; **h,** R^1=R^3=Me, R^4 =Et, R^2R^2C=IPD.

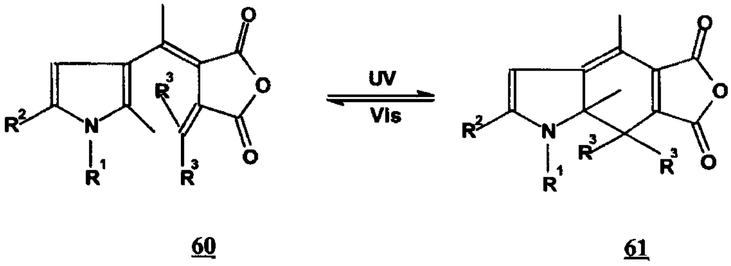
Scheme 18. Photochromism of compounds **58** and **59.**

quantum yield of UV irradiation, and a bulky R^1 and R^2 worked to increase the bleaching quantum yield of visible light irradiation. However, this finding does not apply to the case of indolyl fulgides. For **58f,** the *i*-Pr group does not work well to increase the coloring quantum yield efficiently ($\Phi_{E\rightarrow C}$ =0.066). For the fulgide with an ADD group (**58d, 58e, 58f**), the bleaching quantum yields at irradiation with 403 nm and visible light are both increased. That is, the effect of the *i*-Pr group for **58f** was offset by the ADD group. The substitution of the 2-methyl group of the indolyl ring with an ethyl group decreased $\Phi_{E\rightarrow C}$. In contrast, the $\Phi_{E\rightarrow Z}$ was increased. The absorption spectra data for indolyl fulgides with bulky alkyl substituents are listed in Table 4.14.

The difference in the absorption maximum wavelengths between the E form and Z form was not large. The deviation was only about 10 nm when R^3 was an ethyl group. The λ_{max} of the colored form was 616 nm, which was a 32-nm bathochromic shift compared with the methyl group-substituted fulgide, suggesting that the steric hindrance effect of R^3 on the planar molecular structure of the colored form must be considered.

4.3.4. Pyrryl Fulgides

Little effort has been made to study pyrryl-substituted fulgides during the past few years. Heller[76] suggested that the colored form of pyrryl fulgides showed absorption maxima in the visible region above 600 nm, which is over 100 nm longer than those of the corresponding furyl and thienyl fulgides. However, the overall yield in the synthesis of pyrryl fulgides is very poor and they are difficult to isolate and purify.[77] Photochromic properties of some pyrryl-substituted fulgides (**60**) have been reported by Heller,[76] Harris *et al.,*[77] Matsushima *et al.*[68] The molecular structures and photoreactions are shown in Scheme 19.



Scheme 19. Photochromism of compounds **60** and **61.** **a,** $R^1 = R^2 = R^3 =$ Me; **b,** $R^1 = R^3 =$ Me, $R^2 =$ Ph; **c,** $R^1 = R^3 =$ Me, $R^2 =$ *p*-tolyl; **d,** $R^1 = R^2 =$ Ph, $R^3 =$ Me; **e,** $R^1 =$ Me, $R^2 =$ Ph, $R^3 =$ cyclopropyl; **f,** $R^1 = R^3 =$ Me, $R^2 =$ CN; **g,** $R^1 = R^3 =$ Me, $R^2 = CONH_2$; **h,** $R^1 = R^3 =$ Me, $R^2 =$ H.

Absorption spectral data of fulgides **60** and its colored form (7,7a-dihydroindolyl derivatives) (**DHI, 61**) are summarized in Table 4.15.

Similar photochromic properties are exhibited in a wide range of organic solvents, in rigid plastic matrices, and in the crystalline state. In most photochromic organic compounds, the photocolored form absorbs strongly at the activating wavelengths, acting as an internal filter and inhibiting photocoloration. The UV and visible absorption spectra of **60h** in toluene before and after irradiation with 366-nm light is shown in Ref. 78. Compound **61h** (**DHI**) has a relatively weak absorption in the 300–400 nm region, so that the internal filter effect is decreased. A bathochromic shift for the λ_{max} of **61** was observed.

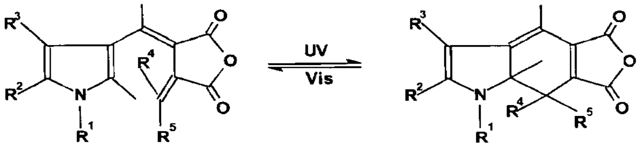
Recently Fan *et a1.*,[78,79,81–84,86,87] Zhao *et al.*,[80] and Fan *et al.*[85] have made an effort to study the molecular design, synthesis, photochromism, and application of pyrryl-substituted fulgides. A series of such fulgides (**62**) has been prepared by Fan's group, and the photochromic reactions investigated. The molecular structures and photochromic reactions are shown in Scheme 20.

Table 4.15. Ultraviolet and Visible Absorption Spectra Data of Fulgide **60** (E) and its Colored Form (**61**) (C)

Compound	R^1	R^2	R^3	Solvent	E/λ_{max} (ϵ_{max})	C/λ_{max} (ϵ_{max})[a]
60a	Me	Me	Me	Toluene	377(7420)	632(7300)
60b	Me	Ph	Me	Toluene	373 (9000)	615 (8580)
60c	Me	*p*-Tolyl	Me	Toluene	374(8600)	615 (8900)
60d	Ph	Ph	Me	Toluene	373 (7830)	605 (10,000)
60e	Me	Ph	Cyclopropyl	—	—	—
60f	CN	Me	Me	PMMA	345	579
60g	$CONH_2$	Me	Me	PMMA	355	629
60h	H	Me	Me	Toluene	364(6980)	620(6980)

Note: λ_{max} (nm); ϵ_{max} (mol^{-1} dm^3 cm^{-1}).

[a] The ϵ_{max} of the colored form (C) was calculated assuming quantitative conversion into colored forms on irradiation (366-nm) of the respective fulgide (E) and no photodegradation.



62 63

Scheme 20. Photochromism of compounds **62** and **63**. **a,** R^1-R^5 = Me; **b,** R^1-R^4 = Me, R^5 = Et; **c,** R^1 = R^2 = Ph, R^3 = H, R^4 = R^5 = Me; **d,** R^1 = Et, R^2 = Ph, R^3 = H, R^4 = R^5 = Me; **e,** R^1 = *p*-methoxylphenyl, R^2 = Ph, R^3 = H, R^4 = R^5 = Me; **f,** R^1 = Me, R^2 = Ph, R^3 = H, R^4 = R^5 = Me; **g,** R^1 = *p*-methylphenyl, R^2 = Ph, R^3 = H, R^4 = R^5 = Me; **h,** R^1 = R^3 = R^4 = R^5 = Me, R^2 = Ph; **i,** R^1 = Et, R^2 = Ph, R^3 = R^4 = R^5 = Me; **j,** R^1 = R^2 = R^4 = R^5 = Me, R^3 = Ph; **k,** R^1 = R^3 = Ph, R^2 = H, R^4 = R^5 = Me; **l,** R^1 = R^3 = R^4 = R^5 = Me, R^2 = *p*-methoxylphenyl; **m,** R^1 = R^2 = R^4 = R^5 = Me, R^3 = *p*-methoxylphenyl; **n,** R^1 = R^4 = R^5 = Me, R^2 = Ph, R^3 = *i*-Pr; **o,** R^1 = R^3 = R^5 = Me, R^2 = Ph, R^4 = *i*-Pr; **p,** R^1 = $C_{18}H_{37}$, R^2 = Ph, R^3 = R^4 = R^5 = Me; **q,** R^1 = $C_{16}H_{33}$, R^2 = Ph, R^3 = R^4 = R^5 = Me; **r,** R^1 = *p*-$C_{18}H_{37}OC_6H_4$, R^2 = Ph, R^3 = H, R^4 = R^5 = Me.

4.3.4.1. Absorption Spectra of Fulgide **62** and its Colored Form (**63**)

Replacing the 3-furyl or thienyl group by a 3-pyrryl group in fulgide molecules causes a major color change in the ring-closed form, a 7,7a-dihydroindolyl derivative (**7,7a-DHI**), from red to purple to blue or blue-green. The fulgide **62** in common organic solvents changed to deep blue or a blue-green color when the solution was irradiated by UV light. The colored form did not fade in the dark, which is attributed to the thermally stable 7,7a-dihydroindole derivatives (**7,7a-DHI, 63**). The reaction can be reversed and the color bleached by exposure to visible light. The absorption spectral change of fulgide **62e** in acetonitrile during photochromic processes is shown in Figure 4.1.

It can be seen from Figure 4.1 that irradiation of **62e** in acetonitrile with UV light caused the UV band (380 nm) to decrease while the visible band (640 nm) simultaneously increased. When the colored form (**63e**) was irradiated with 580-nm light, it was bleached, and the absorption band in the visible region decreased while the UV band increased.

The absorption spectra data of **62** and **63** in organic solvents are shown in Tables 4.16 and 4.17, respectively. The molar extinction coefficients at maximum wavelength ($\in_{max}$) of fulgide **62** range from 10^3 to 10^4 dm^3 mol^{-1} cm^{-1}.

4.3.4.2. The Effect of Solvent Polarity on the Absorption Spectra of Fulgide (**62**) and its Colored Form (**63**)

From Tables 4.16 and 4.17 we can see that the solvent polarity has different effects on fulgide **62** and its colored form (**63**). For fulgide **62,** solvents had little effect on the absorption maxima. However, a strong solvatochromic behavior was observed for the colored forms (**63**). More detailed absorption spectra data for **62** and **63** in various organic solvents are listed in Table 4.18. The polarity of the solvents was represented by the Dimroth scale $E_{T(30)}$.[88]

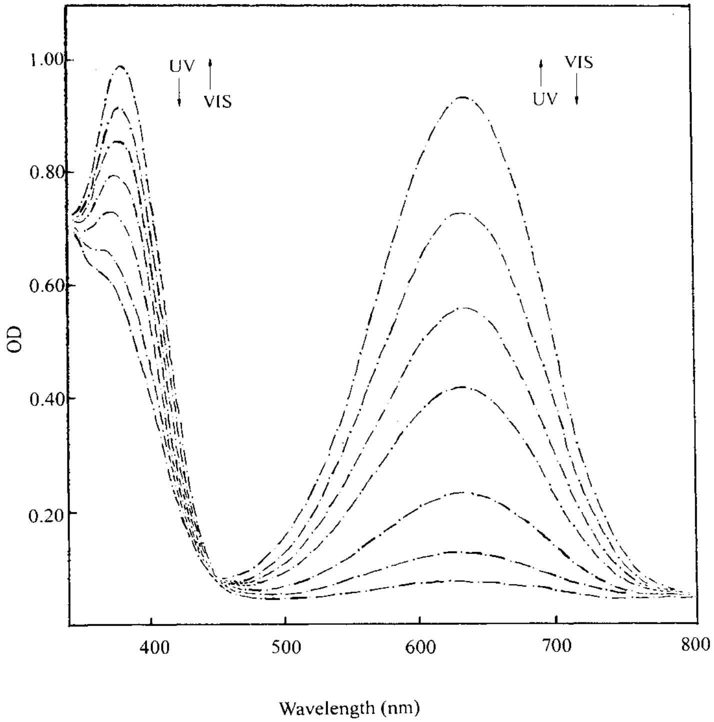
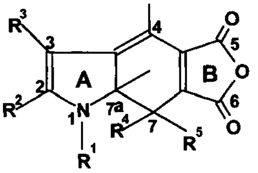


Figure 4.1. Absorption spectral change of the fulgide **62e** in acetonitrile during photochromic processes (366-nm light irradiation for photocoloring; 580-nm light irradiation for photobleaching).

From Table 4.18 it can be seen that the absorption maxima (λ_{max}) of fulgide **62** varied by about 15–30 nm in organic solvents with different polarity, whereas the corresponding absorption maxima of the colored form **63** changed significantly by about 50–100 nm, i.e., the absorption bands of **63** in the visible region were strongly red shifted with increasing solvent polarity. This indicates that the excited state of **63** has a (π,π*) character. The differences between the λ_{max} values of **63** in the various solvents were very large. For example, the absorption maximum wavelengths of **63h** were 715 and 625 nm in methanol and cyclohexane, respectively. This cannot be explained using the empirical criteria for the assignment of orbital configuration with



63

Table 4.16. Absorption Spectra Data of Pyrryl Fulgide **62** in Organic Solvents

						λ_{max} in solvents (nm)		
Compound	R^1	R^2	R^3	R^4	R^5	Acetonitrile	Toluene	Cyclohexane
62a	Me	Me	Me	Me	Me	385	380	—
62b	Me	Me	Me	Me	Et	—	390	—
62c	Ph	Ph	H	Me	Me	—	370	—
62d	Et	Ph	H	Me	Me	—	375	360
62e	*p*MOP[a]	Ph	H	Me	Me	380	370	365
62f	Me	Ph	H	Me	Me	380	370	—
62g	*p*-PM[b]	Ph	H	Me	Me	—	—	375
62h	Me	Ph	Me	Me	Me	387	380	—
62i	Et	Ph	Me	Me	Me	391	—	362
62j	Me	Me	Ph	Me	Me	371	370	338
62k	Ph	H	Ph	Me	Me	352	348	380
62l	Me	*p*-MOP[a]	Me	Me	Me	390	385	360
62m	Me	Me	*p*-MOP[a]	Me	Me	380	365	370
62n	Me	Ph	*i*-Pr	Me	Me	390	380	370
62o	Me	Ph	Me	*i*-Pr	Me	385	370	370
62P	$C_{18}H_{37}$	Ph	Me	Me	Me	385	380	370
62q	$C_{16}H_{33}$	Ph	Me	Me	Me	387	380	370
62r	*p*-OOP[c]	Ph	H	Me	Me	380	380	380

[a] *p*-MOP = *p*-methoxyphenyl.
[b] *p*- MP = *p*-methylphenyl.
[c] *p*-OOP = *p*-octodecoxyphenyl.

$\pi,\pi \rightarrow \pi,\pi^*$.[89] However, it can be rationalized by the formation of an intramolecular charge transfer state between the dihydropyrryl ring (ring A, electron-donating moiety) and the anhydride structure (ring B, electron-accepting moiety) in the colored form.[86]

In fulgide **62,** because of the steric repulsion between the pyrryl ring and the isopropylidene group, the succinic anhydride portion and the pyrryl ring are not coplanar, i.e., they are similar to furyl and thienyl fulgides. X-ray analysis shows that fulgide **62n** has a twisted structure.[87] After irradiation of **62** with UV light, the fused heterocyclic compound, a 7,7a-dihydro-5,6-anhydride indole derivative (**63**), is formed which has a nearly planar structure; ring A and ring B are nearly coplanar. This is why compound **63** possesses absorption maxima in the visible region. The results indicated that planar molecules are polarized much more by polar solvents than less planar molecules. The planar molecule is more favorable for the formation of the intramolecular charge transfer state, i.e., the substituted amino group in ring A acts as an electron donor and the carbonyl group in ring B acts as an electron acceptor. As a result, the absorption maximum (λ_{max}) of compound **63** (the colored form of fulgide **62**) in the visible region is severely affected by the solvent polarity and thus the red shift is consistent with an enlarged conjugated π system.

Table 4.17. Absorption Spectra Data of Compound **63** in Organic Solvents

	λ_{max} in solvents (nm)		
Compound	Acetonitrile	Toluene	Cyclohexane
63a	705	665	630
63b	—	670	—
63c	—	605	—
63d	—	640	—
63e	632	612	590
63f	665	630	600
63g	—	—	—
63h	712	660	625
63i	700	—	—
63j	699	651	620
63k	649	610	596
63l	720	670	640
63m	695	655	630
63n	700	660	630
63o	695	660	630
63p	705	665	640
63q	705	667	635
63r	635	610	590

Table 4.18. Solvent Effect on the Absorption Maximum Wavelength (λ_{max}) of Fulgide **62** and its Colored Form (**63**)

	λ_{max} (nm) in solvents [$E_{T(30)}$]					
Compound	Methanol (55.5)	Acetonitrile (46.0)	Acetone (42.2)	Dioxane (36.0)	Toluene (33.0)	Cyclohexane (31.2)
62e	390	380	380	379	370	360
62f	380	380	375	370	370	365
62h	390	387	385	380	380	375
62k	360	352	350	340	348	338
62a	390	385	385	380	380	375
62p	390	385	385	—	380	370
62r	380	380	378	—	380	380
63e	640	632	620	600	612	590
63f	670	665	660	630	630	600
63h	715	712	695	660	660	625
63k	640	649	635	616	610	596
63a	710	705	705	670	665	630
63p	707	705	694	—	665	640
63r	637	635	626	—	610	590

4.3.4.3. Substituent Effects on the Absorption Spectra of Pyrryl Fulgide **62** and its Colored Form (**63**)

The data in Tables 4.15, 4.16, 4.17, and 4.18 indicate that the substituents on the pyrryl ring have little effect on the absorption maxima of fulgide **62;** the λ_{max} values of **62** range from 360 to 390 nm in organic solvents, except for fulgide **62k,** which has a shorter λ_{max} than the others. However, the substituents have a significant effect on the absorption maxima of the colored form (**63**), as seen in Table 4.18. The following points are addressed: (1) *N*-alkyl-substituted molecules have longer absorption maximum wavelengths than the corresponding *N*-aryl-substituted molecules. For example, for **63e** and **63f,** the maxima are at 632 and 665 nm in acetonitrile, respectively, the difference being nearly 30 nm. For **63c** and **63d,** the λ_{max} values are 605 and 640 nm in toluene, respectively. The length of the *N*-alkyl substituent has little effect on the λ_{max}. For **63h, 63i, 63p,** and **63q,** the λ_{max} values are 712, 700, 705, and 705 nm in acetonitrile, respectively. (2) When R^2 or R^3 is a hydrogen atom, the λ_{max} appears at a shorter wavelength than that of the corresponding substituted molecules. For example, the λ_{max} of **63c, 63e, 63k, 63a, 63h,** and **63j** are 605, 612, 610, 665, 660, and 651 nm in toluene. (3) An electron-donating group in the para position of the phenyl ring can cause a slight red shift for the λ_{max} of **63.** The difference in λ_{max} for **631** and **63h** is 8 nm in acetonitrile. (4) Alkylidene groups (R^4, R^5) have little effect on the λ_{max} of **63.**

4.3.4.4. Crystal Structure of Fulgide **62n**

The X-ray crystal structure of the E form of fulgide **62n** was obtained as shown in Figure 4.2. The figure shows that fulgide **62n** has a considerably twisted structure. The dihedral angle between the succinic anhydride portion and the pyrryl moiety is 128.6°, while the dihedral angle between the phenyl ring and the pyrryl ring is 122.9°. The bond lengths in the cis-hexatriene unit (C1–C2–C16–C18–C21–C22) are partially averaging, in other words, the π-electrons in the conjugated system are partially delocalized. Owing to the steric interaction between the pyrrole ring and the IPD group, the bond angles of C2–C1–C15, C16–C18–C21, and C18–C21–C22 are 131.1(3)°, 132.3(3)°, and 130.6(2)°, respectively, which are much larger than those in a normal hexatriene. The distance between two reactive sites, C1 and C22 atoms, which form the new σ-bond after the intramolecular photocyclization, is 3.56 Å while for furyl, thienyl, and indolyl fulgides the corresponding distances in their E forms are 3.44, 3.90, and 2.04 Å, respectively.

4.3.5. Heteroaromatic Fulgides Containing Two Hetero Atoms

4-Oxazolyl (**64**), 4-pyrazolyl (**65**), 4-thiazolyl (**66**), and 4-isoxazolyl (**67**)-substituted fulgides have been prepared and their photochromic reactions investigated by several groups. The absorption spectra data and quantum yields of their photoreactions are listed in Table 4.19.

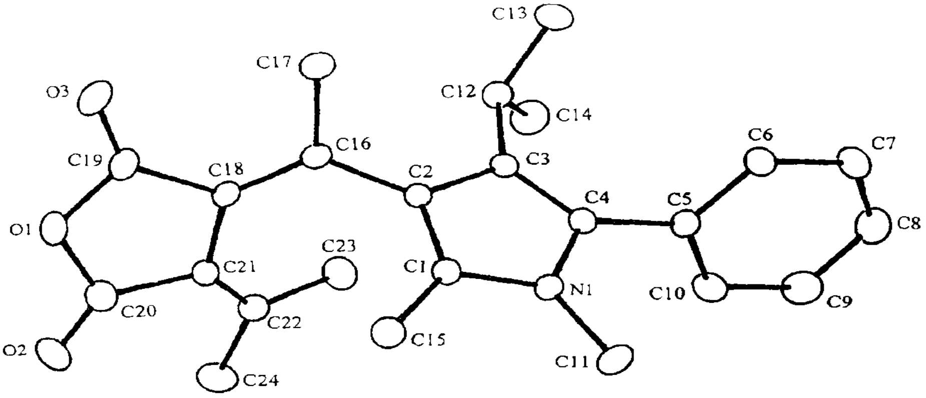
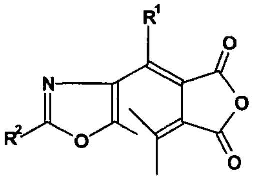


Figure 4.2. Crystal structure of E form of fulgide **62n.** Selected bond lengths and bond angles: C1–C2: 1.381(4) Å; C16–C18: 1.351(4) Å; C21–C22: 1.342(5) Å; C18–C21: 1.484(4) Å; C2–C16: 1.47(5) Å; C15–C1–C2: 131.3(3)°; C16–C18–C21: 132.3°; C18–C21–C22: 130.6(2)°. (Reprinted from Ref. 87 with the permission of the copyright owner, the Chinese Chemical Society.)

Suzuki *et al.*[90] reported that oxazolyl fulgides (**64**) possess good thermal and photochemical stabilities in comparison with 3-furyl fulgide. The quantum yield for coloration ($\Phi_{E \to C}$) of **64b** was 0.42, which is two times larger than that of **64a.** That is, introduction of the bulky alkyl substituent into the α-position was also effective in improving the$\Phi_{E \to C}$ of oxazolyl fulgide, which is similar to that of furyl fulgide. In fulgide **64,** when R^2 is substituted by an electron-donating group or by an extended conjugation chain, the λ_{max} of both fulgides and their colored forms exhibit obvious red shifts, e.g., the λ_{max} of the colored form of **64e** is 538 nm, which is almost 80 nm longer than that of fulgide **64a.**

Matsushima *et al.*[68] studied the photochromic properties of fulgides **65, 66,** and **67.** Their results showed that fulgides **65** and **66** possess an excellent fatigue



64

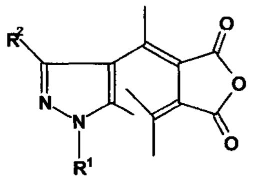
a R^1 =Me, R^2 =Ph

b R^1 =$C_{17}H_{34}$, R^2 =Ph

c R^1 =Me, R^2 =p-$C_6H_4NMe_2$

d R^1 =Me, R^2 =p-CH=CH-$C_6H_4NMe_2$

e R^1 =Me, R^2 =p-$(CH=CH)_2$-$C_6H_4NMe_2$

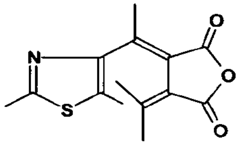


65

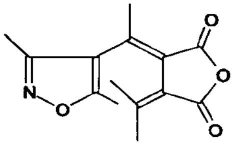
a R^1 =Me, R^2=Me

b R^1 =Ph, R^2=Me

c R^1 =Ph, R^2 =OMe



66



67

Table 4.19. Absorption Spectra Data and Quantum Yields of Photoreactions of Fulgides **64–67** and their Colored Forms (C)

Compound	E/λ_{max} (ϵ_{max})	Z/λ_{max} (ϵ_{max})	C/λ_{max} (ϵ_{max})	$\Phi_{E \to C}$[a]	$\Phi_{C \to E}$[a]
64a	337 (10,100)	347 (13,800)	462 (11,000)	0.18 (366)	0.054 (477)
64b	—[b]	—	—	0.42 (366)	—
64c	325 (33,300)	322 (31,400)	510 (18,300)	0.32 (366)	0.0091 (511)
64d	379 (36,100)	379 (36,800)	528 (26,000)	—	0.00019 (535)
64e	—	403 (37,800)	538 (27,600)	—	0.000049 (535)
65a	336	—	546	—	—
65b	335 (7200)	—	539 (4800)	0.03 (311)	0.28 (556)
65c	—	—	545	—	—
66	296 (18,500)	—	488 (8200)	0.21 (366)	0.061 (477)
67	304	—	435	—	—

Note: λ_{max} (nm); ϵ_{max} (mol^{-1} dm^3 cm^{-1}).

[a] The values in parenthesis refer to the irradiation wavelength of the photoreactions in nanometers.

[b] Not measured.

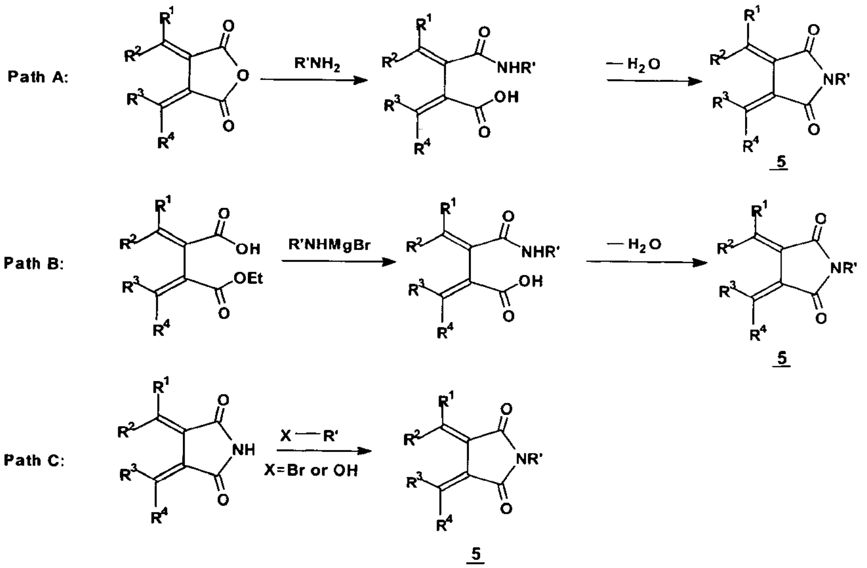
resistance and fairly good thermal stability, but fulgide **66** and its colored form underwent substantial degradation in hydroxylic solvents at room temperature.

4.4. FULGIMIDE, ISOFULGIMIDE, FULGENATE, FULGENOID, AND DICYANOMETHYLENE DERIVATIVES OF FULGIDES

4.4.1. Fulgimides

Fulgimides are the most important fulgide derivatives. They can be synthesized by the dehydration of succinamic acids, which are prepared by either the reaction of a fulgide with ammonia or primary amine, or by the reaction of a succinic half-ester with the Grignard salt of the amine. Some N-substituted fulgimides are prepared by reacting fulgimides with bromo or hydroxy compounds. Scheme 21 illustrates the three pathways for the preparation of fulgimides.

A wide range of aryl and heterocyclic fulgimides with structure **5** have been prepared. Their overall yields and melting points are summarized in Table 4.20.



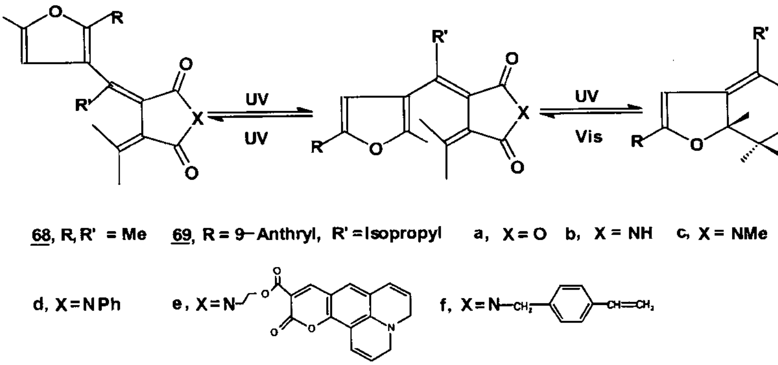
Scheme 21. Preparation methods for fulgimides.

Table 4.20. Synthetic Overall Yield and Melting Point of Fulgimides **5**

Compound	R^1	R^2	R^3	R^4	R^5	Method	Yield (%)	mp (°C)	Ref.
a	Me	Me	2,5-DMF	Me	H	A	58	161	51
b	Me	Me	2,5-DMF	Me	Octadecyl	A	77	—	89
c	Me	Me	2,5-DMF	Me	Benzyl	A	10	79–80	90
d	Ne	Me	2,5-DMF	Me	Vinylbenzyl	C	68	178	52
e	Me	Me	2,5-DMF	Me	*n*-HA	C	40.4	—	91
f	Me	Me	2,5-DMF	Me	*n*-HMA	C	29.3	—	91
g	Me	Me	TMOP	Me	H	A	47	189	21
h	Me	Me	TMOP	Me	Me	A	—	146	21
i	Me	Me	TMOP	Me	Ph	A	—	143	21
j	Me	Me	TMOP	Me	*p*-MOP	A	—	134	21
k	Me	Me	TMOP	Me	*p*-Tolyl	A	—	162–163	21
l	Me	Me	TMOP	H	Ph	A	—	158	21
m	Me	Me	α-Naphthyl	H	Ph	A	—	147–149	17
n	Me	Me	β-Naphthyl	H	Ph	A	35.7	151	17
o	Me	Me	Ph	H	Ph	A	48.1	123	18
p	Me	Me	Mesityl	H	Ph	B	—	180–181	18
q	Me	Me	Ph	Ph	Ph	A	89.5	210–211	18
r	H	Ph	Ph	H	Ph	A	76.2	200–201	17
s	H	Ph	Mesityl	Ph	Ph	B	—	191–192	17
t	Ph	Ph	Ph	H	Ph	A	—	239–240	23
u	Ph	Ph	H	Ph	Ph	A	—	185.5–186	23
v	Ph	Ph	H	Ph	Ph	A	74.2	285	23

Notes: 2,5-DMF=2,5-dimethylfuryl; TMOP=3,4,5-trimethoxyphenyl, *n*-HA=*n*-hexylacrylate, *n*-HMA= *n*-hexylmethyl acrylate.

A photochromic fulgimide can undergo a chemical reaction similar to that of the corresponding fulgide, as shown in Scheme 22.



Scheme 22. Photochemical reactions of compounds **68** and **69**. **68,** R,R' = Me; **69,** R=9-anthryl, R'=isopropyl; **a,** X=O, **b,** X=NH, **c,** X=NMe, **d,** X=NPh, **e,** X=N, **f,** X=N.

Fulgimides were reported to have photochromic properties similar to the parent fulgides, but the absorption bands show hypsochromic shifts. Among them, heterocyclic aromatic fulgimides play an important role for their potential applications in information storage. The quantum yields of the photochromic reactions of fulgimides in solution and polymer matrices are listed in Tables 4.21, 4.22, and 4.23. The quantum yields of ring opening and cyclization of fulgimides were almost equal to those of the corresponding fulgides. In solution, the attachment of side groups of fulgimide onto polymer chains had only little effect on the photochromic behavior, but in solid polymer, both the quantum yields of ring opening and of cyclization were slightly decreased compared with those in solution. In contrast, the isomerization of the Z form into the E form is strongly affected by the lack of mobility below T_g. This effect is most pronounced with the incorporation of fulgimide into a polymer matrix.[51]

A type of donor–fulgimide–acceptor (D–F–A) molecule **69e** (see Scheme 22) has been used to study intramolecular energy transfer. In this molecule, the fulgimide unit is a switch for energy transfer. By controlling the E or C form of the fulgimide molecule, an intramolecular energy transfer is possible, but the transfer mechanism cannot be determined definitely.[91]

Polymers are excellent supporting materials for the practical use of photochromic compounds by introducing stability and easy processibility. Liquid crystalline polymers offer the additional advantage that the macroscopic orientation can be influenced by external forces, such as applied electric or magnetic fields and therefore control of the strongly anisotropic properties can be achieved. A very promising result was reported by Cabrera *et al.*[92] The photocoloring reaction of liquid–crystal polymer **70** was first order in character and the photocolored form of the fulgimide side groups showed excellent thermal stability at room temperature. Polarizing microscope observations revealed that irradiation of compound **70** with

Table 4.21. Quantum Yield of Photocyclization Reaction of Fulgides and Fulgimides in Solution and Polymer Matrix[51,91]

Compound	λ_{irr} (nm)	$\Phi_{E\rightarrow C}$	Solvent or polymer	T (°C)	Remarks
68a	343	0.23	Cumene	22	Independent of solvent λ_{irr} (316, 333, 365 nm) and temperature (17–47°C)
		0.158	PS	25	T_g (PS): 91°C
		0.208	PPMA	50	T_g (PMMA): 26°C
		0.166	PMMA	25	T_g (PMMA): 90°C
68b	316	0.22	Cumene	25	Independent of solvent and temperature (25–80°C)
		0.173	PS	31.5	T_g (PS): 88°C
		0.204	PBMA	31.5	T_g (PBMA): 12°C
68f	316	0.2	Cumene	65	Poly(27f-co-styrene) containing 0.65 mol% of photochrome
		0.124	Poly(27f-co-styrene)	22.1	Below T_g (T_g =31°C)
		0.182		65	Above T_g (T_g =31°C)
69a	366	0.46	Toluene	28	Independent of λ_{irr} (at 313, 334, 366,405 nm)
69e	313	0.18	Toluene	22	
	334	0.13			
	366	0.04			
	405	0.01			

Notes: T= reaction temperature, T_g = glass transition temperature, PS=polystyrene, PMMA=poly(methyl methacrylate), PPMA=poly(propyl methacrylate), PBMA=poly(butyl methacrylate), Λ_{irr}=irradiation wavelength.

Table 4.22. Quantum Yield of Photobleaching Reaction of Fulgides and Fulgimides in Solution and Polymer Matrix[51,91]

Compound	λ_{irr} (nm)	$\Phi_{C\rightarrow E}$	Solvent or polymer	T(°C)	Remarks
68a	494	0.084	Cumene	24	
		0.10		47.4	
		0.12		63.4	
		0.067	Methyl pivalate	24	
		0.07	Hexane		
		0.05	2-butanone		
		0.075	PMMA	50	T_g (PMMA): 90°C
		0.091	PPMA	50	T_g (PPMA): 26°C
	468	0.097	Cumene	24	
68b	494	0.083	Cumene	25	
69a	520	0.10	Toluene	22	
69e	520	0.12	Toluene	22	

Notes: T=reaction temperature, T_g =glass transition temperature, PS=polystyrene, PMMA=poly(methyl methacrylate), PPMA=poly(propyl methacrylate).

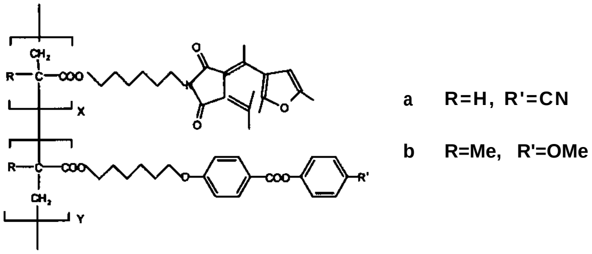
Table 4.23. Quantum Yield of Z → E Isomerization Reaction of Fulgides and Fulgimides in Solution and Polymer Matrix

Compound	λ_{irr} (nm)	$\Phi_{Z\rightarrow E}$	Solvent or polymer	T (°C)	Remarks
68a	343	0.23	Cumene	20.5	Independent of solvent, λ_{irr} and light intensity
		0.28		80	
		0.23	Methyl pivalate	20.5	
		0.046	PMMA	50	T_g (PMMA): 91°C
		0.064	PS	50	T_g (PS): 90°C
		0.194	PPMA	50	T_g (PPMA): 26°C
68b	316	0.206	Cumene	21.5	
		0.23		52.3	
		0.26		70.6	
		0.215	Methyl pivalate	21.5	
		0.23	Ethanol	21.5	
		0.048	PS	31.5	T_g (PS): 87°C
		0.169	PBMA	31.5	T_g (PBMA): 12°C
68f	316	0.026	Poly (Z and E 27f-co-styrene)	22	Below T_g (T_g =39°C)
		0.167		65	Above T_g

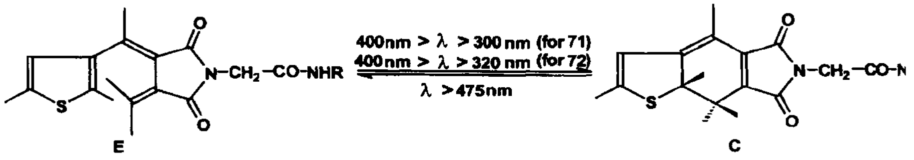
Source: Based on V. Deblauwe and G. Smets, Quantum yields of the photochromic reactions of heterocyclic fulgides and fulgimides, *Makromol. Chem. 189,* 2503–2512 (1988).

Notes: T=reaction temperature, T_g = glass transition temperature, PS=polystyrene, PMMA = poly(methyl methacrylate), PPMA=poly(propyl methacrylate), PBMA=poly(butyl methacrylate).

UV light led to a higher clearing point of the mesophase, thus making compound **70** potentially useful in information storage.



When fulgimides are attached to a protein backbone, they can be used as switches for photoregulation of the activities of the protein. Two kinds of fulgimide-containing proteins were synthesized and their photochromic reactions are shown in Scheme 23. In both cases, the fulgimide structure changed in the photochromic reaction, which resulted in the corresponding structural change of the protein backbone, thus influencing the activity of the protein. The reversible photoregulation of the protein–substrate assembly could be determined.[93–95]



71, R=Concanavalin

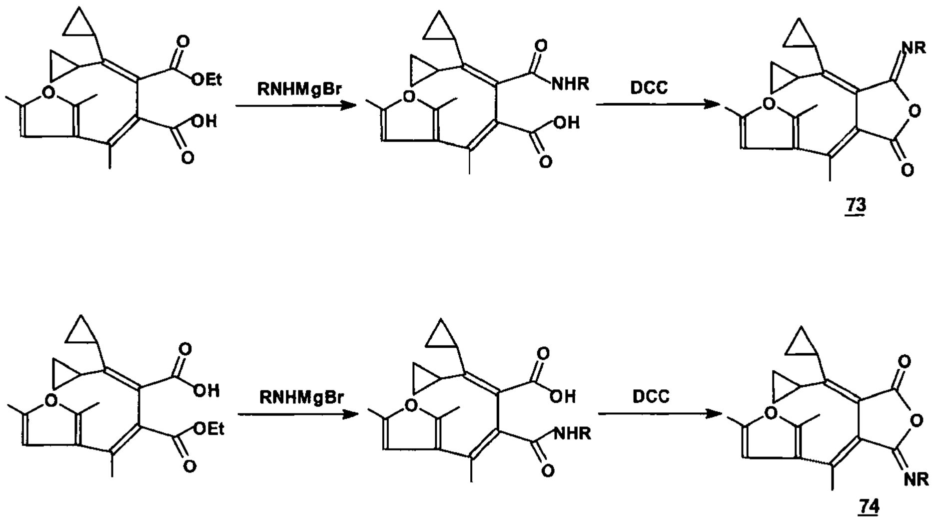
72, R=α-Chymotrypsin

Scheme 23. Photochromism of compounds **71** and **72**.

4.4.2. Isofulgimides

Isofulgimides are isomers of fulgimides in which one of the carbonyl groups of the anhydride ring has been replaced by an imino group. For the fulgide molecule, there are two oxygens that can be replaced. The α-isofulgimide **74** is defined as the one that has the carbonyl group as part of the conjugated system in its corresponding cyclized form, while the β-isofulgimide **73** has the doubly bonded nitrogen as a part of the conjugated system in its cyclized form. They can be prepared by cyclization of the appropriate succinamic acid with dicyclohexyl carbodiimide (DCC), as exemplified by Scheme 24.

The β-isofulgimide **73** shows photochromic properties similar to the corresponding fulgide. The main difference is that the molar extinction coefficient of the long wavelength absorption band of the cyclized form of the β-isofulgimide is greater than that of the cyclized form of the corresponding fulgide.



Scheme 24. Preparation of the isofulgimide (**a**, R=Ph; **b**, R=NHCH$_2$ Ph).

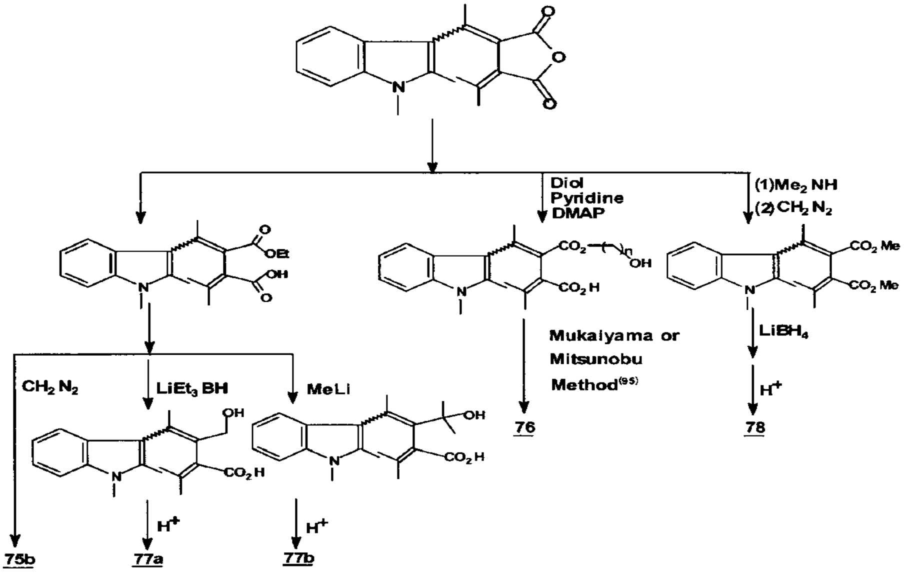
The cyclized form of the α-isofulgimide **74** shows a large hypsochromic shift of its long wavelength absorption band compared with the cyclized forms of the fulgide, fulgimide, and β -isofulgimide.[1]

4.4.3. Fulgenates and Fulgenolides

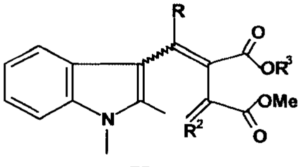
Fulgenate and fulgenolide, named by Yokoyama *et al.*,[7,8,96] are ester and lactone derivatives of fulgide, respectively. Fulgenate **75** could be synthesized by the esterification of the half-ester, which came from the alcoholysis of fulgide or from the Stobbe condensation of the alkylidene succinate with 3-acyl-1,2-dimethyl indole.[8] The cyclic fulgenate **76**[96] and fulgenolides **77** and **78**[7] were also prepared from the fulgide or from the half-ester, as shown in Scheme 25.

The synthesized fulgenates were thermally irreversible photochromic compounds. Their photochromic reaction is shown in Scheme 26.

Compounds **75, 76,** and **77** are photochromic; however, fulgenolide **78** has quite poor photochromic properties. The absorption spectra data and quantum yields of the photoreactions of fulgenates and fulgenolides, together with the parent fulgide, are summarized in Table 4.24.



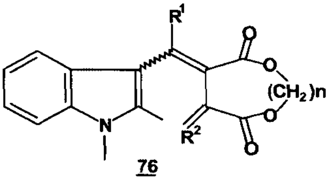
Scheme 25. Synthesis of fulgenate and fulgenolide.



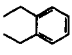
75

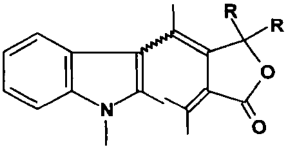
	R^1	R^2	R^3
a	Me	IPD	Me
b	Me	IPD	Et
c	Pr	IPD	Me
d	Me	ADD	Me

IPD=isopropylidene
ADD=adamantylidene



76

a n= 4
b n = 5
c n = 6
d $(CH_2)_n$= 



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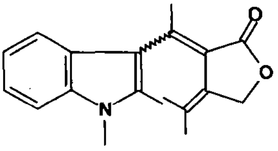
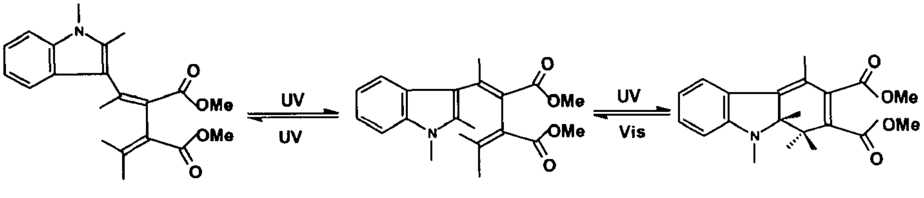


78

From Table 4.24, one can see that all the maximum absorption wavelengths of fulgenate and fulgenolide isomers are shorter than those of the corresponding fulgides. The ratio of the colored species of fulgenates in the photostationary state after UV irradiation is smaller and the bleaching quantum yield is greater than those of fulgides. Bridging of the fulgenate with a tetra or penta methylene chain to a cyclic fulgenate increases the photocyclization quantum yield and shifts the absorption maximum bathochromically, but has little effect on the bleaching quantum yield.



Z-75a **E-75a** **C-75a**

Scheme 26. Photochemical reactions of fulgenate **75a**.

Table 4.24. Absorption Spectra Data and Photochemical Reaction Quantum Yield of Fulgenates, Fulgenolides, and **54a** in Hexane

	λ_{max} (nm)			313-nm Irradiation				446-nm Irradiation
Compound	E	Z	C	$\Phi_{E \to C}$	$\Phi_{C \to E}$	$\Phi_{E \to Z}$	$\Phi_{Z \to E}$	$\Phi_{E \to C}$
75a	293 (11,500)	285 (9300)	437 (7100)	0.065	0.40	0.054	0.10	0.27
75b	293 (11,500)	285 (9000)	437 (7100)	0.060	0.32	0.044	0.10	0.32
75c	293 (11,300)	285 (8900)	445 (7600)	0.043	0.37	0.050	0.030	0.31
75d	293 (12,300)	285 (9400)	585 (7100)	0.071	0.051	0.050	0.10	0.40
76a	331 (5900)	347 (4000)	447 (6900)	0.37	0.32	0.20	0.073	0.25
76b	287 (9800)	284 (10,100)	442 (6700)	0.32	0.37	0.0078	0.056	0.35
76c	292 (10,800)	285 (8500)	432 (7000)	0.026	0.39	0.046	0.098	0.33
76d	334 (4300)	346 (2400)	454 (5200)	0.41	0.40	0.0 15	0.064	0.40
77a[a]	—	—	462 (9800)	0.35	0.41	0.004	0.03	0.23
77b[a]	—	—	464 (11,000)	0.39	0.40	0.011	—	0.20
54a[b]	385 (6800)	—	585 (7100)	0.045	0.16	0.040	0.073	0.051

[a] Irradiation with 366 nm for cyclization.

[b] 2,5-Dimethyl-3-indolyethylidene (isopropylidene) succinic anhydride in toluene irradiation with 405 nm for coloring and 608-nm light for bleaching.

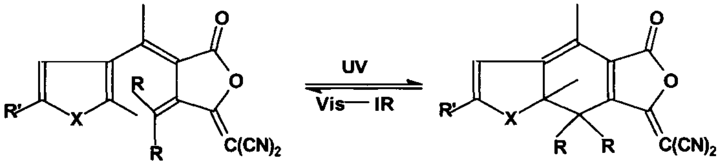
4.4.4. Tetrahydrofuran-2-one Derivatives

Replacement of the one carbonyl oxygen of the anhydride ring in photochromic heterocyclic fulgides by the powerful electron-withdrawing dicyanomethylene group produced another type of fulgide derivative, substituted 5-dicyanomethylenetetrahydrofuran-2-ones (**79**). On irradiation with UV light, compound **79** can undergo photocyclization reactions to give the colored form **80,** and the reverse process can be realized by irradiation with visible light (Scheme 27).[97–100]

Compounds **79** can be prepared by reaction of fulgides with a molar equivalent of malonitrile in the presence of diethylamine, followed by dehydration with acetyl chloride. A typical procedure is described in Section 4.7.

The yellow dicyanomethylene derivative **79** could be photocyclized to give the colored form (**80**), which could be bleached with visible-IR light. The absorption spectra of **79** were similar to those of the corresponding fulgides, but the powerful electron-withdrawing dicyanomethylene group of compounds **80** caused an unexpectedly large bathochromic shift (> 100 nm) of the long-wavelength absorption bands (see Table 4.25).

Another dicyanomethylene derivative of fulgide **81** was also reported. On irradiation with white light, the purple compound **81** underwent an intramolecular [4 + 4] photocyclization reaction to give colorless adducts, which underwent the reverse reaction thermally or photochemically.[35] The results demonstrated that molecular modification of fulgide molecules can significantly affect the photochromic properties of fulgide family compounds.



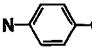
79 80

a X = O R= Me R' = Me

b X = O R= cyclopropyl R'=Ph

c X = O RRC= adamantylidene R' Ph

d X = S R= Me R'= Ph

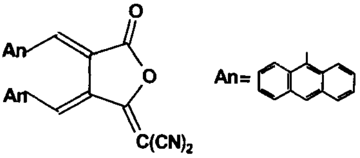
e X = NOMe R=Me R'=Ph

Scheme 27. Photochromism of tetrahydrofuran-2-one derivatives

Table 4.25. Absorption Spectra Data of the Colored Form of Fulgides and their β-Dicyanomethylene Derivatives (**80**)

	λ_{max} (nm)	
Compound	Toluene	Acetonitrile
80a	601	665
7,7a-DHBFa [a]	494	507
80b	636	—
7,7a- DHBFb[a]	500	—
80e	—	825
7,7a-DHIe[a]	612	632
80c	605	—
80d	669	684

[a] 7,7a-DHBF and 7,7a-DHI are the colored forms of the corresponding furyl and pyrryl fulgides respectively.



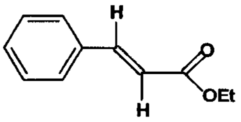
81

4.5. PHOTOCHROMIC MECHANISM

The photochromic mechanism of fulgides can be separated into four parts in this discussion: chromophore and excited state, E → Z isomerization, photocyclization, and heliochromic reaction.

4.5.1. Chromophores and Excited States of Fulgides

The general formula for fulgides is represented as compound **1**. Based on the absorption spectra data, [1–3] fulgide systems can be separated into two largely independent cinnamic anhydride-type chromophores. Freudenberg *et al.*[101] studied the absorption spectra of ethyl *trans*-cinnamate **82** and diethyl-(E,E)-bisbenzylidene succinate **83** and found that the absorption spectrum of compound **83** was similar to that of compound **82,** rather than 1,4-diphenylbutadiene. This indicated that compound **83** had two relatively independent chromophores, which was supported by Heller and Szewczyk.[16] They demonstrated that the UV spectrum of (E,E)-bis-(α–phenylethylidene) succinic anhydride **1t** was almost identical with a 1:1 mixture of (E,Z) and (E,E) isomers of the same fulgide.



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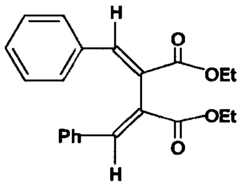
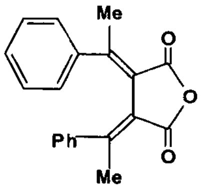


83



1t

Becker *et al.*[9] first studied the nature of the excited states of phenyl-substituted fulgide. They found that when a fulgide was excited by UV light, only the excited singlet state was formed, but that fluorescence could be seen in some fulgides at low temperatures. Later studies[10] of nanosecond laser photolysis experiments on phenyl fulgides confirmed that the excited singlet state has a π,π* character. It is the originating state for photochromism. No triplet transient species was observed and oxygen had no effect on the transient spectra and kinetics of the photochromic reactions, Ilge and Paetzold[102] and Ilge *et al.*[103] found that internal or external heavy atoms effects had no influence on the intersystem crossing, and they also confirmed the π,π* character of the excited singlet state.

Kurita *et al.*,[12] Takeda *et al.*,[13] and Parthenopoulos and Rentzepis[11] used picosecond laser photolysis techniques to study the photochromic processes of furyl fulgide. They found that the excited states of furyl fulgide and its colored form were singlet states and had π,π* characteristics. Takeda *et al.*[13] reported from theoretical studies that the values of the oscillator strength and the radiation lifetime (t_R) were

6.6×10^{-2} and 14 ns, respectively. The decay time t of the luminescence of the colored form of the fulgide was about 1–2 ns according to the experimental data. The values of the decay time were a function of the luminescence photon energy for various concentrations. The results suggested that the nonradiative tunneling process from the excited state to the ground state was responsible for the decay.

Zhao *et al.*[14] and Yu *et al.*[15] used a nanosecond laser photolysis technique to study the mechanism of pyrryl-substituted fulgides. They found that the excited singlet state was the originating state, but the excited triplet state, which originated from the excited singlet state via intersystem crossing, was also involved. This was because oxygen affected the photophysics and photochemical behavior of pyrryl-substituted fulgides.

Is there any (n,π^*) excited state? This is still an open question. In 1974, Heller and Szewczyk[16] studied diphenylmethylene (isopropylidene)-*N*-phenyl succinimide. The rate of electrocyclic ring closure was wavelength dependent. There was a remarkable difference between the absorption wavelength and the radiation wavelength of ring closure. These authors said that the change in sensitivity was related to the weak n,π^* absorption band of imide; the (n,π^*) excitation initiated the cyclization of fulgimide. The short fluorescence lifetime (4.6 ns) of α, α'-diphenyl-δ'-styrylfulgide and the value of the extinction coefficient suggested that a state of π,π^* character was most likely for the lowest excited singlet state.[10] It would not be expected that the fulgimide could be significantly different.

Is the excited state of fulgimide different from that of fulgide? No more studies have been presented to date.

4.5.2. E → Z Isomerization

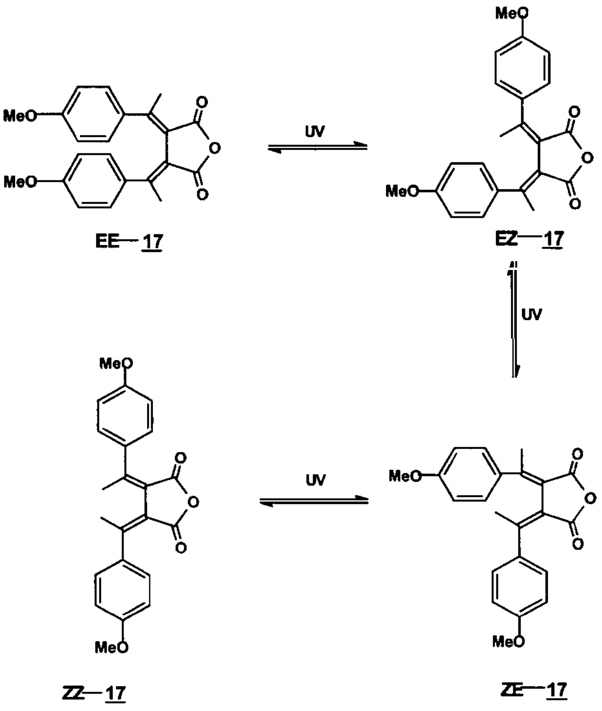
If four groups in compound **1** are totally different, there are four isomers based on two double bond, e.g., (E,E) (E,Z), (Z,E), and (Z,Z) isomers.

Ilge *et al.*[31,103] studied two α,δ-di(4- alkoxyphenyl) fulgides (**17**) in which there are only three isomers, e.g., (E,E), (EZ = ZE), and (Z,Z). The photoisomerizations are presented in Scheme 28.

According to the spectroscopic data and picosecond photolysis results, the torsional angles about the $\alpha-\beta$ and $\gamma-\delta$ double bonds could be assigned as the relevant reaction coordinates for the fulgide system.

The direct photoisomerizations are singlet-state reactions, as shown by their independence of oxygen and the addition of triplet quenchers. Ilge *et al.*[31,103] demonstrated that no potential barriers in the photoisomerizations, EE → EZ, and EZ → ZZ, were found. In contrast, there was a small barrier in the photoisomerization of ZZ → EZ or ZE; a very weak fluorescence was detected at 77 K, and the fluorescence of the ZZ isomer disappeared at temperatures above 130 K.

The isomerization reaction via the excited triplet state was only found in the EE ↔ ZZ and EZ ↔ ZE sensitized reactions. The E↔Z isomerization is a basic photochemical reaction. Different excited states have different chemical behaviors. The results can be summarized in Scheme 29 for phenyl fulgides.



Scheme 28. Photoisomerization of α,δ- di (4-methoxyphenyl) fulgide

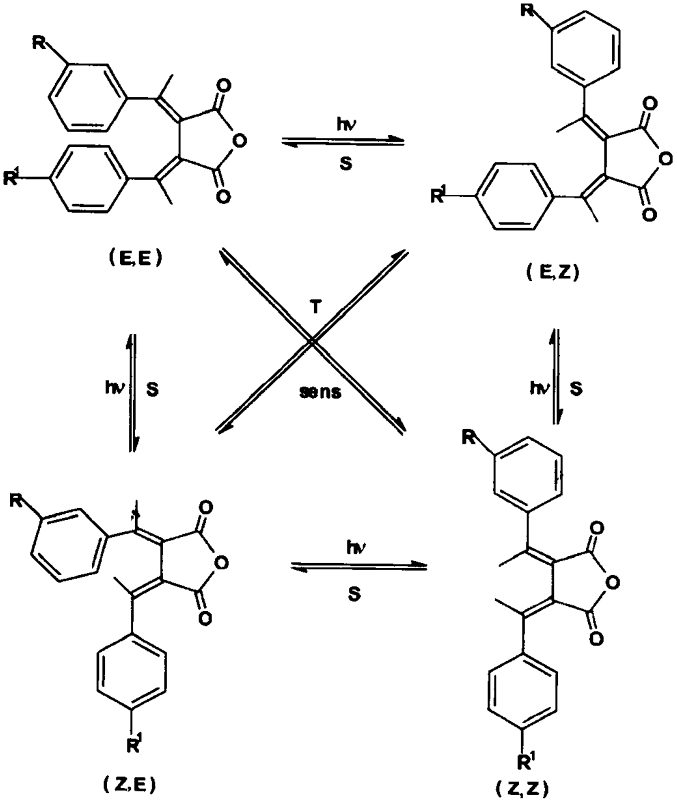
The E↔2 photoisomerization is also involved in heterocyclic fulgides and their derivatives. The quantum yields have been measured for different reactions. Yokoyama *et al.*,[7,8,44,45] Uchida *et al.*,[75] and Yokoyama and Kurita[104] very recently studied the E↔Z isomerization of fulgides in detail.

A typical representation is that for furyl fulgides, as shown in Scheme 30. The quantum yields of E↔Z photoisomerization are summarized in Table 4.26.

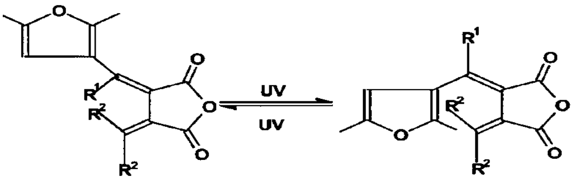
The data in Table 4.26 indicate that when the steric hindrance of R^1 was increased, the quantum yields of E↔Z photoisomerization decreased, but the steric hindrance effect of R^2 was not clear. The quantum yields of E↔Z isomerization for indolyl fulgides in toluene are summarized in Table 4.27. The reaction is shown in Scheme 31.

The substituent effect of R^1, R^2, and R^3 is not different, except for adamantylidene-substituted fulgide, the $\Phi_{E\rightarrow Z}$ of which is 0.11.

Indolyl fulgenate is a new kind of photochromic compound. The E↔Z photoisomerization is also involved, as shown in Scheme 32. The quantum yields of E↔Z photoisomerization are summarized in Table 4.28. In general, the quantum yields of E↔Z photoisomerization of fulgide and its derivatives are much lower than those of photocyclization (see Section 4.5.3).



Scheme 29. E↔Z photoisomerization of phenyl fulgides (R, R^1 are hydrogen or alkyl groups; Singlet state; T= Triplet state; Sens= Sensitized reaction)$^{(102)}$.



Scheme 30. E--Z photoisomerization reaction of compound **84.**

Table 4.26. Quantum Yields of E↔Z Photoisomerization of Furyl Fulgides **84** (Irradiated at 366 nm)

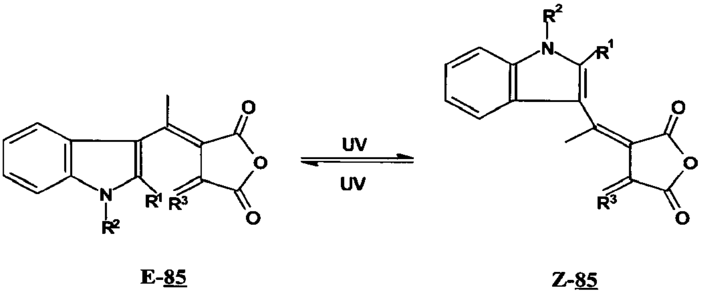
R^1	R^2	$\Phi_{E\to Z}$	$\Phi_{Z\to E}$
Me	IPD[a]	0.13	0.11
Et	IPD	0.06	0.12
Pr	IPD	0.04	0.10
i-Pr	IPD	0.00	0.06
t-Bu	IPD	0.00	—
Me	NBO[b]	0.30	0.42
i-Pr	NBO	0.01	0.01
Me	ADD[c]	0.10	0.10
i-Pr	ADD	0.02	0.05

[a] IPD = isopropylidene.
[b] NBO = norbornylidene.
[c] ADD = adamantylidene.

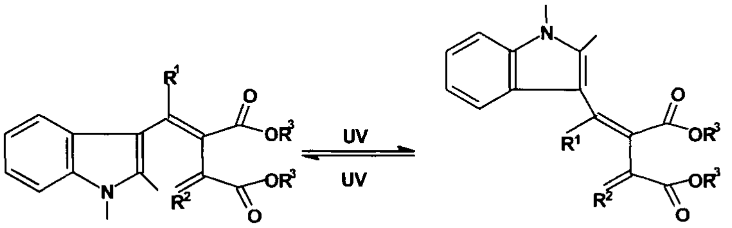
Table 4.27. Quantum Yields of E ↔ Z Photoisomerization of Indolyl Fulgides **85** in Toluene (Irradiated at 405 nm)

R^1	R^2	R^3	$\Phi_{E\to Z}$	$\Phi_{Z\to E}$
Me	Me	IPD[a]	0.040	0.072
Et	Me	IPD	0.057	0.042
Me	Et	IPD	0.048	0.059
Me	Me	ADD[b]	0.110	0.063

[a] IPD = isopropylidene.
[b] ADD = adamantylidene.



Scheme 31. E--Z photoisomerization reaction of compound **85.**



E-86 **Z-86**

Scheme 32. E-- Z photoisomerization reaction of compound **86.**

Table 4.28. Quantum Yields of E↔Z Photoisomerization of Indolyl fulgenate **86** in Hexane (Irradiated at 313 nm)

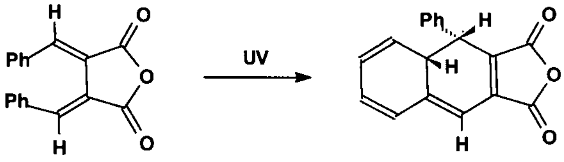
R^1	R^2	R^3	$\Phi_{E\rightarrow Z}$	$\Phi_{Z\rightarrow E}$
Me	IPD[a]	Me	0.054	0.10
Me	IPD	Et	0.044	0.10
Pr	IPD	Me	0.050	0.030
Me	ADD[b]	Me	0.050	0.10
Me	IPD	$-(CH_2)_4-$	0.020	0.073
Me	IPD	$-(CH_2)_5-$	0.0078	0.056
Me	IPD	$-(CH_2)_{10}-$	0.046	0.098
Me	IPD	*p*- $(OCH_2-)_2-C_6H_4$	0.015	0.064

4.5.3. Photocyclization Reaction of Fulgides and Derivatives

Santiago and Becker[9] first suggested that the photochromic reaction of phenyl fulgide (**1a**) was an intramolecular photocyclization reaction, which forms a 1,8a-dihydronaphthalene (1,8a-DHN) derivative, as shown in Scheme 33. Further studies on the photochromic mechanism of phenyl fulgides have been conducted by Heller and Szewczyk[16] and Darcy *et al.*[21] Their conclusion was that the photocyclization reaction of phenyl fulgides occurs by a photochemical conrotatory process, and the thermal electrocyclic ring-opening reaction is a disrotatory process in accordance with the Woodward–Hoffmann selection rules, as shown in Scheme 34.

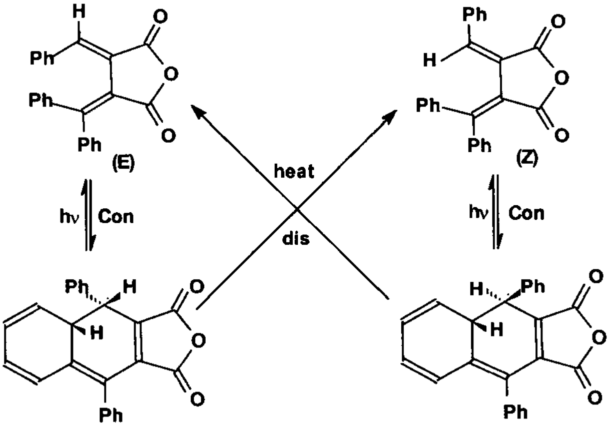
The electrocyclic reactions of phenyl fulgides and 1,8a-DHNs can be photo-induced by a conrotatory process. The electrocyclic ring-opening reaction of cyclohexadiene systems (1,8a-DHNs) can also be induced thermally via a disrotatory process.

Photochromic reactions of the heterocyclic fulgides are also in accordance with the Woodward-Hoffmann selection rules. The molecular structures have dramatic effects on the quantum yields of photoinduced ring-closure and ring-opening reactions of fulgides. The photochemical reactions of furyl fulgides are shown in Scheme 35 and the quantum yields are summarized in Table 4.29.[44,45,104]



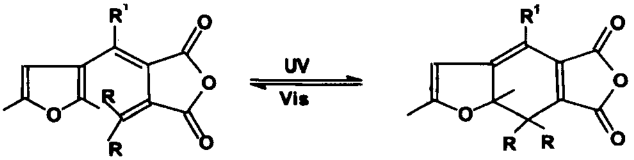
1a 1,8a-DHN

Scheme 33. Photocyclization reaction of fulgide **1a.**



1,8a-DHN 1,8a-DHN

Scheme 34. Photocyclization and bleaching of Phenylfulgide. Con= Conrotatory; dis= disrotatory.



87 88

Scheme 35. Photochromism of compounds **87** and **88.**

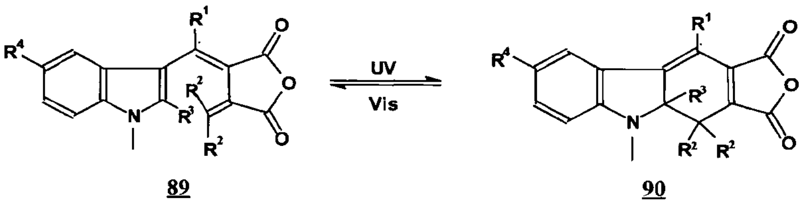
The data in Table 4.29 indicate that the quantum yield of ring closure ($\Phi_{E\rightarrow C}$) increased as the steric hindrance of R^1 increased. In contrast, R groups have a significant effect on the quantum yield of the ring-opening process; for example, if RRC is adamantylidene (ADD)$\Phi_{C\rightarrow E}$ is almost one order of magnitude larger than others.

Table 4.29. Quantum Yields of Ring-Closure and Ring-Opening Reactions of Furyl Fulgides **87**

No.	R^1	RRC	$\Phi_{E\to C}$[a]	$\Phi_{C\to E}$[b]
1	Me	IPD[c]	0.19	0.035
2	Me	IPD	0.18	0.048
3	Et	IPD	0.34	0.027
4	Pr	IPD	0.4	0.044
5	*i*-Pr	IPD	0.2	0.040
6	*i*-Pr	IPD	0.5	0.043
7	*t*-Bu	IPD	0.7	0.034
8	Me	NBO[d]	0.2	0.057
9	*i*-Pr	NBO	0.5	0.049
10	Me	ADD[e]	0.1	0.21
11	*i*-Pr	ADD	0.5	0.26

[a] Irradiated at 366 nm.
[b] Irradiated at 492 nm.
[c] IPD = isopropylidene.
[d] NBO = norbornylidene.
[e] ADD = adamantylidene.

The results of picosecond laser photolysis studies on furyl fulgides[11–13] indicated that photoinduced cyclization of E-fulgide gives a colored C form within a picosecond time scale. The ring-closure reaction is an ultrafast process; it occurs from an excited singlet state and requires no activation energy barrier. In contrast, the ring opening of the closed form has a small activation energy barrier and the luminescence of the closed form can be detected at low temperatures. The observed decay time of the luminescence of the closed form of furyl fulgide is about 1–2 ns and one order of magnitude shorter than the radiative lifetime. These results suggest that the nonradiative tunneling process from the excited state to the ground state is responsible for the decay. The photoreaction of indolyl fulgides is shown on Scheme 36 and the quantum yields are summarized in Table 4.30.[75, 104]



Scheme 36. Photochromism of compounds **89** and **90.**

The steric hindrance of R^1, R^2, and R^3 dramatically affects the quantum yields of photoreactions, $\Phi_{E\to C}$ and $\Phi_{C\to E}$, but for group R^4, the influence on the quantum yield of the photoreactions of fulgide has been attributed to the electronic

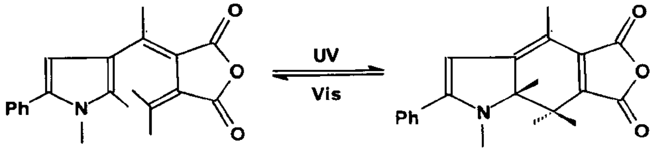
Table 4.30. Quantum Yields of Photoreactions of Indolyl Fulgides **90**

No.	R^1	R^{1}R^{2}C	R^3	R^4	$\Phi_{E\to C}$[a]	$\Phi_{C\to E}$[b]
1	Me	IPD[c]	Me	H	0.045	0.16
2	Me	IPD	Et	H	0.023	0.087
3	*n*-Pr	IPD	Me	H	0.14	0.12
4	*i*-Pr	IPD	Me	H	0.23	0.31
5	Me	ADD[d]	Me	H	0.037	0.52
6	*n*-Pr	ADD	Me	H	0.054	0.22
7	*i*-Pr	ADD	Me	H	0.066	0.91
8	Me	IPD	Me	SMe	0.028	0.027
9	Me	IPD	Me	OMe	0.024	0.024
10	Me	IPD	Me	NMe$_2$	0.015	0.001

[a] Irradiated at 403 nm.
[b] Irradiated at 608 nm.
[c] IPD = isopropylidene.
[d] ADD = adamantylidene.

properties. When the steric hindrance of R^1 increased, both the quantum yields of ring-closure and ring-opening reactions increased. The effect of R^2 had an opposite influence on the quantum yields. When the steric hindrance of R^2 was increased, the quantum yield of the ring-opening reaction ($\Phi_{C\to E}$) was increased but the quantum yield of the ring-closure reaction ($\Phi_{E\to C}$) decreased. When the steric hindrance of R^3 was increased, both quantum yields, $\Phi_{C\to E}$ and $\Phi_{E\to C}$, decreased. If the electron-donating ability of R^4 increased, both quantum yields decreased.

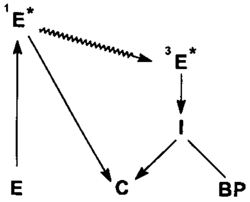
The photochromic processes of pyrryl fulgides[14, 15] has been studied by nanosecond laser photolysis; the photocyclization reactions are shown in Scheme 37.



91 **92**

Scheme 37. Photochromism of compounds **91** and **92.**

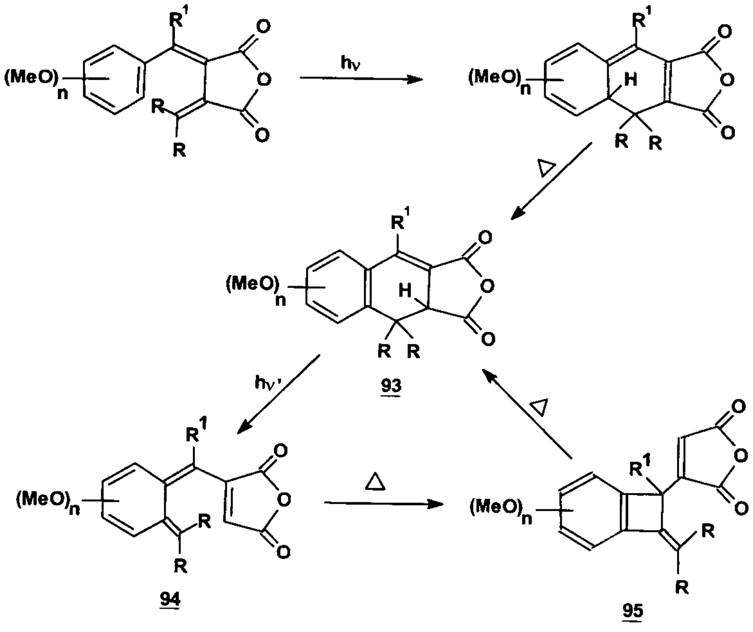
The transient absorption spectra show that besides the ring-closure product (C), a new transient species was found that could be quenched by oxygen. The authors assigned the new species to an excited triplet state. The time-resolved transient absorption spectra indicated that when the time delay was increased, the excited triplet state was decreased and the ring closure product was increased slightly. The decay of the excited triplet state can be fit to first-order kinetics. The lifetime (t) of the transient is 0.8 μs in cyclohexane. The authors noted that the photocyclization process proceeds mainly via the excited singlet state, but the excited triplet state is also involved. The photocyclization reaction mechanism of pyrryl fulgide (E) is summarized in Scheme 38.



Scheme 38. The mechanism of photocyclization of pyrryl fulgides. E = E-form; C = C-form; I = intermediate; BP = by-product.

4.5.4. Heliochromic Reaction

Heller *et al.*[105] studied the heliochromic reaction and synthesized several heliochromic compounds. The chemistry of the heliochromes was reviewed by Whittall.[2] The main idea of heliochromism is that properly substituted aryl or heteroaryl fulgides having a large steric hindrance group, such as an adamantylidene group linked to the succinic anhydride, photocyclized to form 1,8a-DHNs. Because of the presence of a hydrogen in the position of photocyclization, the 1,8a-DHNs could undergo a thermal [1,5] hydrogen shift to form 1,2-DHNs (**93**). These, in turn, underwent an electrocyclic ring-opening reaction by UV light irradiation and gave



Scheme 39. Heliochromic reaction.

$R^1 = H, CH_3$; RRC = adamantylidene; $n = 0 \sim 3$.

the colored *ortho*-quinodimethane derivatives (**94**). In the case of aryl fulgides, the quinodimethane derivatives rapidly underwent a thermal rearrangement to colorless compounds, benzocyclobutane (**95**), through thermal fading to compound **93.** The heliochromic reaction is shown in Scheme 39. Starting with a five-membered ring heteroaryl (e.g., furano) fulgide, the corresponding *ortho*-quinodimethane derivatives revert directly back thermally to the 1,2-DHNs without the formation of the intermediate aryl cyclobutanes. The end result is that the photochromism of the fulgides that had been restricted to a photochemical decoloration mechanism was transformed into a photochromic system that involved a thermal reversion.

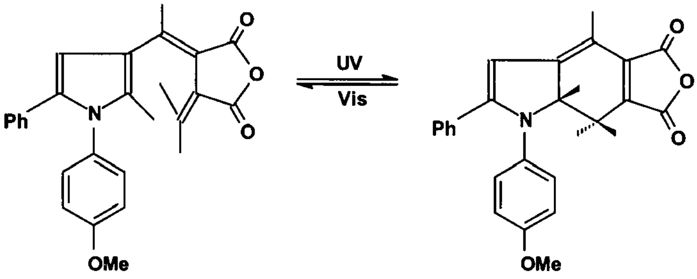
4.6. APPLICATIONS OF FULGIDES AND DERIVATIVES

The applications of fulgides and their derivatives are discussed separately for advanced materials, photochromic inks, and fabrics.

4.6.1. Optical Storage

Photochromic compounds could possibly be used for rewritable optical storage materials. This is one of the reasons for the widespread current interest in photochromics. Hirshberg is the first person who suggested that a photochromic compound could be used as an optical data storage material. Heller *et al.*[3] summarized the basic requirement of photochromic compounds for rewritable optical storage materials.

There are five problems that have to be solved in photochromic optical storage systems. They are (1) thermal stability at ambient conditions, (2) high sensitivity for writing and erasing processes, (3) appropriate fatigue resistance, (4) sensitive wavelength matching with an appropriate laser, and (5) non- or low-destructive readout properties. Recently, Yu *et al.*[106] published a paper on the application of pyrryl fulgides as erasable optical media. The photochromic reaction is shown in Scheme 40.



96 **97**

Scheme 40. Photochromism of compounds **96** and **97.**

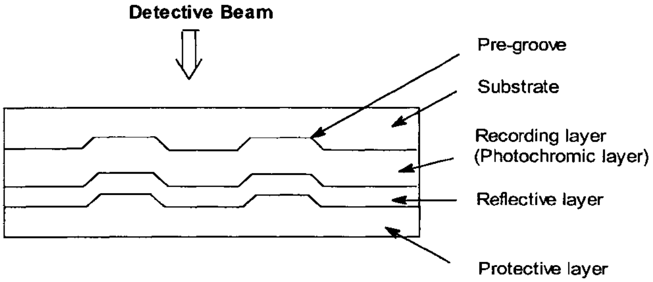


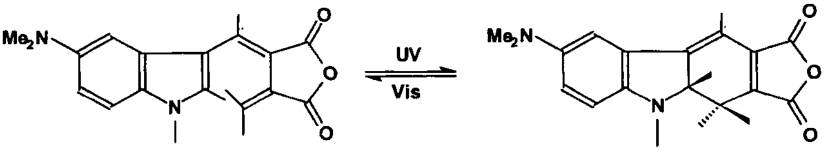
Figure 4.3. Structure of photochromic optical disk sample.

Two methods could be used to prepare the disk samples. One is spin coating. Compound **96** and poly(methyl methacrylate) (PMMA) were dissolved in cyclohexanone and the solution spun coated onto the disk substrate to prepare a photosensitive PMMA thin film on the disk doped with compound **96.** The second method is direct evaporation of pure compound **96** to the disk under high vacuum conditions. The structure of the photochromic optical disk sample is shown in Figure 4.3.

The coloration and bleaching processes consist of irradiation with UV light and a 632.8-nm laser, respectively. After five hundred written-erased cycles on the photochromic disk sample, there was no change that could be observed in the photosensitivity and other properties of the disk. The sample was stored at ambient conditions for over 5 years with its optical properties well preserved.

According to laser photolysis results, the time scale of the coloration of heterocyclic fulgides is shorter than a few nanoseconds and extends to the picosecond time scale. The results indicated that the photoresponse of the photochromic optical disk could be very fast.

How can nondestructive readout be obtained? It is still a serious question. There are several ways to try. Matsui *et al.*[107] presented a fundamental idea for a nondestructive readout method based on finding the wavelength dependence of the bleaching quantum yield of the colored form of the fulgide. An optical disk sample with photochromic compound **56d** has been made. The photochromic reactions are shown in Scheme 41.



56d **57d**

Scheme 41. Photochromism of compounds **56d** and **57d.**

The bleaching quantum yield of compound **57d** irradiated at 550 nm is about 0.00043. When the irradiation wavelength is moved over 750 nm, the quantum yield of bleaching is almost zero ($<10^{-5}$) within the limit of experimental error, but compound **57d** has enough absorbance at that wavelength for detection. It is expected that the readout cycles could be increased over a hundred thousand times under appropriate conditions. This method may be practical.

Another potential method had been suggested. The basic idea is that the wavelength of the detection beam is outside the absorption band of the colored form of the photochromic compound. Wilson[108] showed that the difference in the refractive indices between the two states of the photochromic fulgides in the near-infrared region could be used as a detection method.

The third possibility is to design photochromic materials in which the photochemical bleaching reaction of the colored form has an activity energy barrier that could act as a threshold. Picosecond laser photolysis studies on furyl fulgides[12] demonstrated that the transformation from the excited state of the colored form to the S_0 potential surface of furyl fulgides has an activity energy barrier.

4.6.2. Actinometry

Heller[109] and Wintgens *et al.*[110] studied furyl fulgides, for example, Aberchrome-540 (**35**), as actinometers. The photoreversible reactions are shown in Scheme 7.

Upon UV irradiation, fulgide **35** is converted to compound **36,** with a quantum yield of 0.20 in toluene at room temperature. It is wavelength independent between 313 and 366 nm. In contrast, the quantum yield of photobleaching of compound **36** was found to be temperature and wavelength dependent. The linear-dependent relation in toluene at 21°C is shown in Eq. 4.1.

$$\Phi_{36\rightarrow 35} = 0.178 - 2.4 \times 10^{-4}\lambda \text{ (nm)} \qquad (4.1)$$

This expression leads to $\Phi_{36\rightarrow 35} = 0.059$ at 494 nm. Wintgens *et al.* used Aberchrome-540 as an actinometer for studies of one- and two-laser photochemistry of short-lived reaction intermediates.

4.6.3. Photochromic Inks, Paints, and Fabrics

Several inks[111,112] have been developed for paints and labels of security masks. Furyl fulgide was spun into fibers and woven into a fabric that was used to manufacture photochromic labels. In 1995, the Color Change Corporation (U.S.) exhibited several different color photochromic fabrics as commercial products at the third international symposium on the chemistry of functional dyes.

4.6.4. Applications in Other Advanced Materials

The application of photochromic materials for optical storage is the most important area, as discussed in Section 4.6.1. Many other applications have been developed, for example, nonlinear optical image processing,[108] photoswitches,[92] energy-switchable devices,[91] and optical waveguides.[113] Some of them have been discussed in detail by Whittall.[2]

4.7. SOME EXAMPLES OF DETAILED SYNTHESIS

The synthesis of fulgides has been generally carried out through Stobbe condensations[1] since the beginning of this century, although important improvements have been reported.[2–4] A strong base should be employed in the condensation reaction. It can be any of the following compounds: sodium ethoxide, potassium ethoxide, potassium *tert*-butoxide, sodium hydride, lithium diisopropylamide (LDA), etc. The yield of the condensation reaction is strictly related to the steric hindrance and electronic properties of the ketone, as well as the steric hindrance of the substituted succinate esters. The reaction time and temperature are dependent on the nature of the catalytic base and the reactivity of the carbonyl compounds. In this section we give some examples of fulgide compounds.

The first investigations that led to the synthesis, characterization, and properties of fulgides were carried out on phenyl and substituted phenyl fulgides. Therefore it is essential to describe the synthetic procedure for the preparation of phenyl (substituted phenyl) fulgides. This will be beneficial to understanding the later modifications of the synthetic methods for the heterocyclic-substituted fulgides. Some representative examples follow.

4.7.1. (E,Z)-1-(*p*-Methoxyphenyl) ethylidene (isopropylidene) succinic anhydride[114]

p-Methoxy acetophenone (0.05 mol) and 0.05 mol of ethyl isopropylidene succinate were dissolved in 80 ml of dry toluene; 0.15 mol of sodium hydride (60% mineral oil dispersion) was added to the solution, a few drops of absolute ethanol were added to initiate the reaction, and the reaction mixture was stirred for 36 h at ambient temperature. The reaction mixture was poured into 200 g of ice water and the organic layer separated and extracted with saturated sodium carbonate (2 x 40 ml). The combined water solution was acidified with concentrated HCl; the brown oil was extracted into toluene (3 x 350 ml) and dried with anhydrous $MgSO_4$. The solvent was removed in vacuum, which gave the aryl-substituted monosuccinate ester. This residue was hydrolyzed in 10 g of potassium hydroxide/ 100 ml of ethanol solution for 10 h at refluxing temperature. After cooling, the resulting white solid was collected by filtration and redissolved in 50 ml of water, followed by acidification with hydrochloric acid. The substituted succinic acid was collected by filtration. The dry acid was dissolved in 50 ml of acetyl chloride and stored overnight. The solvent was removed by rotary evaporation and the residue was purified by chromatography on silica gel eluted with chloroform–petroleum ether (60–90°C) (1:1). The eluent was evaporated and gave a yellow solid, which could be recrystallized from chloroform–petroleum ether (60–90°C) (1:1). Yield: 32%; mp 120–122°C.

Calcd. for $C_{16}H_{16}O_4$: C:70.58; H:5.92; found: C: 70.32; H: 5.82. ^1H NMR ($CDCl_3$): 1.20 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.88–7.38 (4H, m, Ar-H). m/z (EI), 272 (M^+).

4.7.2. (E)- and (Z)-2-[1-[(2,5-Dimethyl-3-furyl)-2- methylpropylidene]-3-isopropylidene succinic anhydride (37b)

A mixture of sodium hydride (0.5 g, 12.5 mmol, 2.2 equiv., about 60% dispersed in mineral oil), toluene (15 ml), 2,5-dimethyl-3-isopropyl furan (0.98 g, 6.46 mmol, 1.1 equiv.), and diethyl isopropylidene succinate (1.24 g, 5.78 mmol) was heated to 80°C and a few drops of methanol added. After the evolution of hydrogen gas ceased, the reaction mixture was cooled and was poured into a mixture of ice and 5 mol dm^{-3} aq. HCl. The mixture was extracted with ether, and from the ethereal solution, acidic materials were extracted with 10% aq. Na_2CO_3. To this aqueous solution 1 mol dm^{-3} aq. HCl was added until the solution become strongly acidic, and the liberated only material (mainly composed of the half acid) was extracted with ether. The organic layer thus obtained was dried with anhydrous Na_2SO_4 and the solvent removed *in vacuo.* The acidic material (1.248 g) was then refluxed with a mixture of potassium hydroxide (10 g) in ethanol for 5 h. The reaction mixture was acidified with dilute hydrochloric acid and the mixture extracted with ether. The organic layer was dried with anhydrous Na_2SO_4, and the solvent evaporated. The residue thus obtained (1.123 g) was treated with acetic anhydride (20 ml) at 80°C for 30 min and the acetic anhydride was then removed *in vacuo.* The residue was extracted with toluene; the organic layer was washed with dilute aq. Na_2CO_3 and sat. aq. NaCl and was dried with anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the residue (0.921 g) was purified with column chromatography. Fulgide **37b** was obtained.

E-form of 37b: (124 mg, 7.8%): mp 104–105°C. ^1H NMR (90 MHz, $CDCl_3$) δ = 1.06 (3H, t, J=7.4 Hz), 1.35, 1.95, 2.26, 2.34 (each 3H, s), 3.03 (2H, q, J = 7.4 Hz), 5.94 (1H, s); IR (Nujol) 1800, 1760, 1220, 940 cm^{-1} ; MS (EI, 70 eV); m/z (rel. intensity) 274 (M+, 62), 259 $[(M\text{-}CH_3)^+$ 100]. Anal. calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.62%; found: C, 69.78; H, 6.71%.

Z-form of 37b: (58 mg, 3.7%): mp 123–124°C. ^1H NMR (90 MHz, $CDCl_3$) δ = 1.05 (3H, t, J=7.4 Hz), 2.03, 2.20, 2.27, 2.42 (each 3H, s), 2.45 (2H, d, J = 7.5 Hz), 5.90 (1H, s); IR (Nujol) 1800, 1755, 1215, 920 cm^{-1} MS (EI, 70 eV); m/z (rel. intensity) 274 (M^+, 69), 259 $[(M\text{-}CH_3)^+$, 100]. Anal. calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%; found: C, 69.94; H, 6.68%.

4.7.3. (E)-(1,2-dimethyl-4-isopropyl-5-phenyl)-3-pyrryl ethylidene (isopropylidene) succinic anhydride (62n)

A mixture of 1,2-dimethyl-3-acetyl-4-isopropyl-5-phenyl pyrrole (12.75 g, 0.05 mol) and diethyl isopropylidene succinate (10.7 g, 0.05 mol) in dry toluene (70 ml) was added to a stirred solution of sodium hydride (80% dispersion in oil, 3.8 g, 0.125 mol) suspended in dry toluene (10 ml) under nitrogen atmosphere. A few drops of absolute ethanol were added to initiate the exothermic reaction. The reaction mixture was stirred for about 40 h at ambient temperature until no hydrogen was formed, and finally the reaction mixture was poured into crushed ice-water (100 ml). The organic layer was separated and extracted with saturated sodium carbonate solution (2 x 50 ml). The combined aqueous layer was extracted with toluene (50 ml), and then the aqueous phase was acidified slowly with 5 M hydrochloric acid and washed with toluene (3 x 100 ml). The toluene solution was dried with $MgSO_4$ and the solvent was removed; the half-ester was obtained as a gum.

The crude half-esters were hydrolyzed by boiling with 10% (w/v) ethanolic potassium hydroxide (100 ml) for 8 h. On cooling, the dipotassium salt of the succinic acid was filtered off and washed with a small amount of cold ethanol. Most of the solvent was removed from the filtrate under reduced pressure using a rotary evaporator. The second crop of crystal of the dipotassium salt of the succinic acid was obtained and washed with a small quantity of cold alcohol. The combined potassium salts were dissolved in water (100 ml) and acidified slowly with 5 M hydrochloric acid. The succinic acid was filtered, dried thoroughly, and treated with acetyl chloride (100 ml). The acetyl chloride solution was stored for 30 h at room temperature in the dark. After removal of the excess acetyl chloride, the residue was chromatographed on a silica gel column using chloroform–petroleum ether (60–90°C) (1:1) as eluent. The photochromic fraction was collected and the solvent removed. The residue was crystallized from *n*-hexane-ether to give photochromic fulgide (**62n**) as pale yellow crystals (0.2 g, 1.06%) mp 158–159°C.

Found: C, 76.29; H, 7.32; N, 3.83; $C_{24}H_{27}NO_3$. Required: C, 76.36; H, 7.21; N, 3.71. δ_H (ppm): 0.82 (d, 3H, J=8.5 Hz, CH_3); 1.06 (d, 3H, J=8.5 Hz, CH_3); 1.18 (s, 3H, CH_3); 1.96 (s, 3H, CH_3); 2.32 (s, 3H, CH_3); 2.66 (hepta, 1H, J=8.5 Hz); 2.68 (s, 3H, CH_3), 3.14 (s, 3H, CH_3); 7.22–7.50 (m, 5H, Ar-H). m/z: 377 (M+, 45%), 362 (M+-15, 10%), 238 (100%).

4.7.4. Dicyanomethylene Derivative 79e

Equimolar amounts of pyrryl fulgide (**62e**) and malonitrile were dissolved in dry tetrahydrofuran (THF); 2 equivalent molars of diisopropylamine dissolved in dry THF were added dropwise to this solution. After addition, the mixture was maintained at ambient temperature for 2.5 h and the white precipitate appeared (disalt 30%). The disalt was filtered off and thoroughly dried under vacuum pressure, then dissolved in 1,2-dichloroethane and treated with acetyl chloride for 2 h without exposure to UV light. Removal of the solvent and purification by silica–gel column chromatography using dichloromethane–light petroleum ether (1:2) as eluent gave photochromic compound **79e** as a yellow crystal (40%) after recrystallization from diethyl ether–light petroleum ether; mp 160–162°C.

^{1}H NMR ($CDCl_3$)δ ppm, 1.53 (s, 3H, Me); 1.78 (s, 3H, Me); 2.24 (s, 3H, Me); 2.76 (s, 3H, Me); 3.83 (s, 3H, Me); 6.48 (s, 1H, pyrryl-H); 6.92–7.40 (m, 9H, Ar-H). IR (v, cm^{-1}), 2229 (CN), 1801 (C=O), 1547, 1509, 1483 (Ph). MS (EI), m/z = 475 (100%). Elemental analysis, calcd. for $C_{30}H_{25}O_3N_3$: C, 75.77; H, 5.30; N, 8.84; found: C, 75.12; H, 5.55; N, 8.45.

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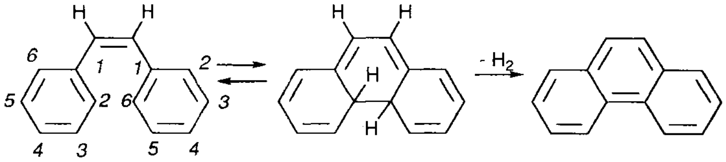
5

Diarylethenes with Heterocyclic Aryl Groups

MASAHIRO IRIE

5.1. INTRODUCTION

Stilbene is well known to undergo a trans-cis photoisomerization upon irradiation with UV light.[1] In addition to this isomerization, stilbene shows a photocyclization reaction to produce dihydrophenanthrene.



Although in the presence of air the dihydrophenanthrene irreversibly converts to phenanthrene by hydrogen elimination with oxygen, it thermally returns to the initial stilbene in the absence of oxygen. When methyl groups are substituted at 2- and 6-positions of the phenyl rings, the compound undergoes a reversible photocyclization reaction, even in the presence of oxygen.[2,3] The lifetime of the dihydro-type yellow closed-ring form is, however, very short and it quickly returns to the colorless open-ring form.

The reactivity of the dihydro-type isomer was found to change dramatically when the phenyl groups were replaced with heterocyclic five-membered rings, such as 2,5-dimethylthiophene.[2] Both isomers, open-ring and dihydro-type closed-ring forms, became thermally stable and cyclization/ring-opening reactions could be repeated many times while retaining adequate photochromic performance. In this

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Masahiro Irie • Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Fukuoka 812, Japan

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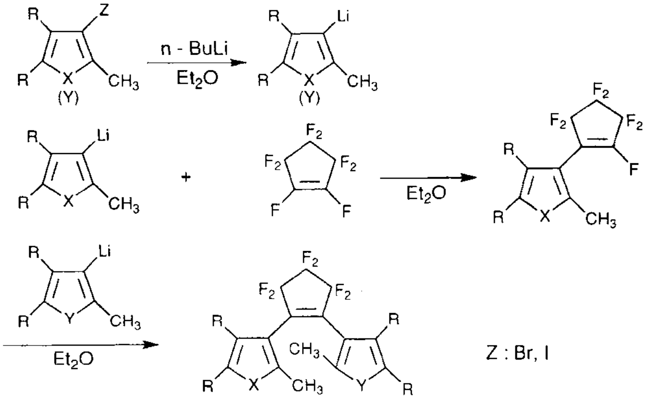
chapter, the synthesis and properties of the diarylethenes with heterocyclic aryl groups are described.

5.2. SYNTHESIS

5.2.1. Diarylperfluorocyclopentenes

Symmetric and nonsymmetric diarylethenes with various heterocyclic aryl groups were synthesized by elimination reaction of perfluorocyclopentene with aryllithium as shown in Scheme 1.[4–8]

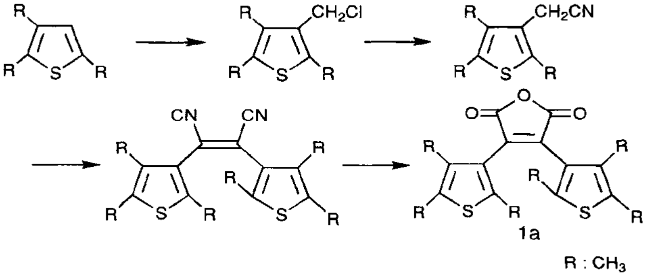


Scheme 1

The mono- and disubstituted perfluorocyclopentenes were selectively prepared by controlling the ratio of perfluorocyclopentene and aryllithium. The monosubstituted compound can be used for the synthesis of nonsymmetric diarylethenes.

5.2.2. Diarylmaleic Anhydride

1,2-bis(2,3,5-Trimethylthiophen-3-yl)maleic anhydride was synthesized from 2,3,5-trimethylthiophene as shown in Scheme 2[2]



Scheme 2

The 2,3,5-trimethyl-3-chloromethylthiophene was converted to a cyanomethyl derivative with NaCN, and then the cyanomethyl compounds were coupled in an NaOH alkaline aqueous solution in the presence of CCl_4. The 1,2-dicyano-1,2-bis(2,3,5-trimethylthiophen-3-yl)ethene was hydrolyzed in an alkaline solution to produce the acid anhydride derivative. The method can be applied to various diarylmaleic anhydrides.

5.3. PROPERTIES

5.3.1. Thermal Stability

Although thermal irreversibility is an indispensable property in applying photochromic compounds to photonic devices, almost all existing photochromic compounds lack this property. One of the isomers is thermally unstable and returns to the other isomer in the dark. Theoretical consideration based on molecular orbital theory revealed that the thermal stability of both isomers of diarylethenes is attained by introducing aryl groups, which have low aromatic stabilization energies.[9] The theoretical prediction was confirmed by the synthesis of diarylethenes with various types of aryl groups shown in Figure 5.1.[2,10–14]

The stability was dependent on the type of aryl groups. When the aryl groups were furan or thiophene rings, which have low aromatic stabilization energies, the closed ring forms were thermally stable and did not return to the open-ring forms in the dark. On the other hand, photogenerated closed-ring forms of diarylethenes with phenyl or indole rings, which have rather high aromatic stabilization energies, were thermally unstable. The photogenerated yellow color of the closed-ring form of 2,3-dimesitylbutene **9b** disappeared with a half-life of 1.5 min at 20°C. It returned quickly to the open-ring form. The closed-ring forms of diarylethenes with indole rings also exhibited thermally reversible reactions. The closed-ring forms **7b** and **8b** returned to the open-ring forms in the dark at 80°C. The different behavior in the thermal stability between diarylethenes with furan or thiophene rings and phenyl or indole rings agrees well with the theoretical prediction that the thermal stability depends on the aromatic stabilization energies of the aryl groups.

It is worthwhile noting that the closed-ring forms **5b** and **6b** were found to be thermally irreversible but photochemically reversible. The result indicates that the closed-ring forms of nonsymmetric diarylethenes become thermally stable when at least one of the heterocyclic rings has a low aromatic stabilization energy.

Diarylethenes having thiazole rings also undergo thermally irreversible photochromic reactions.[8] Introduction of a trifluoromethyl group at the 4-position of the thiazole ring is effective in increasing the thermal stability of the closed-ring form.

5.3.2. Fatigue-Resistant Character

Photochromic reactions are always attended by rearrangement of chemical bonds. During the rearrangement, undesirable side reactions take place to some

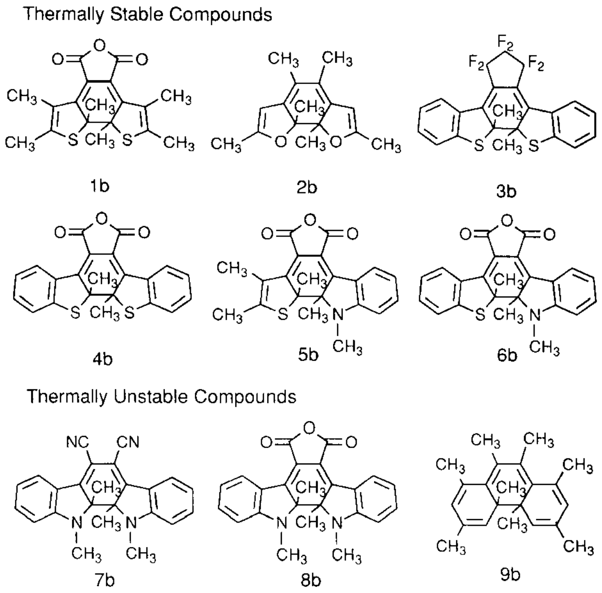


Figure 5.1. Thermal stability of photogenerated closed forms of diarylethenes with various types of aryl groups

extent. This limits the number of cycles of photochromic reactions. The difficulty in obtaining fatigue-resistant photochromic compounds can be easily understood by the following reaction sequence, in which a side reaction to produce B' is involved in the forward process.

$$B' \xleftarrow{\Phi s} A \underset{\lambda_2}{\overset{\lambda_1}{\rightleftharpoons}} B$$

Even if the side reaction quantum yield, Φs, is as low as 0.001 and B perfectly converts to A, 63% of the initial concentration of A will decompose after 1000 coloration–decoloration cycles. Thus the quantum yield for conversion to by-products should be less than 0.0001 to repeat the cycles more than 10,000 times.

The fatigue-resistant character was measured by using the apparatus shown in Figure 5.2. Benzene solutions containing various diarylethenes (~10^{-4} M) were irradiated with shorter wavelength (λ_1) light until the absorption intensity of the colored forms reached 90% of the photostationary state. Then the colored forms were completely bleached by irradiation with longer wavelength (λ_2) light. This operation was repeated many times.

Table 5.1 summarizes the result of repeatable cycle numbers in benzene.[2,4,10,14,15] The repeatable cycle number is the number of photochromic cycles after which the absorption intensity of the colored form decreases to 80% of the first cycle. For

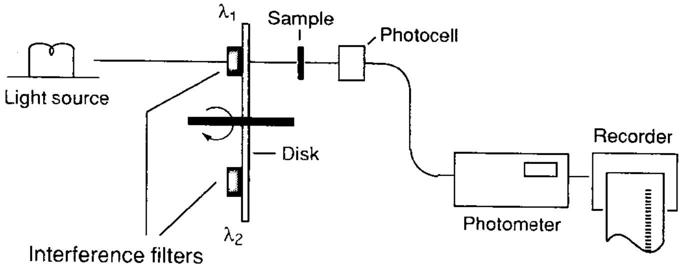


Figure 5.2. An apparatus used to measure fatigue resistant character.

dithienylmaleic anhydride, the repeatable cycle number was limited to less than 480 times even in the absence of air. When the thiophene rings were replaced with benzothiophene rings, the number increased remarkably. Diarylethenes with a 2-ethoxybenso[*b*]thiophene ring on the one end had good fatigue-resistance properties. 2-(1,2-Dimethyl-3-indolyl)-3-(2-ethoxybenzo[*b*]thiophen-3-yl)maleic anhydride kept adequate photochromic properties even after 1.0×10^4 cycles in the presence of air. Diarylperfluorocyclopentene derivatives with benzothiophene aryl groups also showed excellent fatigue resistance. Similar fatigue-resistant properties were observed in a polystyrene matrix. A cycle number as large as 7.0×10^4 was observed for 2-(2-ethoxybenzo[*b*]thiophen-3-yl)-3-(2,4,5-trimethyl-3-thienyl)-maleic anhydride in polystyrene film covered with poly(vinyl alcohol), which prevents oxygen diffusion, in the presence of singlet oxygen quenchers, such as nickel complexes.

5.3.3. Absorption Spectra

From the viewpoint of applications in optical memory media, it is desired to develop photochromic compounds that have sensitivity in the region of wavelengths of 650–830 nm. Although many symmetric diarylethenes with various heterocyclic rings were synthesized, the absorption maximum was shorter than 620 nm.[2] The longest absorption bond was observed for 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride. The closed-ring colored form was, however, thermally unstable and returned to the open-ring form in the dark. In an attempt to obtain thermally stable photochromic compounds having absorption bands at longer wavelengths, unsymmetrically substituted diarylethenes having an indole ring on one end and a thiophene or a benzothiophene ring on the other end were synthesized.

Table 5.2 summarizes the absorption maxima of various nonsymmetric diarylethenes. When an electron-donating group was introduced into the indole ring and/or an electron-withdrawing group into the thiophene ring, the absorption maxima shifted to longer wavelengths. The closed-ring form of 2,3-diarylmaleic anhydride with a 5-methoxyindole ring on one end and a thiophene ring on the other end (**12b**)

Table 5.1. Fatigue-Resistant Properties of Diarylethenes in Benzene

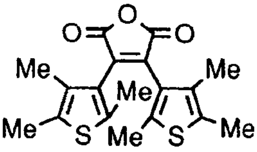
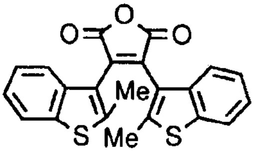
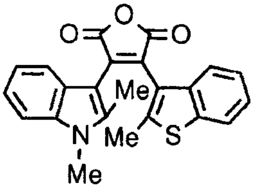
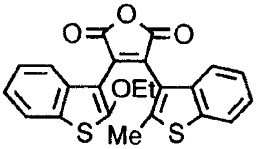
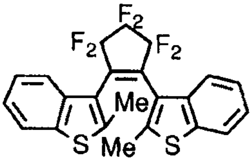
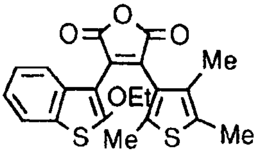
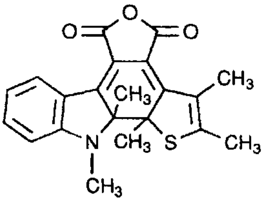
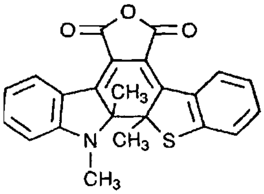
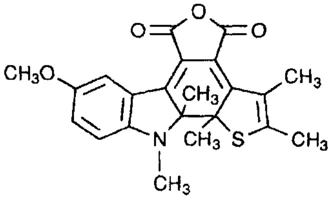
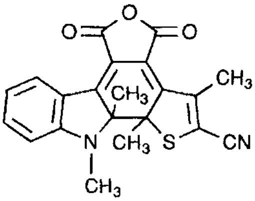
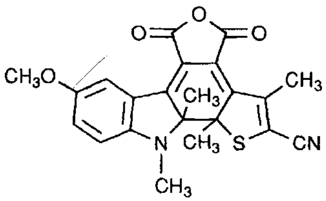
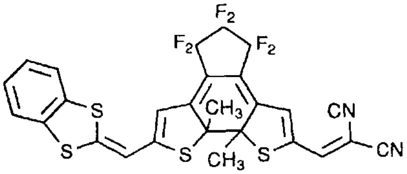
Compound		Repeatable cycle number	
		In air	Under vacuum
	**1a**	70	480
	**4a**	3.7×10^3	1.0×10^4
	**6a**	—	$> 1.1 \times 10^4$
	**10a**	$> 1.0 \times 10^4$	—
	**3a**	$> 1.3 \times 10^4$	—
	**12a**	3.0×10^4 in polystyrene	7.0×10^4 in polystyrene protected with PVA in the presence of single oxygen quenchers

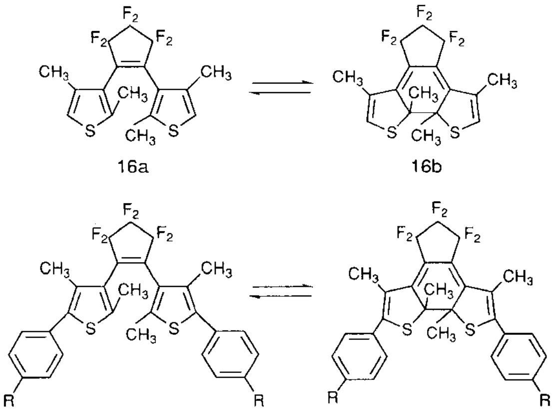
Table 5.2. Absorption Maxima of Nonsymmetric Diarylethenes in Hexane

Compound	λ_{max}	(nm)
	**5b**	578
	**6b**	583
	**12b**	611
	**13b**	626
	**14b**	680
	**15b**	828 (in benzene)

had a maximum of 611 nm in hexane, while the derivative with an indole ring and 5-cyanothiophene ring (**13b**) absorbed at 626 nm. The closed ring form having both electron-donating and -withdrawing substituents (**14b**) shifted the maximum to a longer wavelength at 680 nm, and the absorption edge was extended to 860 nm. The closed-ring forms of these compounds were thermally stable at 80°C.

When the strong electron-donating CH=benzodithiole and strong electron-withdrawing dicyanoethyl substituents were introduced into 5- and 5' positions of the thiophene rings, the absorption maximum of the closed-ring form **15b** was further shifted to 828 nm in benzene.[16] This is the longest absorption band so far synthesized. The closed-ring form was, however, thermally unstable. It returned to the open-ring form with t = 186 min at 60°C in benzene.

Another important absorption characteristic is an absorption coefficient. High sensitivity requires high absorption coefficients and high quantum yields. The following diarylperfluorocyclopentenes with various electron-donating or -withdrawing substituents were synthesized to reveal the effect of the substituents on the absorption coefficients (ε).[5]



16a

16b

17a: R = H

18a: R = OCH_3

19a: R = $N(C_2H_5)_2$

20a: R = CN

17b: R = H

18b: R = OCH_3

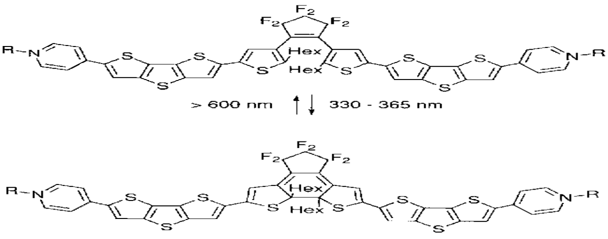
19b: R = $N(C_2H_5)_2$

20b: R = CN

Scheme 3

1,2-bis(2,4-Dimethylthiophen-3-yl)perfluorocyclopentene (**16a**) has an absorption maximum at 234 nm ($\varepsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) in hexane. Upon UV irradiation, it converts to the closed-ring form, with an absorption maximum at 534 nm ($\varepsilon = 5.05 \times 10^3$ M^{-1} cm^{-1}). The ε value is rather low. To increase the molar absorption coefficient (ε), electron-rich phenyl groups were introduced at the 5- and 5′-positions. Upon UV irradiation, a colorless hexane solution containing **17a** turned blue-violet and the absorption maximum was observed at 562 nm ($\varepsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}). The ε value was twice that of **16b.** The introduction of phenyl groups is effective in increasing the coefficient. To further increase the coefficient, the effect of introducing electron-donating and -withdrawing substituents to para-positions of the phenyl groups was examined. Table 5.3 summarizes the results. The absorption maxima and the coefficients increase with increasing electron-donating ability. The electron-withdrawing cyano-substituents shifted the absorption maximum to a longer wavelength, but did not increase the ε value. The value of **19b** is 3.6 times larger than that of the unsubstituted closed-ring form **16b.** When the diethylamino groups were protonated by the addition of trifluoroacetic acid, the protonated closed-ring form **21b** showed an absorption maximum at 582 nm in ethyl acetate and the ε value decreased to 55% of the neutral form. The cyclization and ring-opening quantum yields are also shown in Table 5.3.

Electron-rich dithieno(thiophene) groups are also effective in increasing the ε value of the closed-ring form (Scheme 4).

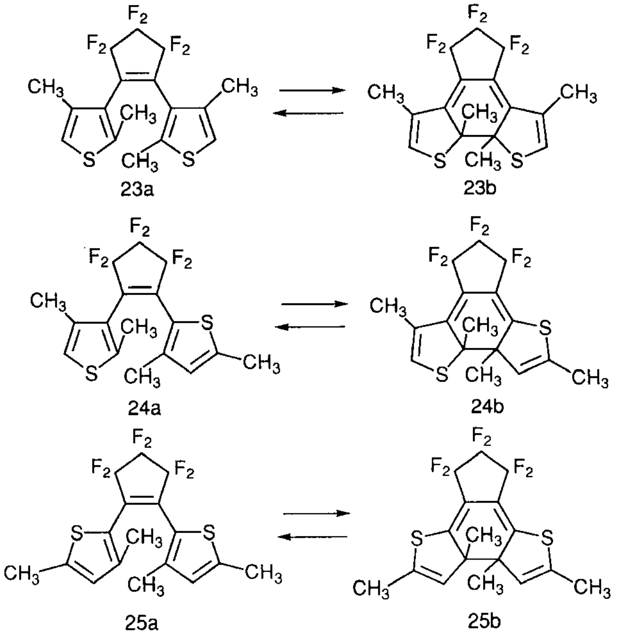


22: R = CH_3^+, anion = $CF_3SO_3^-$

Scheme 4

The compound **22b** has a very large ε value (704 nm, $\varepsilon = 4.3 \times 10^4$ M^{-1} cm^{-1}) in CH_3CN. The molecule has an interesting fluorescence property. Although **22a** gives a strong fluorescence, **22b** has no fluorescence. Such a fluorescence property change, along with the photochromic reaction, can be potentially used for readout in optical memory.[17]

When we apply diarylethenes to full color display, it is indispensable to synthesize yellow-developing compounds. We found that the color of the closed-ring forms of dithienylethenes changes dramatically, depending on the substitution position of the thiophene rings in the ethylene moiety.[18]



Scheme 5

Table 5.3. Absorption Characteristics and Photoreactivity of Dithienylethenes in Hexane

Compound	λ_{max} (nm) (ε/$10^4 M^{-1} cm^{-1}$)[a] a	λ_{max} (nm) (ε/$10^4 M^{-1} cm^{-1}$)[a] b	Quantum yield: Cyclization	Quantum yield: Ring opening 22°C	Quantum yield: Ring opening 80°C	Conv./%[b]
16	234 (1.3)	534 (0.50)	0.21	0.13	—	62
17	262 (2.8)	562 (1.1)	0.46	0.015	0.037	79
18	270 (3.3)	570 (1.4)	0.48	0.0080	0.018	88
19	305 (4.0)	597 (1.8)	0.37	0.0025	0.010	> 99
20	300 (3.0)	570 (1.1)	0.50	0.018	0.034	98

[a] Absorption coefficient at the absorption maximum.
[b] Conversion from the open- to the closed-ring forms in the photostationary state under irradiation with 313-nm light.

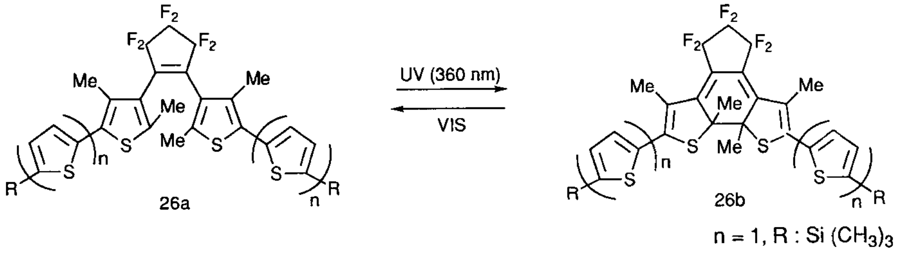
When the thiophene rings are attached to the ethylene moiety at the 3-position, such as compound **23a,** the closed-ring form has an absorption at 534 nm. The colorless solution turned to red upon UV irradiation. On the other hand, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**25**) exhibited a different color change. Photoirradiation of a hexane solution containing **25a** with 366 nm in the presence of air led to a decrease of the absorption at 336 nm and formation of a yellow solution, in which a new band appeared at 425 nm. The new absorption band disappeared by irradiation with light of wavelength > 440 nm. The quantum yields of the cyclization and the ring-opening reactions were determined to be 0.40 and 0.58, respectively. The blue shift of the absorption band of **25b** suggests that the π-conjugation in the closed-ring form is localized in the cyclohexadiene structure. The π-electron delocalization of **25b** is completely different from that of **23b,** in which π-conjugation extends through two thienyl moieties. The open-ring form **25a,** on the other hand, gave an absorption band at longer wavelengths than **23a.** The red shift suggests that π-conjugation in the open-ring form extends throughout the molecule. In **23a,** the π-conjugation is localized in the hexatriene structure. The substitution position controls the absorption maxima of both isomers.

5.3.4. Response Time

The dynamics of cyclization and ring-opening reactions of diarylethenes has been studied by using pico- and femtosecond laser photolysis experiments. Both cyclization and ring-opening reaction rates were measured for compound 1.[19] The open-ring form was excited with a 355-nm laser pulse (fwhm: 22 ps) in hexane and the formation of the closed-ring form was followed at 560 nm. A rapid spectral evolution in a few tens of picoseconds was observed. This is attributable to the photocyclization reaction. The rise curve was reproduced by taking into account the pulse duration and the time constant of formation (8 ps). Since the laser pulse duration is rather long, it is difficult to determine the rapid time constant precisely. The result, however, clearly indicates that the formation process is rapid–less than 10 ps–.

The ring-opening reaction was followed by exciting the closed-ring form in hexane with a 532-nm laser pulse. Immediately after the excitation, an increase in absorption of around 560 nm and a decrease in absorption of around 600–750 nm were observed. The increased absorption is ascribable to an S_1–Sn transition. The absorption decrease is assigned to the bleaching of the closed-ring form. The bleached signal intensity slightly recovered and reached a constant value. The time constant of 2–3 ps reproduced the recovery of the decreased absorption, indicating that the ring-opening reaction took place within 2–3 ps.

In the above measurement, the pulse duration is longer than the rates of the cyclization and ring-opening reactions. To determine the rates precisely, it is desirable to employ a shorter laser pulse. We measured the response time of the following dithienylethene in 1,2-dichloroethane by using a femto laser (180 fs) photolysis apparatus.[20]



Scheme 6

Absorption at 650 nm was found to increase in around 1 ps in accord with the decay of the absorption at 515 nm after irradiation with a 360-nm laser pulse (fiyhm: 180 fs). The absorption bands at 515 and 650 nm were assigned to S_1 – Sn transitions of the open-ring form (or some intermediate produced from the excited state of the open-ring form) and the closed-ring form, respectively. By taking into account the pulse duration and the time constant of formation of 1.1 ps, this kinetic analysis reproduced the decay and the rise profile. This result clearly indicates that the photocyclization of the dithienylethene took place in 1 ps.

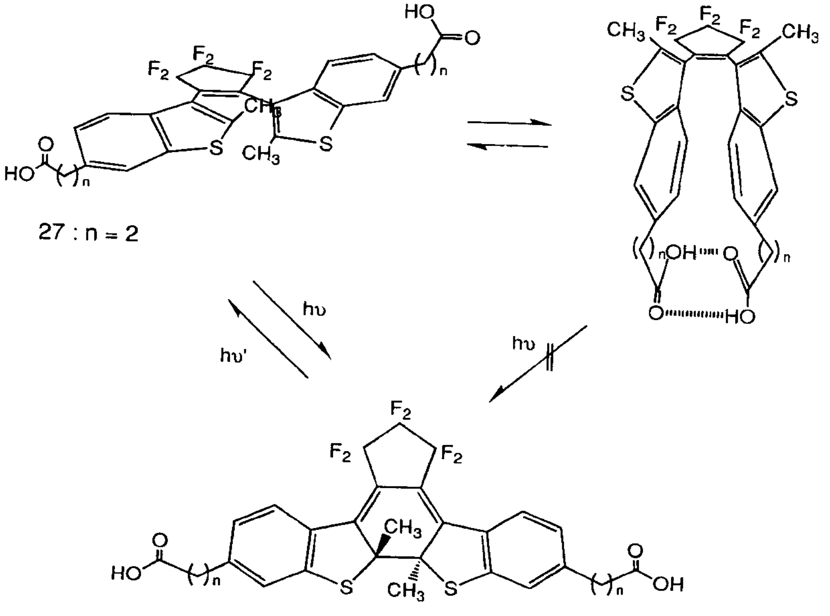
5.4. MOLECULAR SYSTEMS WITH CONTROLLED FUNCTIONALITY

5.4.1. Gated Reactivity

Photochromic reactions in general proceed in proportion to the number of photons absorbed by the molecules. Such a linear-response characteristic cannot be used as the basis of photonic devices. Memories or images are erased during storage under room light or after many readout operations. One possible way to avoid such a problem is to introduce gated photochromic reactivity in the molecules. The gated reactivity is the property that irradiation with any wavelength causes no molecular change, while a photoreaction occurs when another external stimulant, such as a chemical, heat or light of another wavelength, is present. Diarylethene derivatives having such a nonlinear response property have been synthesized.[21,22]

A diarylethene with heterocyclic rings has two conformations, with the two rings in mirror and C_2 symmetries, and its cyclization reaction can proceed only from the conformation with the two rings in C_2 symmetry. This means that photocyclization is prohibited if the heterocyclic rings are fixed to the mirror symmetry or have parallel orientation, while the reaction is allowed when the conformation converts to the C_2 symmetry, or antiparallel orientation, as shown in Scheme 7.

The photoreaction of **27** was completely prohibited in cyclohexane. The addition of a very small amount of ethanol to the cyclohexane solution resulted in photochromic reactivity. In the mixed solvents of cyclohexane and ethanol, the



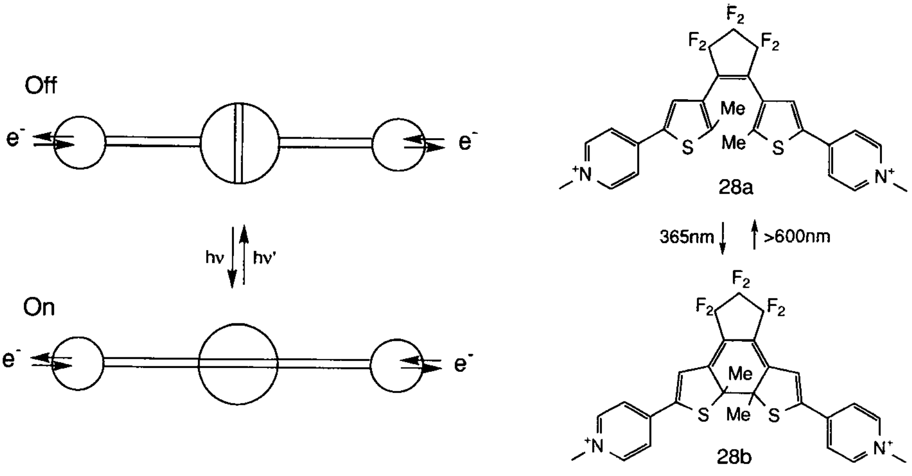
Scheme 7

photocyclization quantum yield increased with increasing ethanol content and reached a plateau value of 0.51 in the solvent containing 15 vol% ethanol. NMR measurement of the methyl protons at the 2-position of benzothienyl rings gave information concerning the relative population of the two conformations. The signals at around 2.4 and 2.1 ppm are assigned to methyl protons in the parallel and antiparallel conformations, respectively. In cyclohexane, the signal at 2.1 ppm was not observed, while it appeared with the addition of ethanol. This clearly indicates that the molecule was in a parallel conformation in cyclohexane, and converted to an antiparallel conformation upon the addition of ethanol. In cyclohexane, the intrahydrogen bonds fasten the molecule in the parallel conformation and make the molecule photochemically inactive. Conversely, ethanol acts as a switch to unlock the system.

The hydrogen bonds can also be broken by heating. In decalin, photocyclization did not occur below 60°C, while it was clearly observed at temperatures higher than 100°C. The molecule has both chemical- and thermal-gated reactivity.

5.4.2. Photoswitching of Electrochemical Properties

A switching function that allows for the reversible modulation of electrochemical properties by photoirradiation is of basic importance for the development of molecular electronic devices.[6,16,23] Such a function can be introduced into a molecule by incorporating a photochromic unit. A switching device that can control electron flow in a molecular system is shown in Scheme 8.[6,16]



Scheme 8

In the open-ring form, two pyridinium rings are electronically separated from each other and there is no appreciable interaction between them. This is the "off" state. On the other hand, in the photogenerated closed-ring form, the π-conjugation delocalizes between the two pyridinium rings and the absorption spectrum shifts to a longer wavelength, from 352 to 662 nm. This is the "on" state. Cyclic voltammetry indicated that whereas no electrochemical process occurs for the open-ring form in the +0.6 to – 0.6-V region, a clearly reversible and monoelectronic reduction wave was observed for the closed-ring form at a potential $E_{1/2}$ = – 230 mV vs. standard calomel electrode. The compound represents a prototype of a switchable molecular wire in which electron flow may occur in the closed-state, on/off switching being triggered by irradiation with light of well-separated wavelengths.

5.5. CONCLUSION

Diarylethenes having heterocyclic five-membered rings as the aryl groups, such as thiophene or benzothiophene rings, were found to undergo thermally irreversible and fatigue-resistant photochromic reactions. Theoretical consideration based on molecular orbital theory revealed that the photogenerated closed-ring forms of diarylethenes are thermally stable when the aryl groups have low aromatic stabilization energies. Most of the diarylethenes having benzothiophene rings underwent photochromic cycles more than 1.0 x 10^4 times. The absorption maximum of the closed-ring forms could be varied from 425 to 825 nm by changing the aryl groups and introducing various substituents into the groups. The maximum also changed dramatically, depending on the substitution position of the aryl groups in the ethylene moiety. The response times of both cyclization and ring-opening reactions were less than 10 ps. Thermal or chemical control of photochromic reactivities could be achieved by introducing intramolecular hydrogen bonding groups into the diarylethenes.

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6

Photochromism of Dihydroindolizines and Related Systems

HEINZ DÜRR

6.1. INTRODUCTION

The photochromism of dihydroindolizines (DHIs) – a new class of photochromic molecules – was discovered only in 1979.[1,2] These molecules are among the few new photochromes discovered in the past 20 years.[3] Their synthetic access has been exploited in detail and their photochemical and photophysical parameters have been studied in a broad sense.[3–7] The potential applications are vast and compare favorably with those of the known photochromes.[8] The chemistry and photochemistry of the DHIs have been described previously in several surveys.[3–7] This review will serve as a short introduction to the field. It will as well include typical preparation modes for the class of dihydroindolizines as well as their aza-homologs, typical five-membered heterocycles. A new class of photochromics derived from these photochromic heterocycles (DHIs) that allows for supramolecular interactions is presented. Some typical applications that are close to commercially useful systems are discussed.

The characteristic structural feature of the dihydroindolizines-based molecules is a five-membered ring, typically a cyclopentene anion. The substitution of the carbanion in this molecule by a heteroatom generates heterocyclic five-membered rings.[9–15] These can undergo a ring opening to zwitterionic species or neutral heteropentadienes. The process can be induced photochemically and is reversed either thermally or photochemically. Thus a new photochromic system based on a five-atom, six-electron $(4n + 2)\pi$ system is created. This system can in principle be

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Heinz Dürr • Fachbereich 11.2 - Organische Chemie, Universität des Saarlandes, Im Stadtwald, D-66041 Saarbrücken

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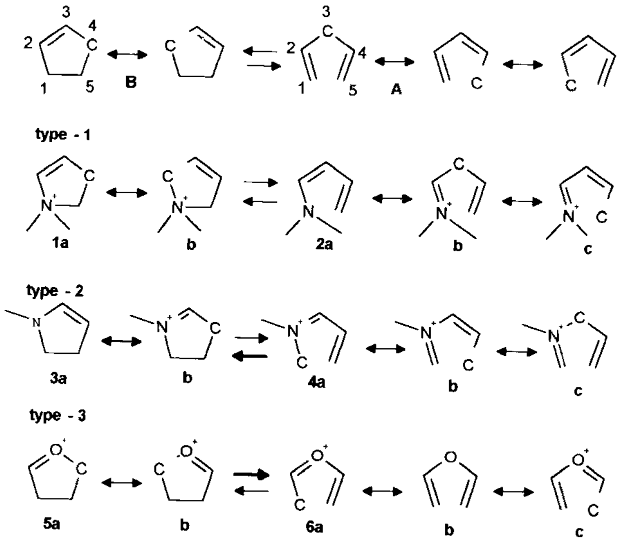


Scheme 1

the essential structural unit of many photochromic systems, such as those shown in Scheme 1.[9–14]

Type-1 systems (heteroatom in position 1) possess a formally charge-free resonance formula such as **2a.** The cyclic structure can be represented only by the charged formulas **1a, b.** This is the reason the more stable species in this case is the open-ring form **(2).**

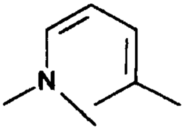
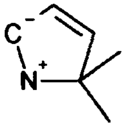
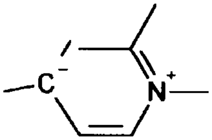
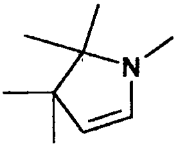
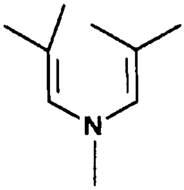
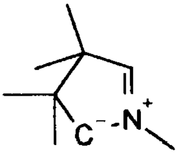
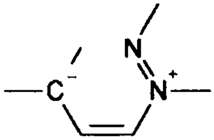
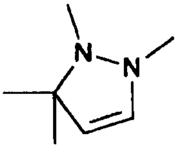
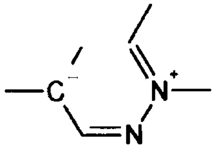
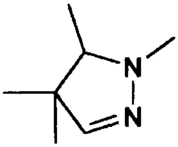
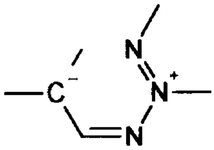
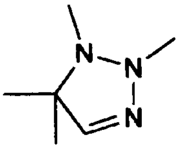
In Type-2 systems the heteroatom is in position 2 allowing a uncharged resonance formula **3a** for the cyclic molecule to be drawn, thus favoring the latter. In Type-3 systems only the open-ring **6b** can be written in a nonpolar form, which becomes here the most probable structure in the equilibrium shown. To our knowledge, photochromic examples for Type 1 systems have not been described so far.

With Type-3 systems, reversibility is not clear. However, Type-2 and the mixed systems, Type-1,2; Type-2,3; and Type-1, 2, possess photochromic properties when substituted properly. The classes of these photochromic molecules described in this chapter are shown in Table 6.1.

6.2. SYNTHESES OF PHOTOCHROMIC MOLECULES BASED ON A 1,5-ELECTROCYCLIC REACTION

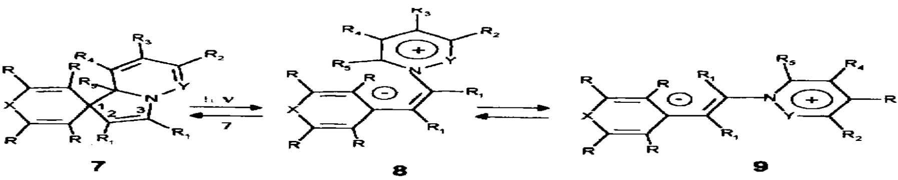
Viewing photochromic systems on the basis of a 1,5-electrocyclization and its reverse, molecules must be envisaged in which the open ring as well as the cyclic structure have a similar energy content. This is the challenge in synthesizing molecules with tailor-made photochromic properties in connection with easy access to these molecules.

Table 6.1. Categories of 1,5-Electrocyclizations in New Photochromic Systems Discussed

Category of 1,5-Electrocyclization	Dipolar structure	Cyclic structure	
Type 1			
Type 2			Δ^2 Pyrroline
Type 3			Δ^1 Pyrroline
Type 1,2			Δ^3 Pyrazoline
Type 2,3			Δ^2 Pyrazoline
Type 1,2,3			Δ^3 Triazoline

6.2.1. Type 2 Systems

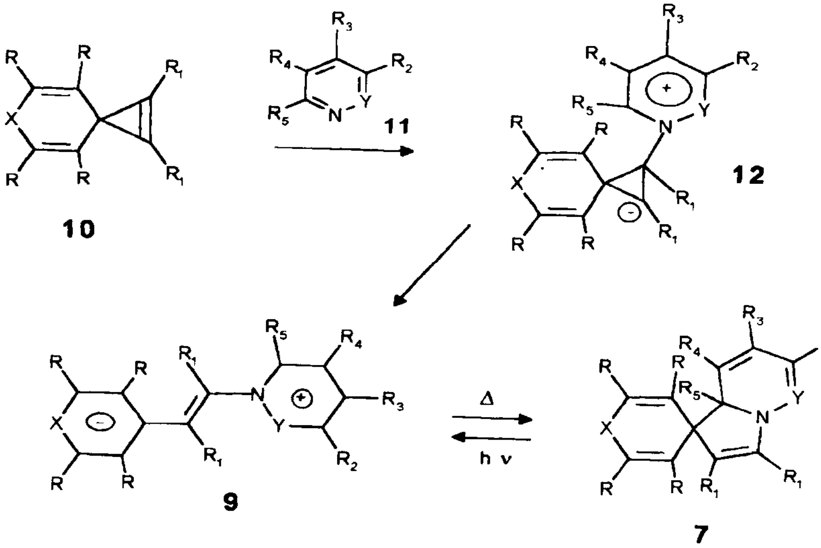
The type-2 systems are the basis of a new type of very potent photochromic compounds. Several routes to this type of system have been developed recently. Incorporation of a Δ^2-pyrroline ring into a more complex molecule has led to a very efficient new class of photochromic compounds (Scheme 2).[1–7]



Scheme 2

6.2.1.1. Cyclopropene: Route (a)[1-7,16,17]

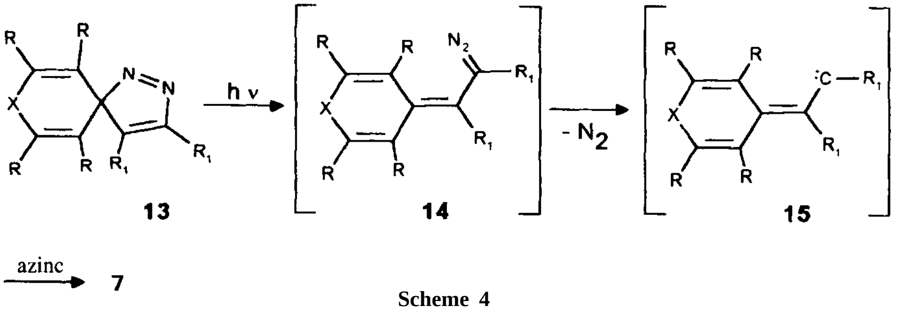
Reactions of the easily obtainable spirocyclopropenes **10**[15a] with aza-heterocycles or azines such as pyridines, pyridazines, quinolines, isoquinolines, azaphenanthrenes, and others afford spiro (1,8a) dihydroindolizine **7** in good yields (50–84%) (Scheme 3). The intermediate in this synthesis is the colored betaine **9.** Typical dihydroindolizines have been made via this route.[1-7,16-18]



Scheme 3

6.2.1.2. Pyrazole: Route (b)

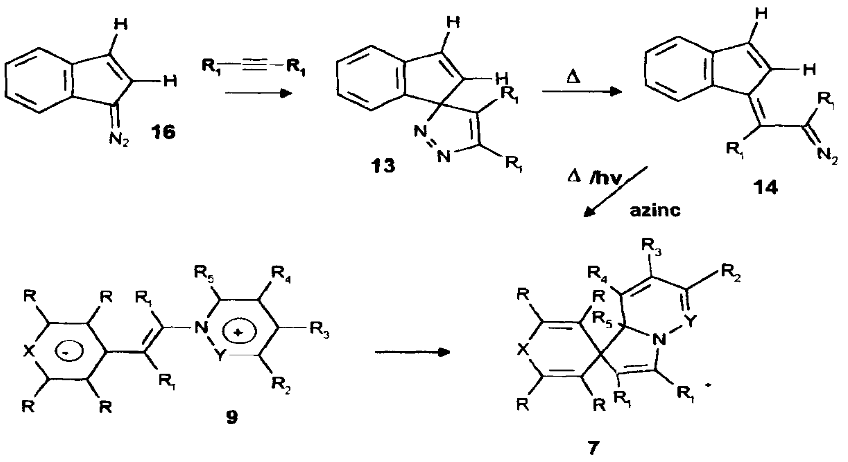
In some cases i.e., when strongly electron-attracting groups such as CN (or CF_3) in **7** are desirable), the cyclopropene route cannot be used. An alternative synthesis has been developed in which spiropyrazoles are photolyzed directly in an azine–solvent mixture. Intermediates in this process are the vinyldiazoalkanes **14** and carbenes **15.**[19,20,21] Overall yields are between 40 and 70% (Scheme 4).



Scheme 4

6.2.1.3. Retro- 1,5-Electrocyclization: Route (c)

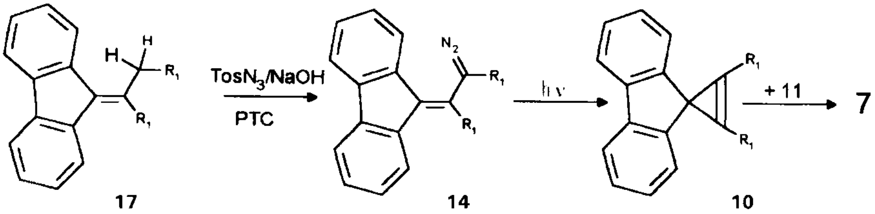
Routes (a) and (b) give access only to DHI **7** bearing identical substituents R[1] or mixtures of regioisomers. However, it was shown that the properties of DHI **7** depend strongly on the substitution pattern of double bond 2,3. Therefore two additional routes were devised. Route (c) starts with diazoalkane **14,** which is formed from **16** via intermediate **13.** The vinyldiazoalkane **14** is converted to **7** in the same way as in the pyrazole route (Scheme 5).[22–24]



Scheme 5

6.2.1.4. Diazo–Route (d)

The diazo–route uses a classical entry via the fulvene **17** into the diazoalkane series **14.** Identical conversions via **10** or **11** (azinc) lead to the DHI **7** in 30–50% yields (Scheme 6). Recently, new compounds of type **7** belonging to molecules with supramolecular properties have been prepared.[25]

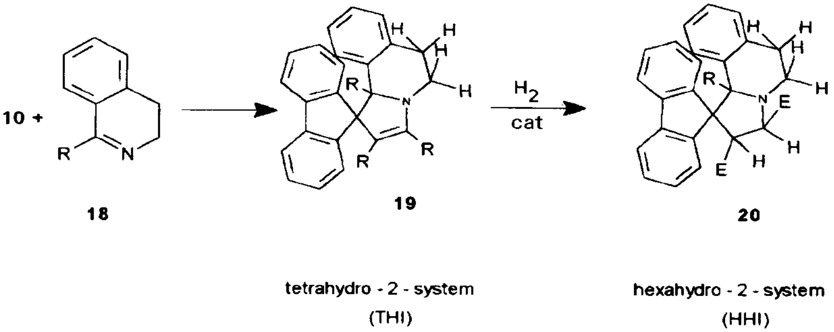


Scheme 6

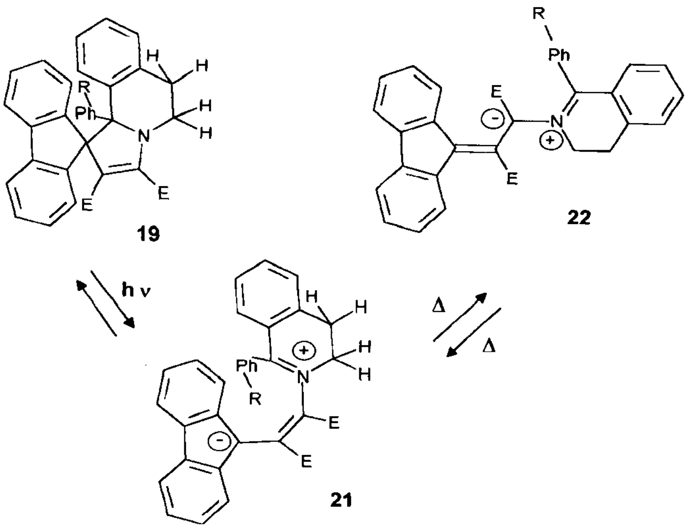
6.2.2. Tetrahydro- and Hexahydroindolizines

Tetrahydro- or hexahydroindolizines (THI and HHI) (Type 2 systems) were also synthesized. Reacting **10** with dihydroisoquinoline **18** in ether–methylene chloride solution gave the tetrahydroindolzine **19** in good yields (Scheme 7).[26] The catalytic hydrogenation of **19** afforded the hexahydroindolizine **20** (Scheme 7).[27,28]

UV or visible light converts spiro-tetrahydroindolizine **19** into deep blue or blue-green betaines **22** (Scheme 8).[26–28]



Scheme 7



Scheme 8

6.2.3. Biphotochromic Systems

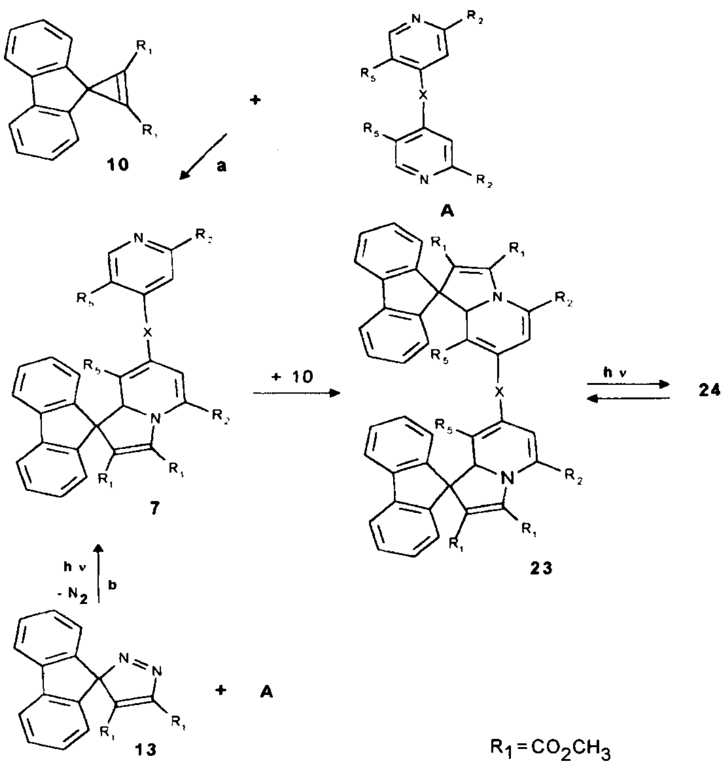
Applying one of the four synthetic approaches (a–d) (see Sections 6.2.1.1 to 6.2.1.4) in combination with the same or a second approach, can lead to biphotochromic systems.[30–33] In principle, these are symmetrical systems such as DHI–DHI and unsymmetrical systems such as DHI-a–DHI-b: DHI, photochromic systems-c are possible.

6.2.3.1. Route 1: Type a and Type b Systems

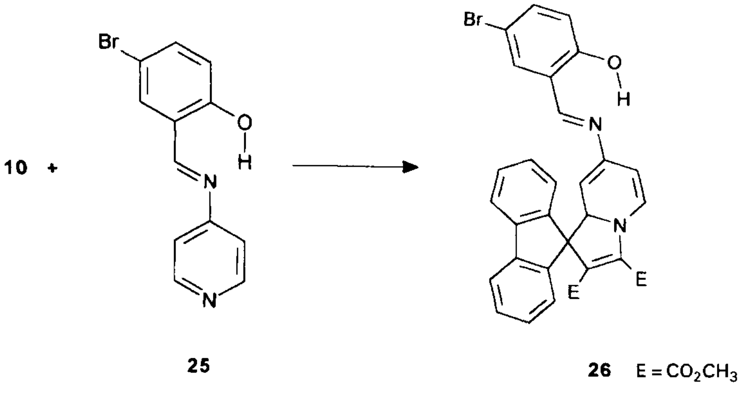
The addition of spirene **10** to 1,3- or 1,4-diazines gives the potential photochromic bisadducts.[3] The reaction of **10** with the bisazine **A** affords the photochromic 1:1 adduct **7** and biphotochromic 2:1 adduct **23,** depending on reaction conditions. By controlling the molar ratio of **10** to bisazine, or reacting **7** with **10,** symmetrical and unsymmetrical bichroomophoric DHI compounds **23** are accessible selectively (overall yields 40–70%) (Scheme 9).[30–32]

6.2.3.2. Type c Systems

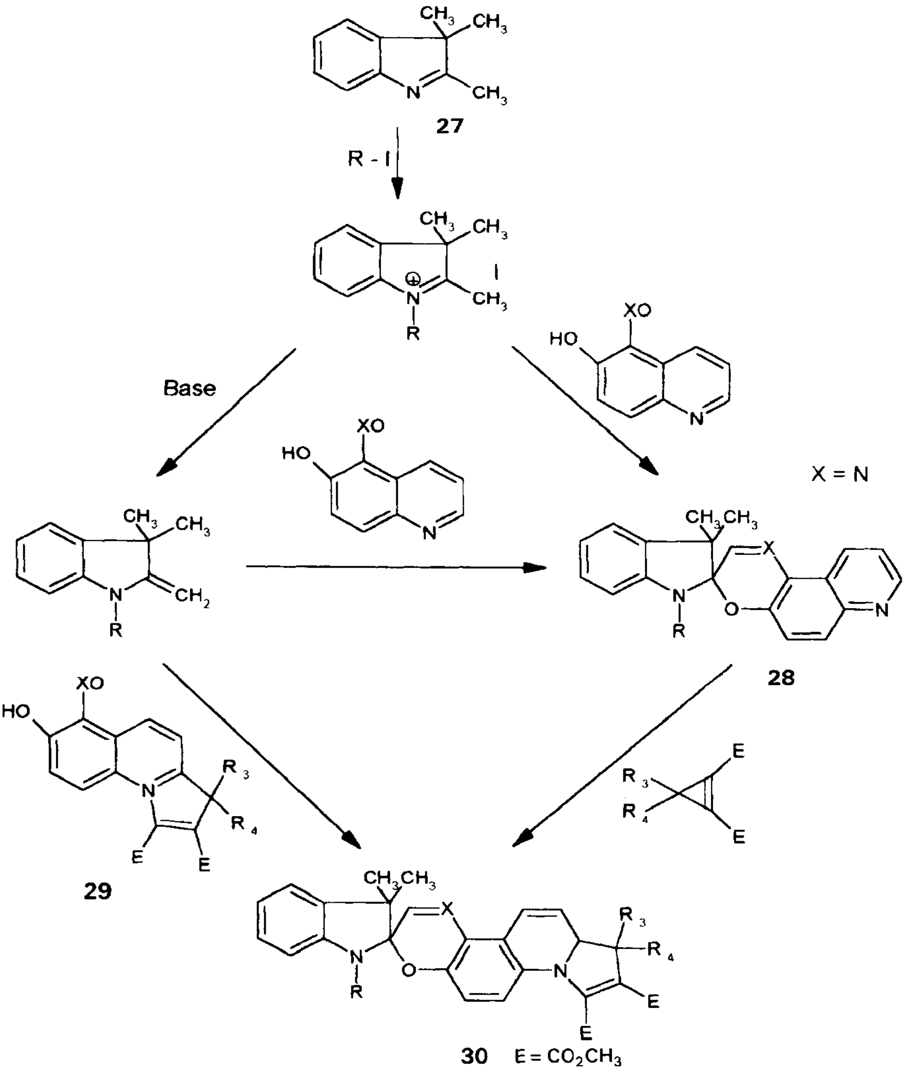
A typical system for an unsymmetrical photochromic compound is molecule **26.** It is prepared by reaction of **10** with pyridosalicylideneanil (Scheme 10).[33]



Scheme 9



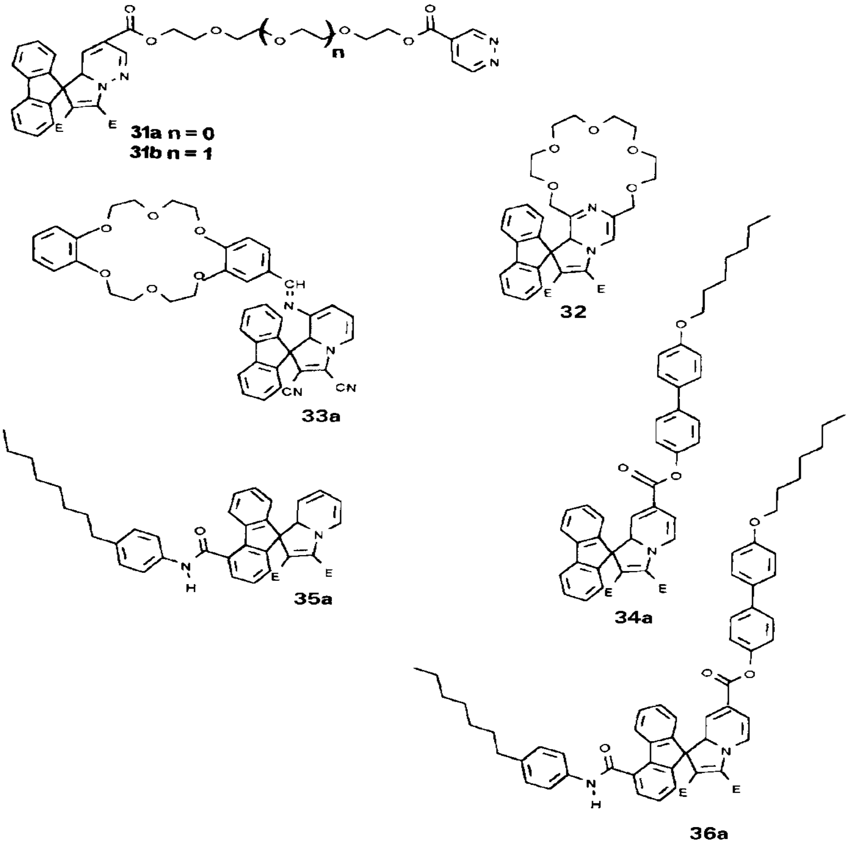
Scheme 10



Scheme 11

Unsymmetrical biphotochromic molecules[30] combining spiroxazine- and spirodihydroindolizine structures have been prepared recently (Scheme 11).[34]

DHIs **31–33** containing podand crown ether groups were obtained by routes (a) or (b).[35,36] DHI molecules of types **34–36** possessing long alkyl chains were prepared analogously (Scheme 12).[35–38]



Scheme 12

6.3. PHOTOCHROMIC SYSTEMS WITH ONE HETEROATOM

6.3.1. Spectra of the Colorless and Colored Forms

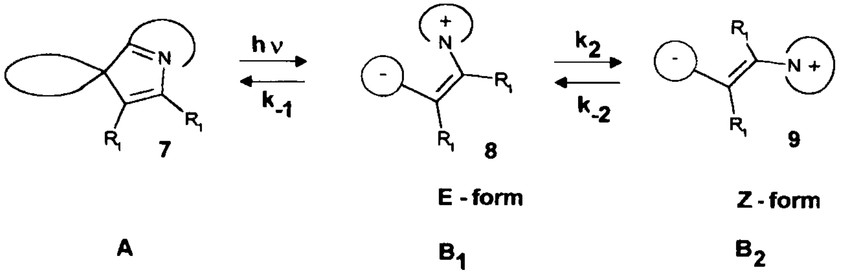
The UV spectra of spiro[1,8a]dihydroindolizine **7** show two typical maxima, one at 240–250 and the other at 360–410 nm. The colored form (betaine) **9,** absorbs in the range of 500–700 nm. Similar absorption ranges are observed for the molecules shown in Refs 1–7. The DHIs **7** are therefore almost colorless or slightly yellowish compounds. The colored forms, however, depending on substitution absorb in almost all regions of the visible spectrum.

The different absorption bands in DHI **7** can be assigned to the following excitations: The band at 360–410 nm results from a locally excited π–π^* transition. It is located in the butadienyl-vinyl-amine chromophore of DHI **7**.$^{1-17, 19-21}$ According to a modified intermediate neglect of differential overlap (MINDO)/3 calculation, the highest occupied molecular orbital (HOMO) of a dicyanoDHI **7** shows a wave function similar to the lowest unoccupied molecular orbital (LUMO). Thus a locally excited (LE) transition (n-π^*) is most probably hidden under this band. The assignment of a second band of **7** is less clear.

If the colored form has a relatively fast fading rate, the maxima of the extinction coefficient cannot be recorded correctly. The procedures described in Ref. 3 can be employed in this case.

6.3.2. Spectra of Colored Forms

Irradiation of the spiro[1,8a]dihydroindolizines **7** with long-wavelength UV or visible light (λ_{max}= 400–450 nm) affords the colored betaine.$^{1-7,16-38}$ Typical spectra are given in Fig. 6.1 and 6.2. The zwitterion can in principle exist in E–**8** or Z–**9** configuration. However, as has been shown earlier by semiempirical calculations, the energy barrier between E–**8** and Z–**9** is small so that only one form being close to **9** is observed with standard techniques (see earlier discussion). For **9** and **8**, resonance formulas are possible where the bond C–2/C–3 is in fact a single bond.



Scheme 13

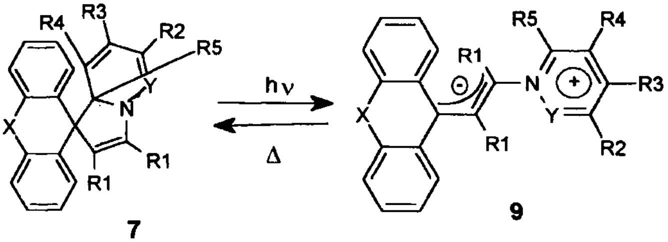
In the new photochromic systems (**7**/**9**) based on the ring opening of an azacyclopentene ring and 1,5-electrocyclization, the basic process is the breaking or reforming of a σ bond (Scheme 13).

The forward reaction can be induced photochemically and the back reaction normally thermally. The products **8, 9** formed in this conversion can only be written in a zwitterionic form. This is the basic difference from spiropyrans or spiroxazines which also undergo a 6π-electrocyclic reaction, yielding, however, an electroneutral molecule.

A typical spectrum for a selected example for a simple DHI **7** is given in Figure 6.1. Spectral data of DHI **7** are collected in Table 6.2A and Ref. 5.

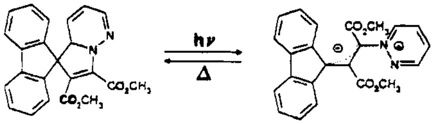
The assignment of the betaine bands in **9** is complicated. The long wavelength band is most probably a charge transfer (CT) transition. This has been shown to be

Table 6.2.A Uv-visible data of selected Spiro[1,8a]dihydroindolizines (DHI) **7** prepared by cyclopropene route (a) or pyrazole route (b). Solvent: CH_2Cl_2/Ether and half life ($\tau_{1/2}$) at 293 K.



X	R_1	Y	R_2	R_3	R_4	R_5	λ_{max} [nm] **7**	λ_{max} [nm] **9**	$\tau_{1/2}$ [s]
Route (a)									
7a –	CO_2CH_3	N	H	H	H	H	380	518	64.8
7b –	AC/E	N	H	H	H	H	402	529	36
7c –	CO_2CH_3	N	CH_3	H	H	CH_3	410	560	16800
7d –	AC/E	N	CH_3	H	H	CH_3	389	612	26
7e –[a]	CO_2CH_3	N	CH_3	H	H	CH_3	394	603	2.13
7f' –[b]	CO_2CH_3	CH	H	H	H	H	401	645	21.5
7g –[b]	CO_2CH_3	N	H	H	H	H	388	529	17,3
7h –	CO_2CH_3	CH=CH–CH=CH		H	H	H	360	470	0.123
Route (b)									
7i –	CN	CH	H	H	H	H	410	560	13800
7j –	CN	N	H	H	H	H	395	535	3375
7k –	CN	N	Cl	H	H	H	397	537	3010
7l –	E/CN	N	H	CH=CH–CH=CH		H	385	550	0.038
7m –	CN	N	H	CH=CH–CH=CH		H	385	577	0.87
7n –	CF_3	CH	H	H	H	H	327		
7o –	CF_3	CH	H	CH=CH–CH=CH		H	338		
7p C=O	CN	CH	H	H	H	H	418		
7q C=O	CN	N	H	H	H	H	392		
7r C=O	CN	CH	H	$N(CH_3)_2$	H	H		685	stable[c]
7s S	CO_2CH_3	CH	H	H	H	H	376	500	2280
7t S	CO_2CH_3	CH	H	CH=CH–CH=CH		H	380	600	
7u H,H	CO_2CH_3	CH=CH–CH=CH		H	H	H	355	726	12540
7v H,H	CO_2CH_3	CH	H	CH=CH–CH=CH		H	376	572	578

a) methyl in 2-position of fluorene ring
b) $CONHC_6H_4$-OCH_3 in 5-position of fluorene
c) stable betaine
AC = $COPCH_3$
E = CO_2CH_3



15 (CO_2CH_3) **15′ (CO_2CH_3)**

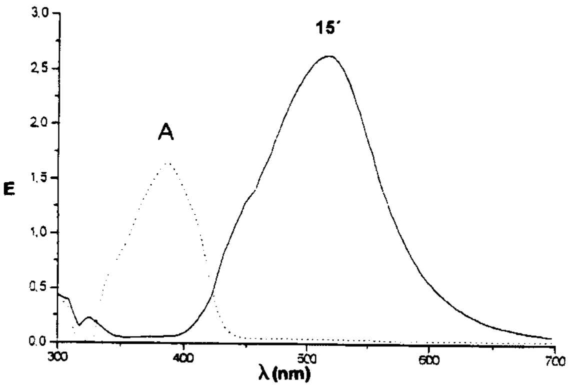


Figure 6.1. UV/VIS spectra of uncolored **15'** and colored species in dichloromethane (c_{7a} = 2.72 x 10^{-4} mol/liter.

the case for the closely related pyridinium-cyclopentadienylylid, studied by Kosower.[39,40] In betaine **9** and related molecules, the CT transition should occur between the symmetrical molecular orbitals (MOs) of the donor and acceptor regions of the molecule. This is in good agreement with rules published by Fabian[41] for similar compounds.

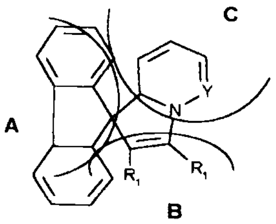
In fast-bleaching betaines **9,** the UV maxima were recorded using flash spectroscopy. A typical setup is described in the following section.[42,43]

6.3.3. Solvent Effects on the Colored Forms

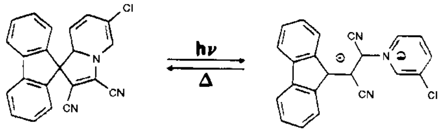
In a study of the colored forms **9** in various solvents, an interesting effect on the long-wavelength band is observed. Most of the DHI **7** investigated showed a negative solvatochromic effect. This is consistent with earlier reports on spiropyrans.[8]

For a structural correlation of photophysical parameters, the DHI molecule is divided into three regions, i.e., A, B, and C.[3–7] Typical partial structures are given in Scheme 13.

Using the Fischer procedure,[3–7] a conversion rate of 94% for dicyano **7i,j** (R^1 = CN, Y = CH or N) is calculated. For the diester **7i,j** (R^1 = CO_2CH_3), the conversion rate drops to only 52%, in contrast to fulgides, where this parameter is 60%.[3] This shows that the dicyano-DHI **7i,j** is very efficiently colored (Figure 6.2).



Scheme 14



15 (CN) **15'(CN)**

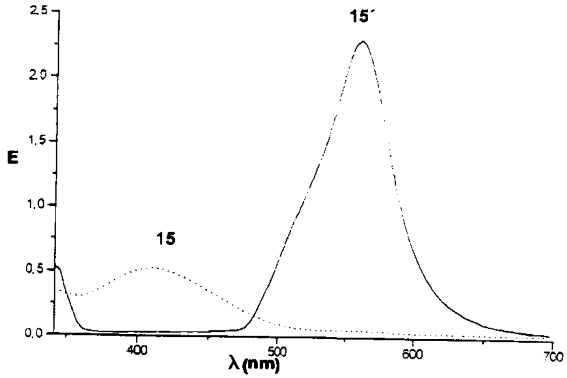


Figure 6.2. UV/VIS spectra of dicyano **15** and **15'** in dichloromethane (c = 1.83 x 10^{-4} mol/liter).

6.3.4. Thermal Reactions in Solution/Structure – Fading Rate Relationships

Irradiation of the photochromic DHI **7** gives rise to the colored forms **8** and **9.** The thermal back or fade reaction **9** → **7** (i.e., the 1,5-electrocyclization), can be easily studied kinetically using UV spectroscopy. The rate constant k thus determined can be converted by the equation:

$$t_{1/2} = \ln 2/k \tag{6.1}$$

to the half-lives of **9.**

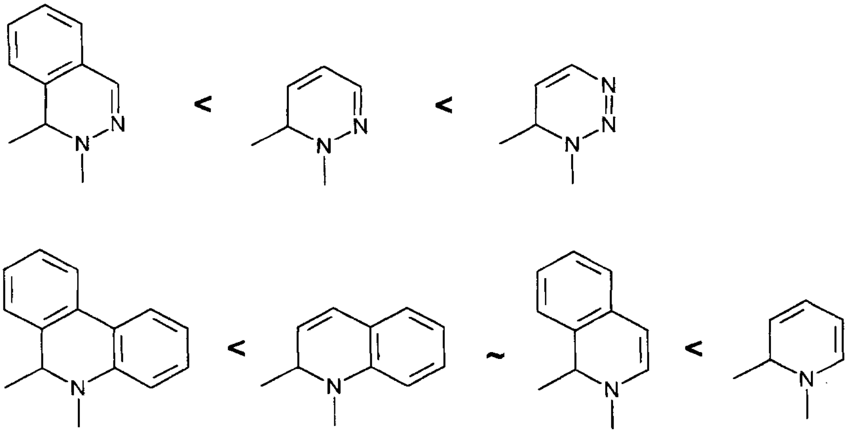
The kinetic scheme for analyzing the thermal fade rate (see Scheme 12) is given by Eq. 6.1. Neglecting a photochemical back reaction **9** → **7** (see earlier discussion), the system can be characterized using the rate constants of the thermal steps k_{-1}, k_2, and k_{-2}. All spectroscopic data (see later discussion) indicate that the equilibrium B_1, B_2 is very fast ($k_{-1} < k_2$, and k_{-2}); thus in a first-order analysis, the thermal fade rate k should depend only on k_{-1} . The values obtained experimentally clearly follow first-order kinetics, and the parameters obtained by standard evaluation were given in Ref. 3.

In the case of regio- or stereoselective reactions of **9** → **7** as well as in biphotochromic systems **(24** → **23),** the kinetics become more complicated (see Refs. 30 and 33). The $t_{1/2}$ values can be used as a rough order for a structure-fade rate relationship. Again, to analyze the data in a simple way, DHI **7** is divided into the regions A, B, and C (see earlier discussion).[3–7]

Region A: In going from the anthronyl, tetraphenyl-cyclopentadienyl, indenyl, and fluorenyl to the diphenyl group, $t_{1/2}$ increases steadily.

Region B: Substitution of R_1 = hydrogen by electron withdrawing groups such as trifluoromethyl-, benzoyl-, acetyl-, methoxy-carbonyl- and cyano leads to increasing $t_{1/2}$ values R_1: CN > $CO_2R > COR > CF_3 >$ H .

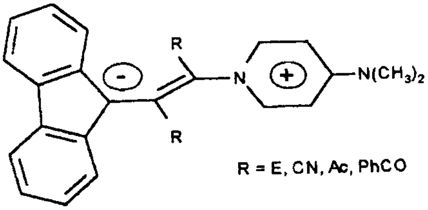
Region C: Introduction of the dihydroazine moiety into region C derived from the aromatic heterocycles such as phenanthridine, benzo[*c*]quinoline, quinolines, or isoquinolines and azines increases the $t_{1/2}$ values constantly. In going from left to right, the positive charge in betaine **9** is stabilized more efficiently (Scheme 15).



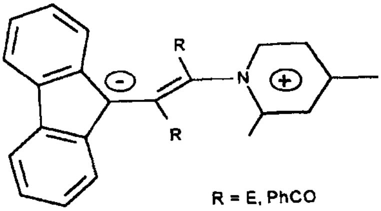
Scheme 15

In special cases betaine **9** becomes so stable, that it does not cyclize. Typical structural prerequisites for such a behavior are (1) donors or rings in region C, or (2) a ring between region B and C. This is shown in Scheme 16.

1) DONOR in Region C

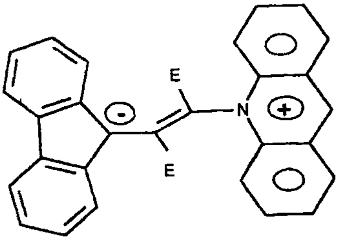


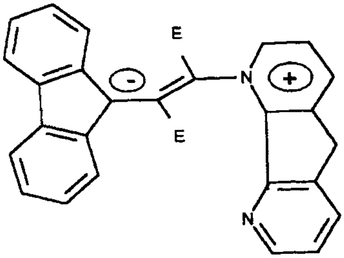
R = E, CN, Ac, PhCO



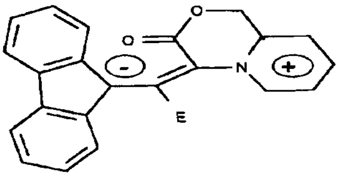
R = E, PhCO

2) Ring-Effect in Region C





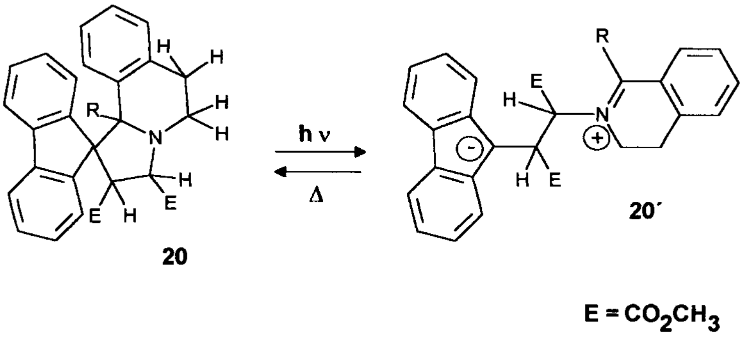
3) Ring Chain



Scheme 16

6.3.5. Modified Systems: Tetra and Hexahydroindolizines

Partially hydrogenated molecules of the DHI type, such as THI and HHI, possess photochromic properties as well. The colored species deriving from THIs **19** can exist in two conformers, **21** or **22,** of which we favor **22** (see Scheme 8). This is again a very powerful, new photochromic Type 2 system; however, here the chromophore is not a butadienylvinylamine (see earlier discussion) as in **7,** but rather a simple enamine unit. The colored form is also a conjugated system that can exist again in all colors. The maximum wavelength of betaine **22** is affected by substitution. Typical UV/VIS spectra are shown for **19** in Tables 6.2 and 6.3. HHIs **20** show photochromism as well. The process responsible for photochromism is no longer a 1,5-electrocyclization and its reverse, but rather, a simple bond breaking to a zwitterionic structure.[27,28]



Scheme 17

Table 6.2B. Absorption Maxima of THI **19**[27] and Colored Form 22 (EtOH)[a]

R	λ_{max} (THI) (nm) **19**	λ_{max} (Betaine) (nm) **22**	$\Delta\lambda$ (Betaine) (nm) R = Me
Methyl	320	715	0
Propyl	320	740	+25
Pentyl	320	747	+32
Heptyl	324	700	-15
i-Propyl	327	765	+50

[a] Σ not determined.

6.3.6. Mechanism of Photocoloration

Recent laser flash photolysis studies of the kinetics of the process **7** → **9** suggest that following photoexcitation with time-resolved spectroscopy, an isomer **8** (E form) is formed in the nanosecond or microsecond time domain which undergoes a first-order conversion to the Z form **9.**[42,43] Details will be published elsewhere.

Table 6.3. Absorption Maxima and Half-Lives of **19** (EteOH)[a]

R	λ_{max} (nm) (THI) **19**	λ_{max} (nm) (Betaine) **22**	$\Delta\lambda$ (nm) vs. R = methyl	$t_{1/2}$ (s)
Methyl	329	675		32.8
Propyl	330	690	–15	15.6
Pentyl	330	680	+ 5	16.2
Heptyl	330	678	+ 3	25.2
i-Propyl	329	700	–25	10.4

[a] Σ not determined.

A triplet route using benzophenone as sensitizer is also possible, but with reduced efficiency.[42] The kinetic scheme for the photoprocess is shown in Figure 6.3 (see also Refs. 3–7).

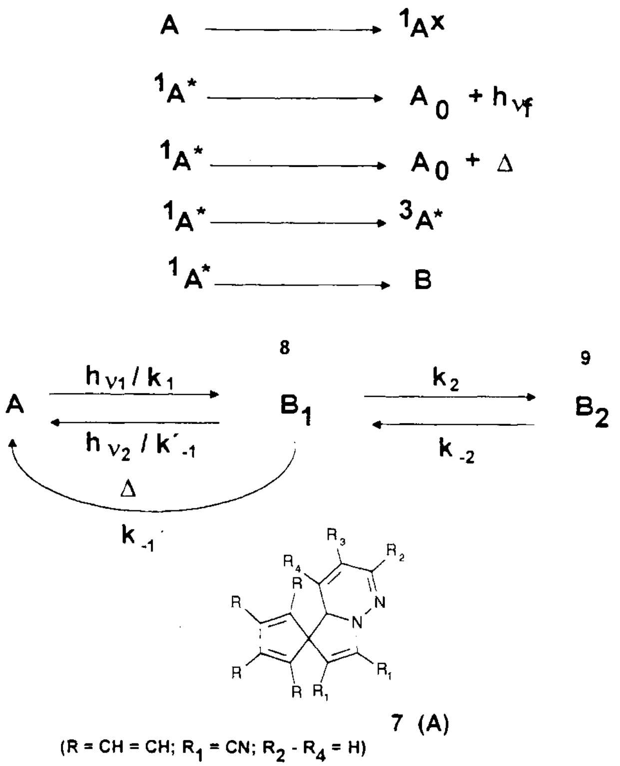


Figure 6.3. Kinetic scheme of photoreaction of DHI 7s (A ≙ **7**; B₁ ≙ **8**; B₂ ≙ **9**).

6.3.7. Quantum Yield of Photocoloration and Photobleaching

The determination of the quantum yield for ring opening of **7** is not a trivial problem. The general scheme can be formulated on the principle that the reaction is not only thermally but also photochemically reversible. This means that the reverse photochemical reaction (rate constant k'_{-1}) is superimposed on the thermal back reaction (rate constant k_{-1}). The analysis must be carried out using nonlinear optimization methods (see Ref. 44).

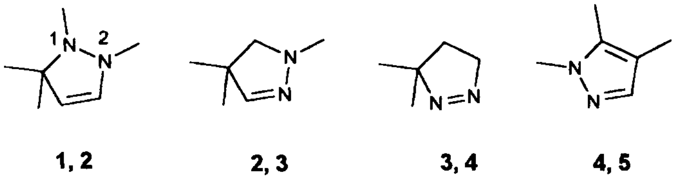
The exact values for ϕ_A and ϕ_B, being on the order of 0.4–0.8 and about 0.05, respectively, are collected in Ref. 3. Approximate data for $\phi_R = \phi_B$, neglecting the reverse thermal and photochemical reactions, do not deviate dramatically from the exact parameters. The quantum yields are in some cases slightly wavelength dependent whereas in others they remain rather constant. No simple explanation has so far been found for these facts.

Phosphorescence was seen in many cases. A clear emission at rather long wavelengths can be observed, which is due to a triplet. The problem of photodegradation has been dealt with in Ref. 3.

6.4. PHOTOCHROMIC SYSTEMS BASED ON PENTADIENYL ANIONS WITH TWO HETEROATOMS

According to the definition given in Section 6.1 and 6.2, pentadienyl anions may contain more than one heteroatom. Thus various systems become possible (only N as heteroatoms with a vicinal arrangement are shown).

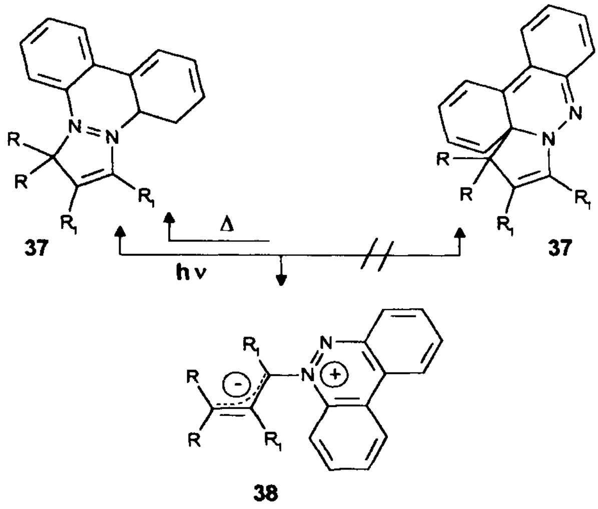
The numbers 1,2, etc. in Scheme 18 were chosen for systematic reasons and are not in accord with International Union of Pure and Applied Chemistry rules. From these molecules, Type 1,2 and 2,3 have proved to be relevant to photochromism. For the azoderivatives Type 3,4, photochemical extrusion of N_2 is possible; this has been widely used in generating cyclopropanes.[45–47]



Scheme 18

6.4.1. Type 1,2 Systems

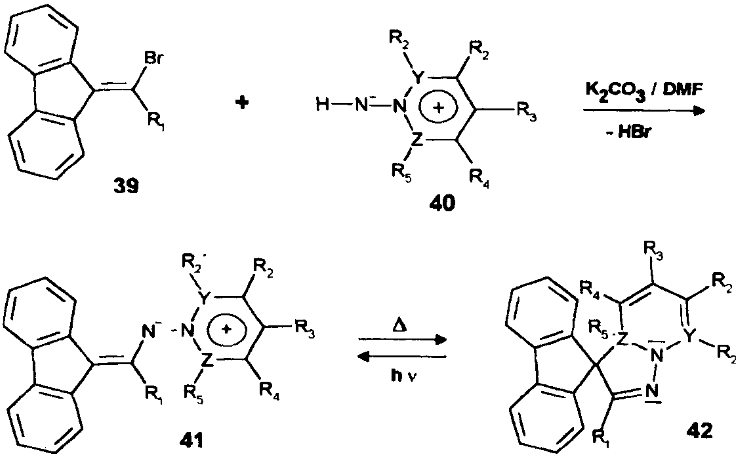
The use of dibenzoannellated 1,2-diazines such as benzo[*c*]cinnoline in the cyclopropene route (a) affords interesting 1,2 systems of Type **37.**[48,49] The photochromism is due to the 1,5-electrocyclic reaction, as shown in Scheme 19.



Scheme 19

6.4.2. Type 2,3 Systems

Substitution of two carbons in position 2,3 of the pentadienyl anion (see Section 6.1) creates a type 2,3 system. Such molecules are the dihydropyrazolopyridines (DHPP) **42.**[50,51] The 1,3 dipolar cycloaddition reaction, which is so effective as a method for synthesizing five-membered rings, can also be used to prepare spiroheterocyclic compounds of the 2,3 type. If a suitable bromo-substituted dibenzopentafulvene is reacted with pyridine the pyrazolo–pyridine **42** is formed in 30–90% yields (Scheme 18).

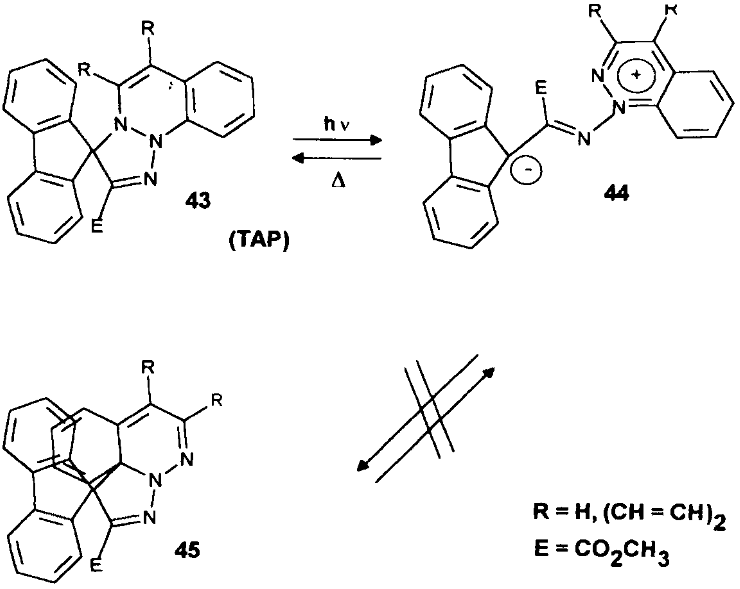


Scheme 20

Irradiating **42** forms the colored species **41,** which (see earlier discussion) can undergo a thermal 1,5-electrocyclization to **42** again. In unsymmetrical molecules, regioselective ring closure may occur. A typical UV spectrum for the color changes in the DHPP **42** in reacting to **41** was reported in Ref. 3.

6.5. PHOTOCHROMIC SYSTEMS BASED ON PENTADIENYL ANIONS WITH THREE HETEROATOMS

Substitution of three carbon atoms with heteroatoms in the pentadienyl anion leads to the structures shown in Scheme 21 (only vicinal N-substitution is considered). The resulting heterocycle is a triazoline ring. Photochromic molecules **43** containing this structural element have been made (Scheme 21).[51,52]



Scheme 21

Here again the 1,5-electrocyclization of betaine **44** is only possible to **43.** A formation of **45** is energetically unfavorable because of the destruction of the aromatic system. The UV/VIS spectra of **43** and **44** show maxima at 400 and 586 nm (in CH_2Cl_2), respectively, with half-lives of the colored species of **44** of $t_{1/2}$ = 60s.

Fluorescence is observed at 614 nm, with a rather low quantum yield of $\phi_F = 7.6 \times 10^{-3}$, showing a value similar to those observed for DHI **7** and DHPP

42. The photochemistry of this new photochromic system has not been studied in more detail.

6.6. SUPRAMOLECULAR AND ENVIRONMENTAL EFFECTS AND APPLICATIONS

The properties of photochromic molecules such as DHI **7** and related compounds are dependent not only on structure but to a large extent also on their environment. Clear differences are to be expected if solution or solid phases of photochromic molecules are compared, i.e. (1) containing supramolecular anchor groups, (2) in liquid crystalline phases, or (3) polymer-containing photochromic systems. It is necessary to use the appropriate spectral methods for the detection of different properties. In addition to normal methods, photoacoustic spectroscopy (PAS), polarized light, and others may be applied.

6.6.1. Supramolecular Systems

Linking a suitable chain or a ring to a dihydroindolizine generates photochromic systems of Type A, B, or C (See Figure 6.4).

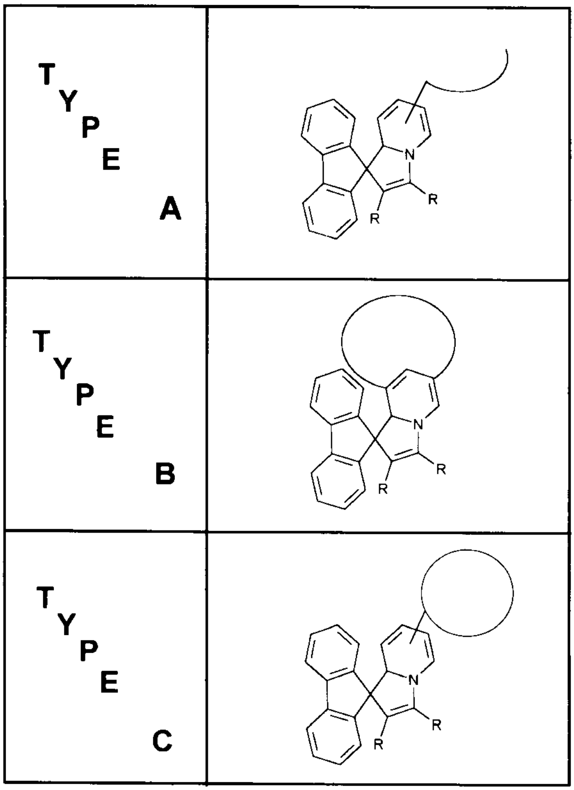


Figure 6.4. Molecules of Type A, B, and C containing anchor groups for supramolecular interaction.

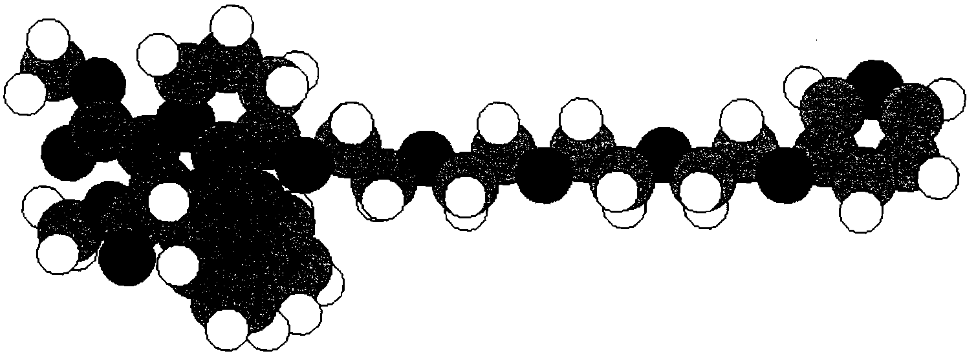


Figure 6.5. CHARMm calculation of Type A molecule **31a** (see p. 232).

These molecules are set up for supramolecular interactions with inorganic (salts) or organic guests. This concept has been applied to mono- or biphotochromic dihydroindolizines **23** and **31–33.**[35,36,52–55]

A model calculation for Type A molecules using the force-field method CHARMm (Chemistry in Harvard Molecular Modeling) showed a linear arrangement of the poly(ethylene glycol) chains for the compound **31a** (Figure 6.5).

Adding metal salts demonstrated a weak but clear effect on $t_{1/2}$ in the presence and absence of metal ions, which results from folding the chain around the metal ion. A schematic representation indicating the conformation change from a linear to a more cyclic (helical) structure is shown in Figure 6.6.

This geometry change is clearly borne out by the salt effect of compound **46** (Figure 6.7).[35,55]

A very interesting effect is seen for the supramolecular systems of Type B. Here the 19-N-oxa-6-crown in DHI **32** is obviously protonated in methanol solution. In the presence of triethanolamine/MeOH, the base binds the proton and the free crown DHI **32** is present in solution. Adding Li^+, Na^+, or K^+ shows a strong hyperchromic

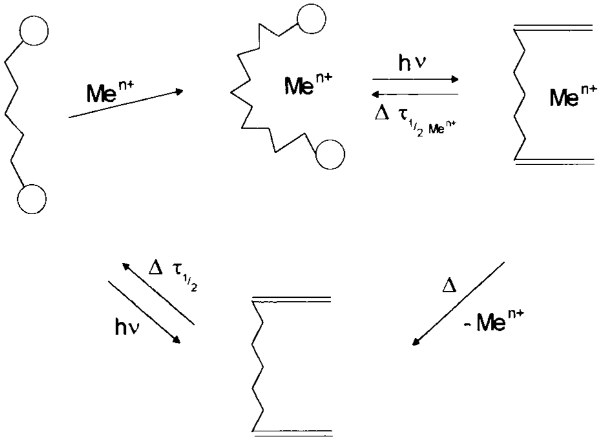


Figure 6.6. Host–guest interaction in supramolecular assemblies of Type A.

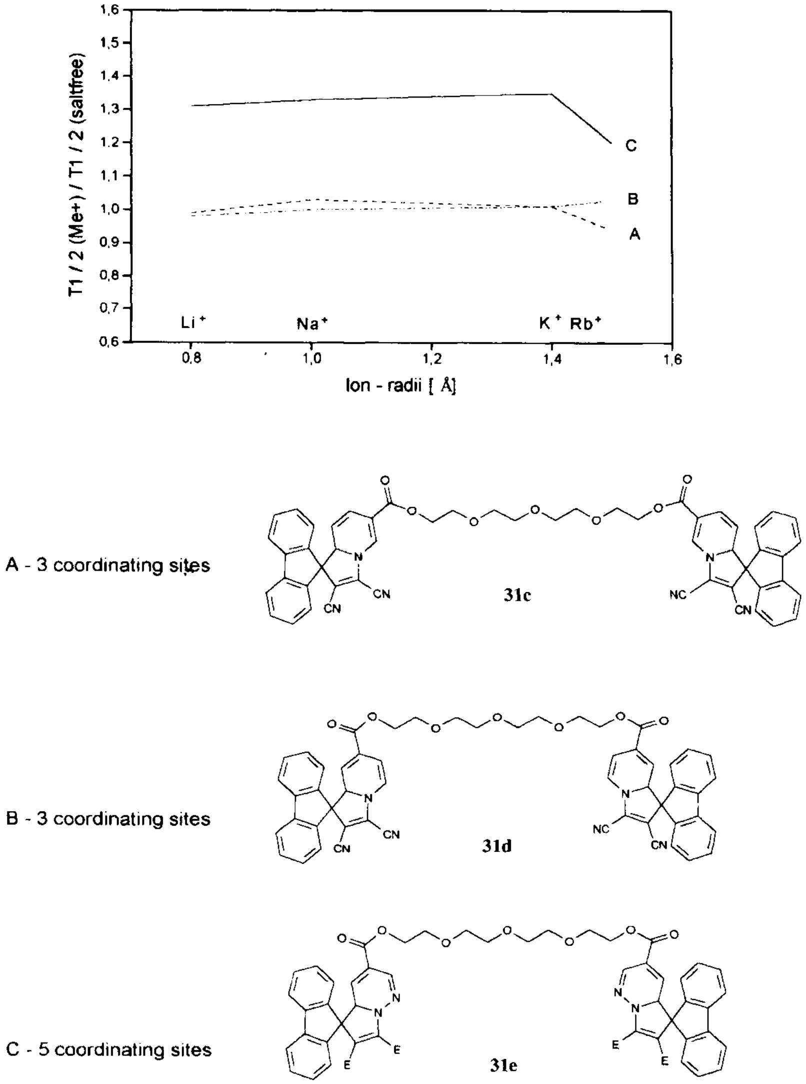


Figure 6.7. Relative changes of 1,5-electrocyclization rates of **31c–e** reflected in $t_{1/2}$ in the presence of alkaline guests in methanol (c = 1.8 x 10^{-4}mol/liter) (A = **31c**; B = **31d**; C = **31e.)**

and a slight bathochromic effect on the UV (Figure 6.9). Dramatic changes have been seen in the half-lives $t_{1/2}$. Li^+ shows the strongest decrease of $t_{1/2,}$ by a factor of about 10^6. These supramolecular assemblies can be clearly regarded as molecular switches, where in the supramolecular assembly the half-life of the colored form is clearly affected (Figure 6.8).

All these molecules must be regarded as molecular switches since light triggers a molecular function.[56] Here the stronger or weaker binding of a salt can be felt in the reactivity, i.e., in the changes of $k_r \approx 1/t_{1/2}$ of the electrocyclic process. Similar results were obtained for compounds of Type C, as demonstrated[54] by the decrease

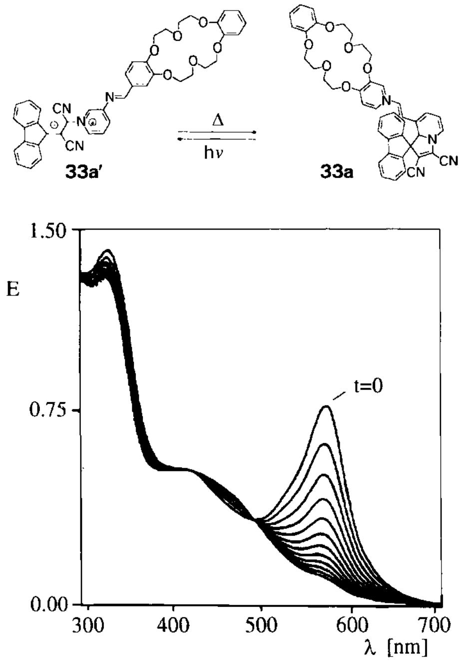


Figure 6.8. Reaction spectrum for the electrocyclization of a supramolecular betaine **33a'**/DHI **33a** assembly (CH_2Cl_2, $C_7 = 5 \cdot 10^{-5}$ mol/liter) (Type B).

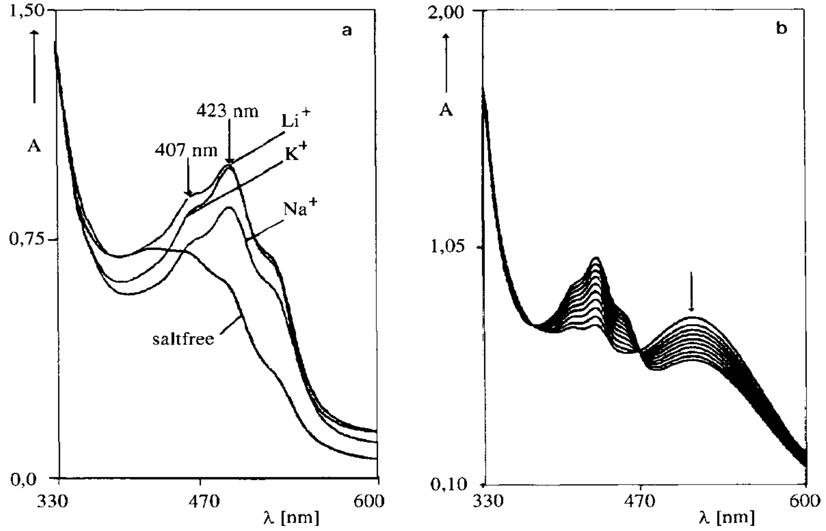


Figure 6.9. Effect of salt ions and reaction betaine spectrum **32** → **32** for molecules containing a cyclic anchor group (c = $1.8 \cdot 10^{-4}$ mol/liter, MeOH/triethanilamine 1 : 1) (Type C).

of $t_{1/2}$ in the presence of K^+ or Ba^{2+}. This indicates that the reaction rate can be reduced by supramolecular structure of K^+ or Ba^{2+} and molecule **33.**

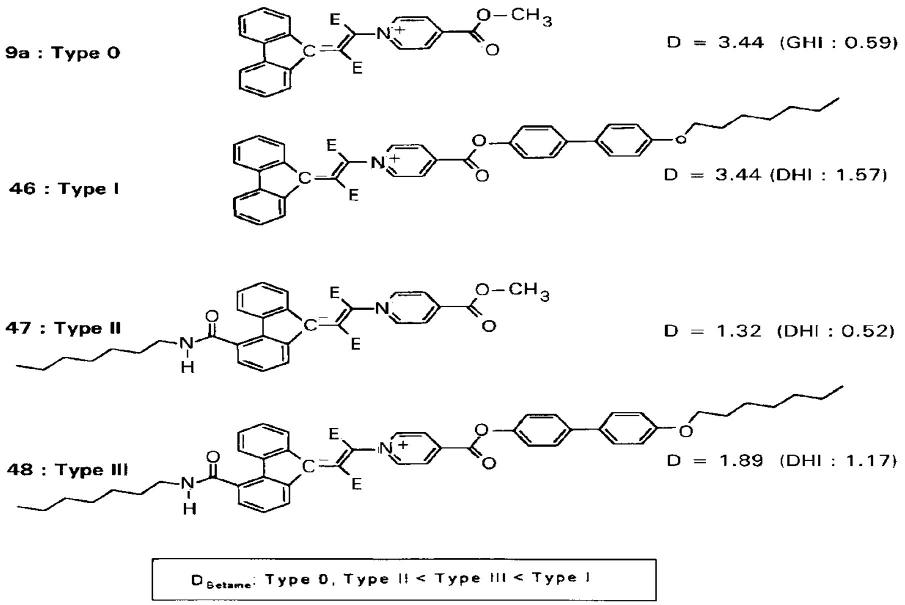
6.6.2. Photochromic Systems in Liquid Crystalline Phase

If the photochromic molecules are especially tailored to contain long alkyl groups, they may be oriented in suitable solvents such as liquid crystals. In DHI **7** alkyl chains may be introduced in regions A, B, or C (see Scheme 14). Appropriate substitution of regions A and C has been achieved in the molecules **34–36** indicated (Scheme 22).[37,38]

Using **34,** a Type I molecule, one can orient these molecules in liquid crystal (LC) phase such as a nematic ZLI-2452 (LC phase commercially available from Merck & Co). Using polarized light, a different ratio D of the absorption $E_{\parallel}$ and $E_{\perp}$ is possible. The dichroic ratio

$$D = E_{\parallel}/E_{\perp} \tag{6.2}$$

is small in DHI **34** (Type I) but large in betaine **46** (Type I). So we can switch a function, namely, the dichroic ratio D in a Type I molecule (Figure 6.10).



Scheme 22

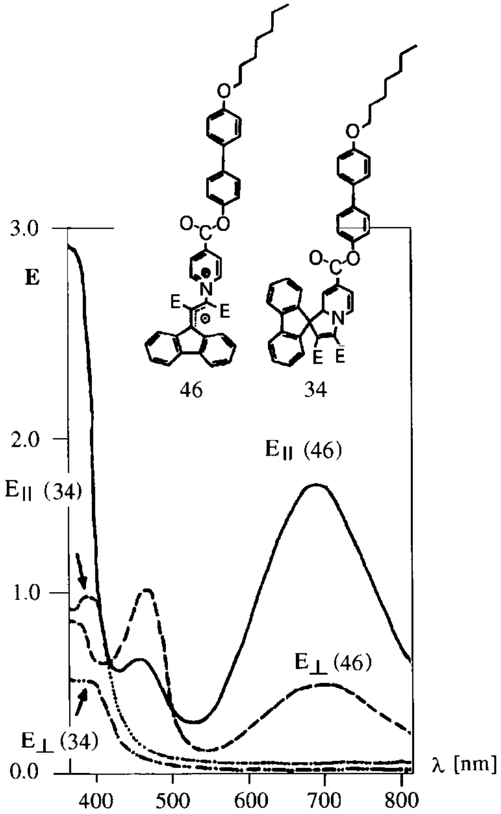


Figure 6.10. Effect of polarized light on oriented DHI **34**/LC (nematic) assemblies. $E_{\parallel}$ is the extinction when the polarized light is parallel to the electric vector of the light ($E_{\perp}$: perpendicular). Molecules were oriented mechanically in the nematic phase. $E_{\parallel}$ or $E_{\perp}$ refers to the extinction measured for **34** or **46** with parallel (or perpendicular) light in the nematic ZLI-2452 (Merck) phase (Type I).

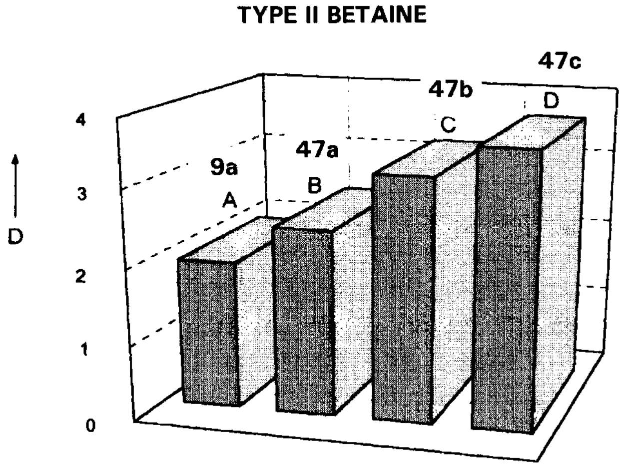
Besides *D*, Type I–III molecules are characterized by the order parameter *S*, which is defined as

$$S = (D - 1)/(D + 2) \tag{6.3}$$

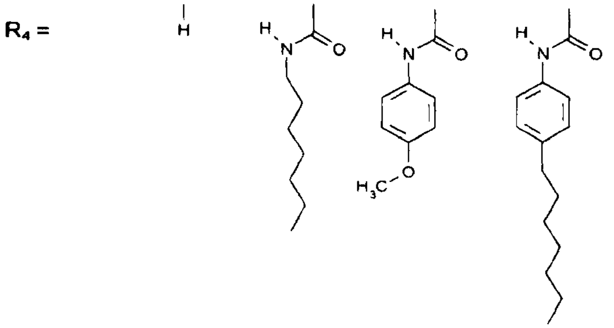
A similar, more pronounced effect is seen in **35** (Type II systems).

Summarizing the results of these studies led to the following conclusions: (see Figure 6.11): For DHIs, the dichroic ratios *D* (and *S*) decrease in the sequence **34** (type I) » **35** (type II) > **36** (type III).

For betaines the order parameters decreases from **46** (Type I) (0.63) » **47** (Type II) (0.46). (See Figure 6.11).



D =	1.94	2.44	3.19	3.59
	9a	**47a**	**47b**	**47c**
S:	0.25	0.32	0.42	0.46



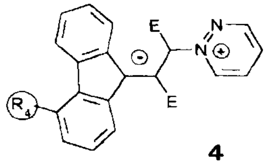


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Figure 6.11. Dichroic ratio $D = E_{\parallel} / E_{\perp}$ and order parameters for Type II betaines **47** in ZLI-2452.

Optimal effects are obtained with Type I molecules. However, the effect is reduced in **48** (Type III molecules). Here the orientation and reorganization of the colored form **48** probably disturbs the LC phase considerably, thus reducing the dichroic ratio *D* and the order parameter *S*.

6.6.3. Photochromic Systems in Polymers

Photochromic molecules may be dissolved in, adsorbed on, or bound to a suitable polymer. Depending on these three different environments, their properties may change in a very subtle way.

6.6.3.1. DHI Dissolved in Polymers

The easiest technique to establish a polymer–photochromic molecule (PC) interaction is to dissolve the photochrome in a polymer solution from which the solvent is evaporated afterwards. DHI **7** has been incorporated by this technique into poly(methyl)- or poly(*n*-butyl methacrylate), vinylidene chloride, acrylonitrile (Saran F), polycarbonate, and polystyrene–butadiene copolymer (Panarez).

Two results obtained in this way are (1) the half-life of the colored form can be increased and (2) number of cycles is enormously augmented. In a rigid polymer matrix, the colored betaine **9** is less able to cyclize. The kinetics of this cyclization are frequently more complicated than in solution.[3]

The number of cycles in DHI **7** increases since oxygen is excluded, which, after activation to $^1O_2$, causes destruction of the colored betaine **9**.[3] The number of Z cycles measured (e.g., in Saran) exceeds $Z_{50} = 600$. The Z_{50} equals the number of cycles leading to 50% of the original extinction of the colored form (Z_{80} equals 80% of the original E). Similar matrix effects have been observed with spiropyrans.[57] Typical values are given in Table 6.4. In a poly(vinyl butyral) (Trosifol^R) matrix, the number of cycles for DHI **7** → **9** exceeds $Z_{50} = 5000$.[3–7]

Using poly(thiourethane) (PTU) as a polymer matrix for DHIs is a method for generating transparent polymers that may be used for different purposes, such as in ophthalmic lenses or information recording material. The compounds shown in the scheme (Scheme 23) were studied in such a PTU matrix. Typical fading or bleaching

Table 6.4. Number of Cycles of **7** in Polymer Matrices

Number of cycles[a]	Z_{80}[b]	Z_{50}[c]
1 in ethanol	130	250
2 in ethanol	> 600	>>600
2 in Saran film	370	> 600
2 in plexigum film	80	240
2 in ethyl cellulose film	70	200

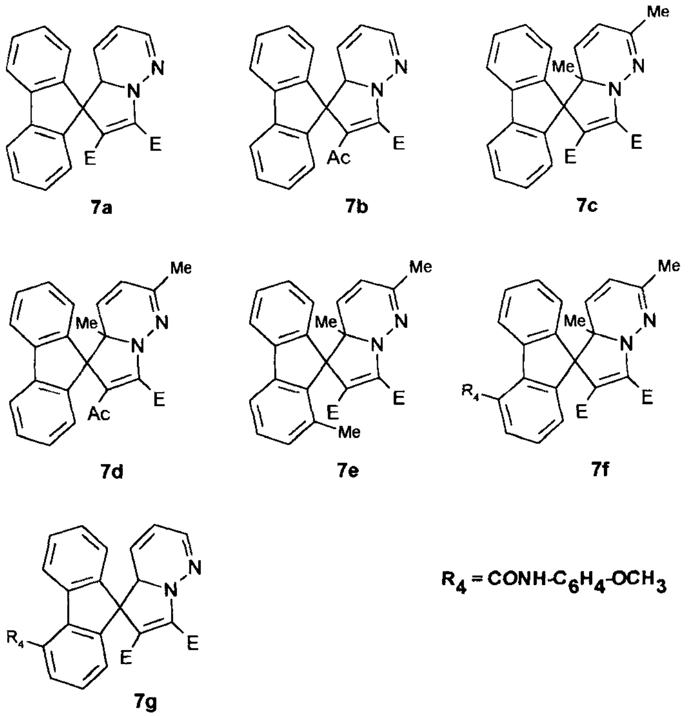
[a] Conditions: 10s irradiation, tungsten lamp, 3h dark.
[b] Number of cycles leading to 80% of original extinction.
[c] Same leading to 50% of original extinction.

values for the polymers compared with solution (CH_2Cl_2) effects are shown for $t_{1/2}$. The polymer does in general slow down the cyclization or bleaching rate of DHIs. (Table 6.5.).

Table 6.5. Bleaching Rates t_{80} and t_{60} for Decrease of the original Extinction to 80 or 60% for various DHIs **7** in polymer PTU Matrices

Polymer	DHI/betaine	c_i (10^{-3} mol/kg)	t_{80}(P) (s)	$t_{1/2}$(P) (s)	t_{80}(S) (s)	t_{80}(P)/t_{80}(S)
P1	**7a/9**	5	580	94	30	19
P3	**7b/9**	10	460	26.6	8.5	54
P2	**7c/9**	6	2050	714	228	9
P4	**7d/9**	2	620	32.4	10.4	60
P6	**7e/9**	10	900	0.64	0.20	4367
P14	**7f/9**	5	1030	77	24.6	42
P11	**7g/9**	8	4350	21.4	6.8	637

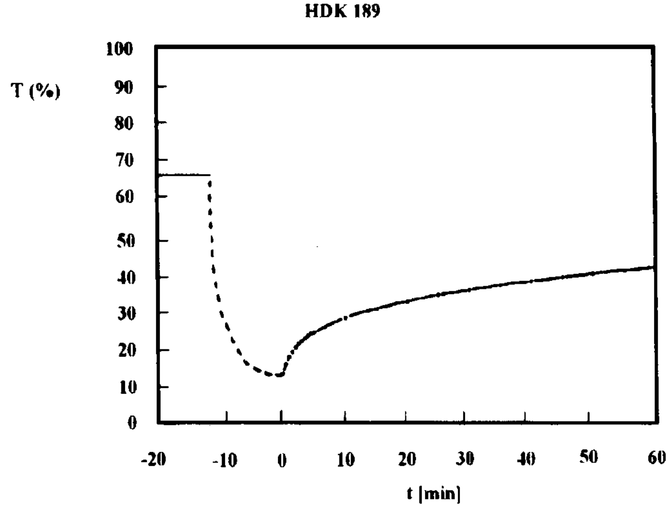
Notes: P=Polymer; L=liquid; S=solution. Polymer: Decrease of $t_{1/2}$: **7g** > **7c** > **7f** > **7e** > **7d** > **7a** > **7b'** . Solution: Decrease of $t_{1/2}$: **7c** > **7a** > **7f** > **7d** > **7b'** > **7g** > **7e** .

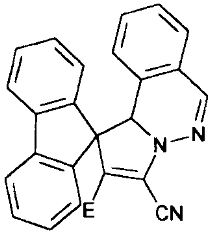


Scheme 23

Photochromic materials for information storage can be envisaged on the basis of the system shown in Figure 6.12. The dicyano DHI is a molecule that can be photochemically switched from the colorless form **7** to the colored form **9** and vice versa. So information could be stored with light of λ_{max} = 400 nm and erased by light of λ_{max} = 580 nm. Thus a dicyano-DHI/poly(thiourethane) matrix can be used to record information. In an initial study, the information was shown to last at least a week (Figure 6.12).[58,59]

7l





7m

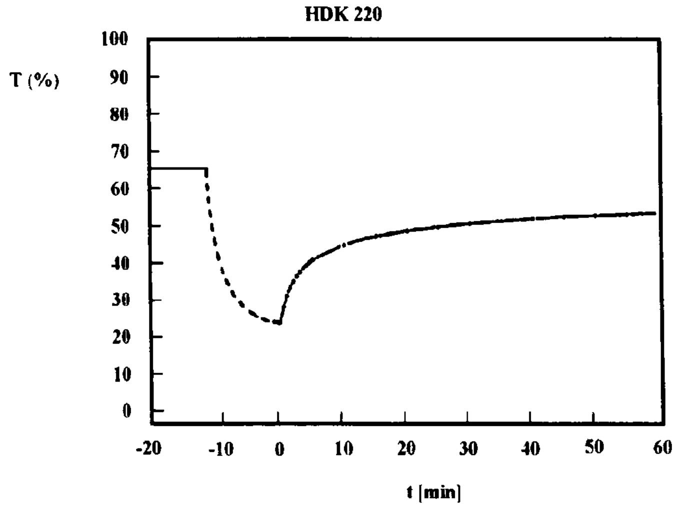


Figure 6.12. Bleaching curves of betaine form of selected DHIs in a PTU matrix (c = 4.97 x 10^{-7} mol/liter).

6.6.3.2. Polymer-Linked Systems

Special effects are envisaged when photochromic molecules are linked to the polymer backbone. Two approaches are possible as shown in Figure 6.13. Such a material would be extremely interesting for molecular information storage devices.[60,61]

The first steps in this field were made in reacting a polypyridazine with spirocyclopropene to form a polymeric material (PN–15) with photochromic pendant side chains.[3]

A different approach for linking photochromic dihydroindolizines uses functional groups like $-\text{Si(OR)}_3$ that can be attached easily to molecules containing active hydrogen. Thus for instance a polymeric inorganic backbone can be connected to a DHI linked to $-\text{Si(OR)}_3$ via a variable spacer molecule. The polymers obtained in such a way are called organic modified ceramics (ORMOCER).[62] The typical structure of an ORMOCER lattice containing photochromic DHI has been described in Ref. 61.

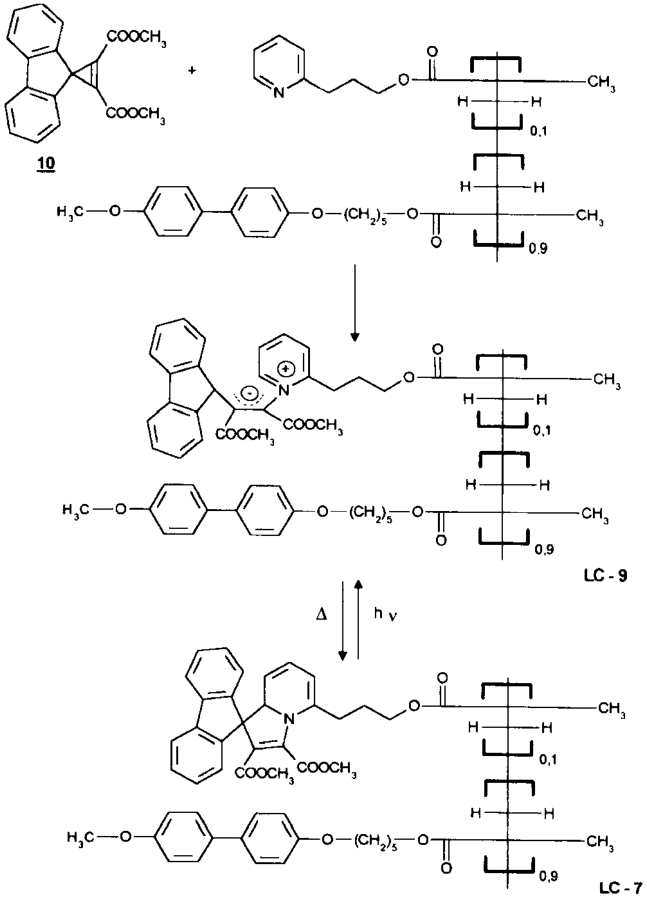
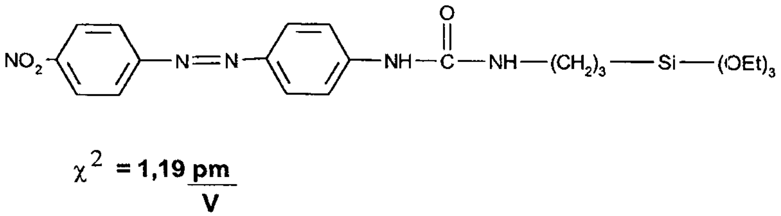


Figure 6.13. Typical covalently linked supramolecular photochromic polymers.

This material can be used for nonlinear optical (NLO) effects. Typical χ^2 values for the DHI–NLO material obtained are at 0.03 pm/V.[61,63] Using LC building blocks to form a polymeric structure, one can prepare an LC polymer showing photochromic behavior. A typical approach is shown in Fig. 6.13. Employing this route to an LC polymer, **7** was prepared and showed a very large mesophase transition temperature of 141°C.[64]

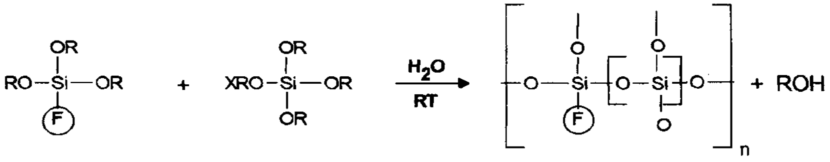


Scheme 24

An ORMOCER is made from alkoxysilanes, which hydrolyzes in the following way:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + n\,ROH$$
$$\times\, M(OH)_n \rightarrow \times MO_{0.5n} + 0.5\,nx\,H_2O$$

If part of the R groups do not hydrolyze then ORMOCERs are obtained. A functionalized group (F) such as a photochrome, or a nonlinear optical active group may be introduced as shown in Scheme 25 [64].

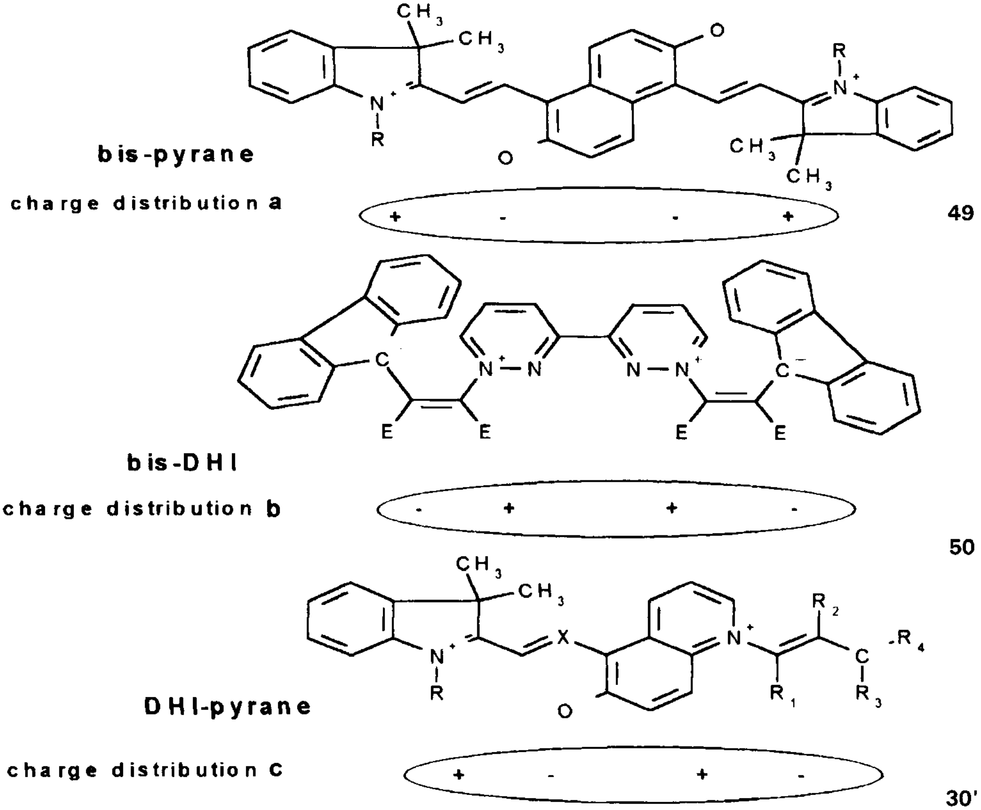


Scheme 25

6.6.4. IR-Sensitive Materials

The combination of two photochromic units as in molecules **30'**, **49**, **50** (Scheme 23) can result in very interesting materials. Irradiation of the mixed biphotochromic system **30'** leads to a colored form absorbing in the infrared. Thus IR-sensitive materials become available. A detailed description of this new material is given in Ref. 34, 65. The charge, distribution in the colored ring open form can be schematically represented as shown in Scheme 26.

There are in principle two colored forms for **30'**, **49**, **50** possible. Depending on the different molecules the fully opened structure **30'** has the charge distribution + – + –. For applications as light sensitive dental material see Ref. 66.



Scheme 26

6.7. DESCRIPTION OF APPARATUS

For most studies mentioned in this chapter, standard photochemical techniques were used. A problem arising frequently with photochromes is the short lifetime of the colored form. The λ_{max} of the colored species as well as its half-life cannot be measured unambiguously in such cases. In the studies presented here, a homemade flash photolysis apparatus was employed which is described briefly. It was constructed as follows (Figure 6.14). A commercial photoflash was employed to excite the solution in the probe, using a reflecting deck to ensure maximum irradiation. The analyzing light entering perpendicular to the flash was provided by an Osram-tungsten-halogen lamp (type HLX 12 V/50 W) and focused on a lens biconvex to the probe. The filters (Oriel, WG 360; GG 375; GG 400; GG 435),

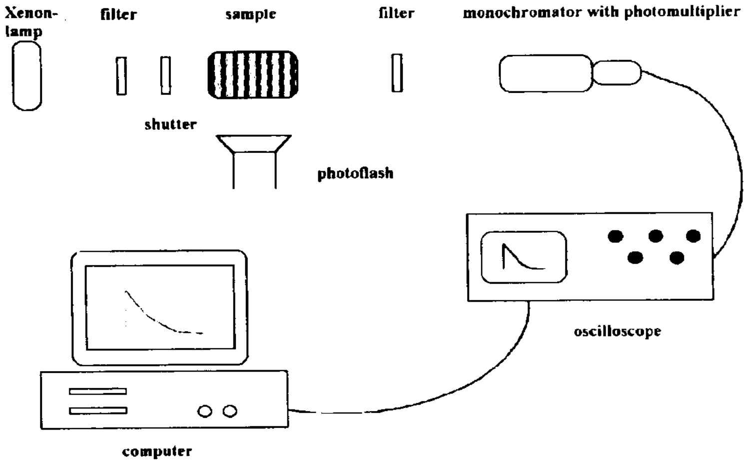
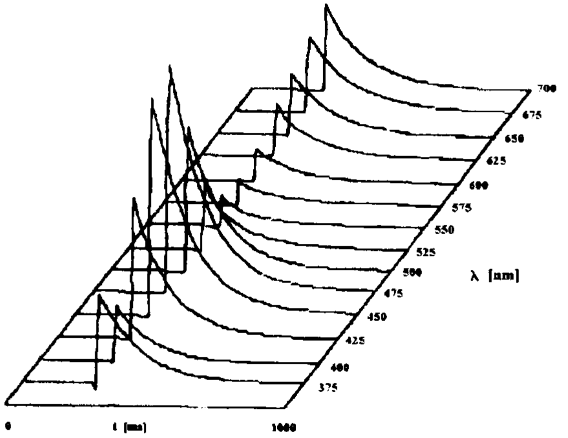
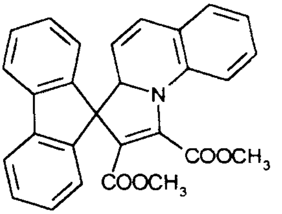


Figure 6.14. Flash photolysis apparatus.

which were consecutively adjusted in the light path, were used to select the appropriate band with the analyzing light. Access was controlled by a manually triggered shutter. The probe was thermostated. Light was passed through the probe, a shutter, glass filters, and a biconvex lens and was collected by a Bausch and Lomb





7h

Figure 6.15. Decay curve of DHI **7h** at various wavelengths in dichloromethane ($c = 7.8 \times 10^{-4}$ mol/liter).

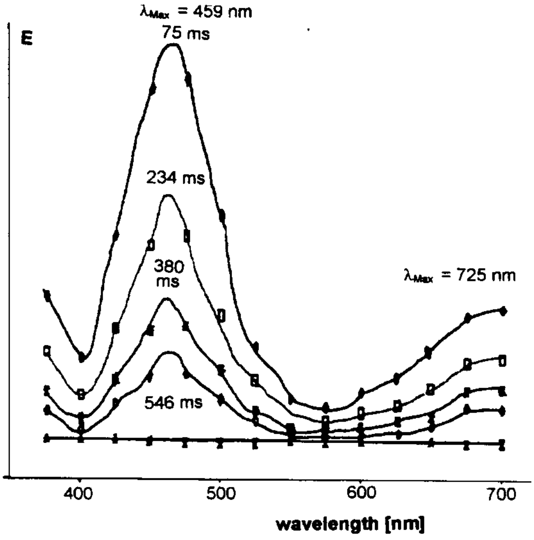


Figure 6.16. Transient spectrum derived from Figure 6.15.

monochromator linked to a Hamamatsu R 955 photomultiplier. A BNC cable connected it with a digital oscilloscope (Tektronix 2212, 60 MHz) for data collection. The RS 232 C interface linked it to a computer. The data were analyzed using the kinetic program Turbo Pascal Borland of R. Bonneau (University of Bordeaux, Talence, France).

A typical example is as follows: Molecule **7h** was studied in the flash photolysis apparatus.[42,67] A solution of **7h** was irradiated at varying wavelengths between 375 and 700 nm. From the 19 decay curves registered, the spectrum of the transient **8h** was determined (see Figures 6.15 and 6.16).

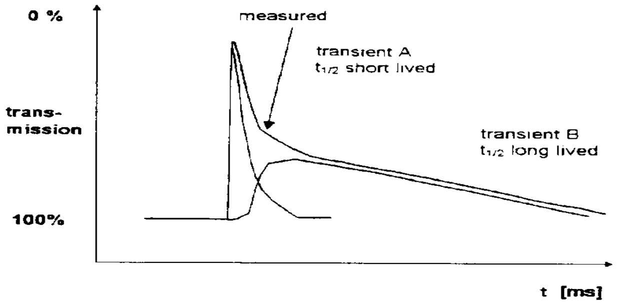


Figure 6.17. Kinetics of a photoreaction A→B→C (stable and nonabsorbing).

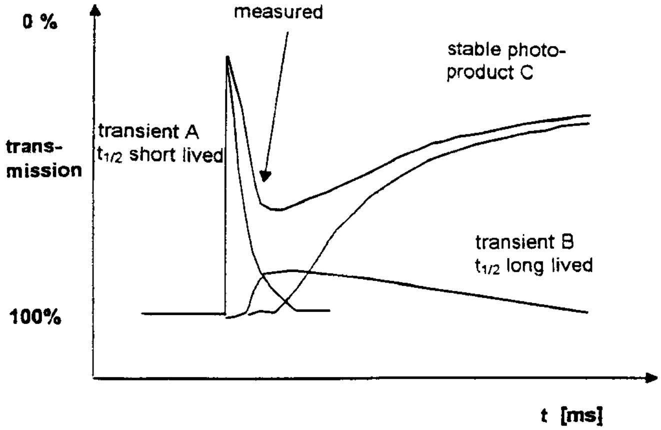
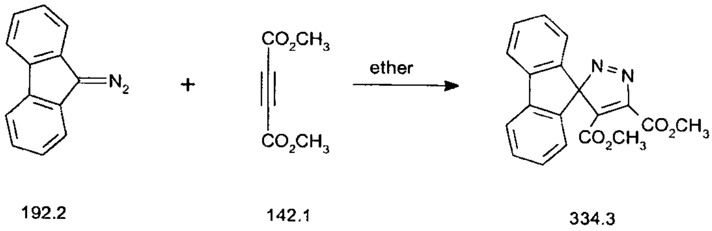


Figure 6.18. Kinetics of a photoreaction A →B→C (stable and absorbing).

The data determined are (1) the half life $t_{1/2}$ of the colored or transient species and (2) the transient's spectra. Using the Turbo Pascal Borland Program, three cases can be distinguished: (1) the formation and decay of the transient are first order. (2) Transient A decays to transient B, giving the nonabsorbing product C. (3) Transient A decays to transient B, which forms the absorbing molecule C (see Figures 6.17 and 6.18).

6.8. SYNTHESIS OF KEY EXAMPLES

6.8.1. 4,5-Dicarbomethoxy-3*H*-pyrazole-(3-spiro-9)-fluorene [68,69,70,71]

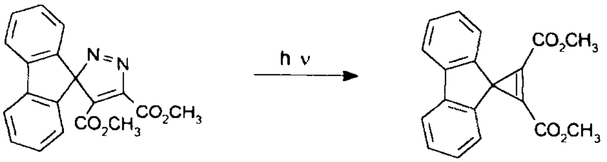


Scheme 27

A mixture of 1.90 g (9.89 mmol) of 9-diazofluorene and 1.70 g (11.96 mmol) of dimethyl acetylenedicarboxylate was dissolved in 10 ml of dry ether. After standing for 24 h, the precipitated yellow crystals were separated in almost quantitative yield, mp 110°C (methanol).

Anal. calcd. for $C_{19}H_{14}N_2O_4$: N 8.38; found: N 8.65.

6.8.2. 1,2-Dicarbomethoxycyclopropene-(3-spiro-9)-fluorene[3 - 7, 72, 73]



334.3 306.3

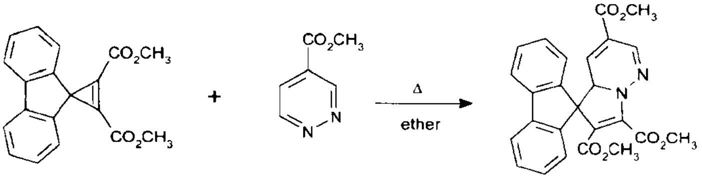
Scheme 28

Irradiation of 1.00 g (2.98 mmol) of 4,5-dicarbomethoxy-3*H*-pyrazole-(3-spiro-9)-fluorene in 150 ml of tetrahydrofuran (high-pressure mercury lamp, Hanau Q 81 Pyrex vessel, at 30°C gave a quantitative amount of nitrogen and 0.64 g (70%) of the product. Crystallization from methanol or ether–petroleum ether afforded colorless crystals in 70% yield, mp 146°C.

^{1}H-NMR ($CDCl_3$, 60 MHz): $\delta = 3.1$ (s), 7.2–7.1 (mm). UV ($CHCl_3$): λ_{max}(log ε) = 266 nm (4.45).

Anal. calcd. for $C_{19}H_{14}O_4$: C 74.5, H 4.61; found: C 74.29, H 4.78.

6.8.3. 1'H-2'3'-6 Tricarbomethoxy-spiro[fluorene-9-1'-pyrrolo[1,2- *b*]-pyridazine]



306.3 80.1 386.4

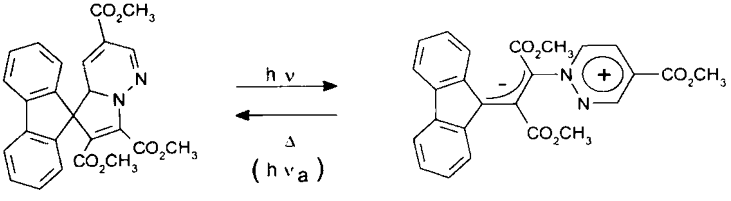
Scheme 29

To a solution of 0.50 g (1.63 mmol) of 1,2-dicarbomethoxycyclopropene-(3-spiro-9)-fluorene in 75 ml of ether was added 0.23 g (1.63 mmol) of 4-alkoxycarbonylpyridazine while stirring in the dark at room temperature. Evaporation of ether and treatment of the residue with methanol afforded 0.52 g as yellow crystals, mp 106°C.

UV (CH_2Cl_2): λ_{max} (log ε) = 415 nm (3.62). ^{1}H-NMR ($CDCl_3$ 90 MH_2): $\delta = 2.85$ (s, 3H, CH_3), 3.29 (s, 3H, CH_3), 3.33 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 4.00 (s, 3H, CH_3), 4.03 (s, 3H, CH_3), 5.35 (d, J = 1.8 Hz, 1H, 8'-H), 5.72 (d, J = 2.2 Hz, 1H, 8a'-H), 5.87–5.88 (m, 1H, 8a'-H), 6.43–6.44 (m, 1H, 7'-H), 7.05 (d, J = 3.9 Hz, 1H, 6'-H), 7.21–7.77 (m,gH,Arom.-H,6'-H) ppm.

6.8.4. 1-(1,2-Dicarbomethoxy-2-fluorene-9-yl-ethenyl)-4-alkoxycarbonylpyridazinium [3–7]

The yellow solution of 1'/H-2',3'-6 tricarbomethoxy-spiro[fluorene-9,1'-pyrrolo[1,2-*b*]pyridazine] in chloroform was irradiated, after flushing with argon, in a 13 cm cuvet (HPK 125 W Hg lamp, Pyrex filter, external irradiation). The solution turned red-violet with the formation of the betaine form. The color of the betaine faded with a half-life of $t_{1/2}$ = 30 s (k = 2.3 × 10^{-2} s^{-1}).

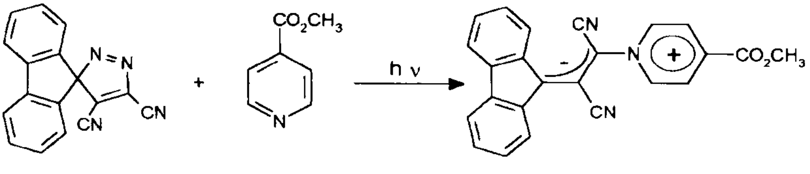


Scheme 30

Color: red.

UV ($CHCl_3$): λ_{max} DHI = 415 nm; λ_{max} betaine = 490 nm.

6.85. 1-(1,2-Dicyano-2-fluorene-9-yl-ethenyl)-4-methoxy-carbonyl-pyridinium [3–7]

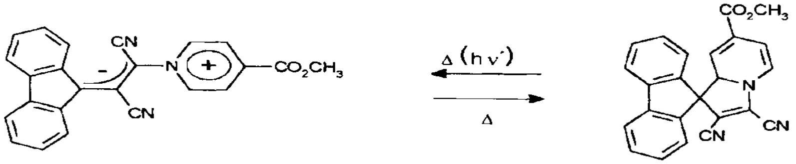


Scheme 31

A pale yellow solution of 0.50 g (1.86 mmol) of the 4,5-dicyano-3*H*-pyrazole-(3-spiro-9)-fluorene in 200 ml of dry ether and 2 ml of 4-methoxy-carbonyl-pyridine was flushed with nitrogen and irradiated (HPK 125 Philips, 125 W/Pyrex filter). The solution turned into a deep color after 1 min. After nitrogen evolution had ceased (about 1 h), the solvent was evaporated and the dark residue chromatographed using silica gel/CH_2Cl_2. Yield: 10% dark crystals; mp 163°C(from ether).

UV (CH_2Cl_2): λ_{max} = 578 nm.

6.8.6. 1'H-2',3'-Dicyano-7-methoxy-carbonyl-spiro[fluorene-9,1'-pyrrolo-[1,2-*b*]pyridine

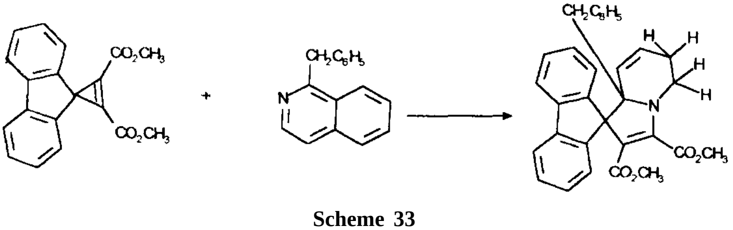


Scheme 32

A suspension of 0.590 g (1,84 mmol) of the betaine 1-(1,2-dicyano-2-fluorene-9-yl-ethenyl)-4-methoxy-carbonyl-pyridinium in ether–petroleum ether was stirred in the absence of light at room temperature for 24 h. The reaction product was separated on a silica gel column with methylene chloride as eluent. Yellowish-green needles precipitated from ether–pentane in a dry ice mixture. Yield: 0.480 g (81.3%); mp: 163°C. The decolorization of the betaine solution can also be brought about by irradiation (bandpath filter, $\lambda = > 570$ nm Philips 125 HPK, Hg lamp).

^{1}H-NMR (CDCl$_3$, 90MHz): δ = 7.82–7.25 (m, 8H, Arom.-H), 6.76 (d, J_{56} = 7.7 Hz, 1H, 5'H), 5.86 (dd, J_{65} = 7.6Hz, 1H, 6'-H), 5.65 (m, 1H, 8a'-H), 5.54 (m, 1H, 8'-H), 3.62 (s, 3H, CO$_2$CH$_3$) ppm.

6.8.7. 1',5',6'-*H*110-b'benzyl-2',3'-dimethoxycarbonyl-spiro[fluorene-9,1'-pyrrolo[2,1-*a*]isoquinoline[74]



Scheme 33

To a solution of 460 mg (1.5 mmol) spiro-cyclopropene in 50 ml of dry ether an equimolar amount (32.2 mg = 1.5 mmol) of 1-benzyl-3,4-dihydroisoquinoline was slowly added at room temperature. After 24 h of stirring in the dark, the precipitate was filtered off. Column chromatography in SiO$_2$ with CH$_2$Cl$_2$ and recrystallisation from ether afforded the tetrahydroindolizine. Yield: 420 mg (53.2%); mp: 238°C.

UV (CH$_2$Cl$_2$): λ_{max}(log ε) = 329 nm. IR (KBr): 3060, 2980 (CH), 2900, 1740 (C=O), 1730 (C=O) cm^{-1}. H-NMR (CDCl$_3$ 90 MHz): δ = 2.15 (td, ^{2}J = 10.2 Hz, ^{3}J = 3.6 Hz, 1H, 6'-H); 2.25 (d, ^{2}J = 10.2 Hz, 1H, 6-H); 2.80 (m, 1H, 5'-H); 3.07 (d, ^{2}J = 12.7 HZ, 1H, CH$_2$); 3.21 (m, 1H, 5-H); 3.31 (s, 3H, 2'-CO$_2$CH$_3$); 4.06 (s, 3H, 3'-CO$_2$CH$_3$); 4.16 (d, ^{2}J = 12,7 Hz, 1H, CH$_2$); 6.28 (d, ^{3}J = 7.8 Hz, 1H, 10'-H); 6.69

(m, 3H, Ar-H); 6.75 (t, $^3J = 6.8$ Hz, 1H, Ar-H); 6.85 (dd, $^3J = 6.8$ Hz, $^4J = 0.9$ Hz, Ar-H); 6.99–7.11 (m, 5H, Ph-H); 7.30 (t, $^3 = 7.0$ Hz, 1H, Ar-H); 7.42 (m, 2H, Ar-H); 7.70 (d, $^3J = 7.6$ Hz, 1H, Ar-H); 7.84 (d, $^3J = 7.6$ Hz, 1H, Ar-H) ppm.

6.9. CONCLUSIONS

1,5-Electrocyclization is an efficient reaction that has been employed in creating new photochromic systems (see also Ref. 3). The main challenge in the field is to prepare colorless and colored forms having almost equal energy content. 1,5-Electrocyclization of the colored betaine to the colorless cyclic structure can be controlled by the substitution pattern of the molecules. Tailor-made molecules with appropriate properties can thus be prepared. This basic concept has been extended from monoaza- (DHI), to diaza-(DHPP) and finally to triaza-5-ring heterocycles. Partially hydrogenated systems are possible as well.

Normally the formation of a C–N bond in electrocyclization is not favorable. It can be forced in this direction, however, by annelating aromatic rings in suitable positions.

The characteristics of the photochromic systems based on 1,5-electrocyclization are (1) a neutral molecule as educt gives a zwitterionic species as primary product, and (2) reversibility is possible only if secondary reactions leading to heteroatomic compounds are suppressed. Typical structural elements are therefore spiro(or gem-) substituted to avoid rearomatization.

Ring opening of the photochromic 5-ring heterocycles can be induced only photochemically. The photoreaction of the colorless form to the betaines involves a singlet species in all cases studied so far. Triplet routes to the photoproducts may be populated with lower efficiency. The reverse process, however, can be brought about thermally or photochemically.

Applications or potential applications for these molecules have been demonstrated. Molecular switches can be built using supramolecular or LC photochromic materials.[1] Photochromic polymers can be used in phototropic glasses or as a basis for information recording. IR-sensitive materials have been made using biphotochromic molecules. Light sensitive dental materials have been developed.

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7

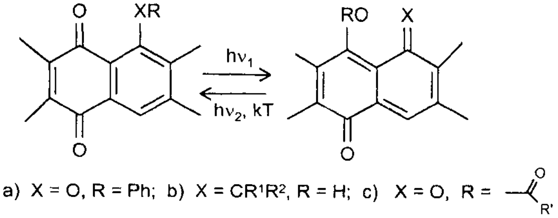
Photochromic Quinones

V. A. BARACHEVSKY

7.1. INTRODUCTION

Photochromic quinones are a class of organic photochromic compounds that have become known as photochromic substances quite recently compared with other compounds.[1] They were discovered during the synthesis and studies of the properties of anthraquinone derivatives.[2–4] It turned out that anthraquinone derivatives with an aryloxy group at the peri-position relative to the carbonyl group change color reversibly in the presence of UV light. In succeeding years, various photochromic quinones have been synthesized. The properties of these compounds have been analyzed in books[1,5] and many papers.[6–10]

At present, the photochromism of quinones is explained by the reversible photoinduced para-ana-quinoid transformations due to photochemical migration of different hydrogen, aryl, and acyl groups (Scheme 1).[8] In this chapter the results of the studies on quinone photochromism have been systematized with regard to recent advances in this field.



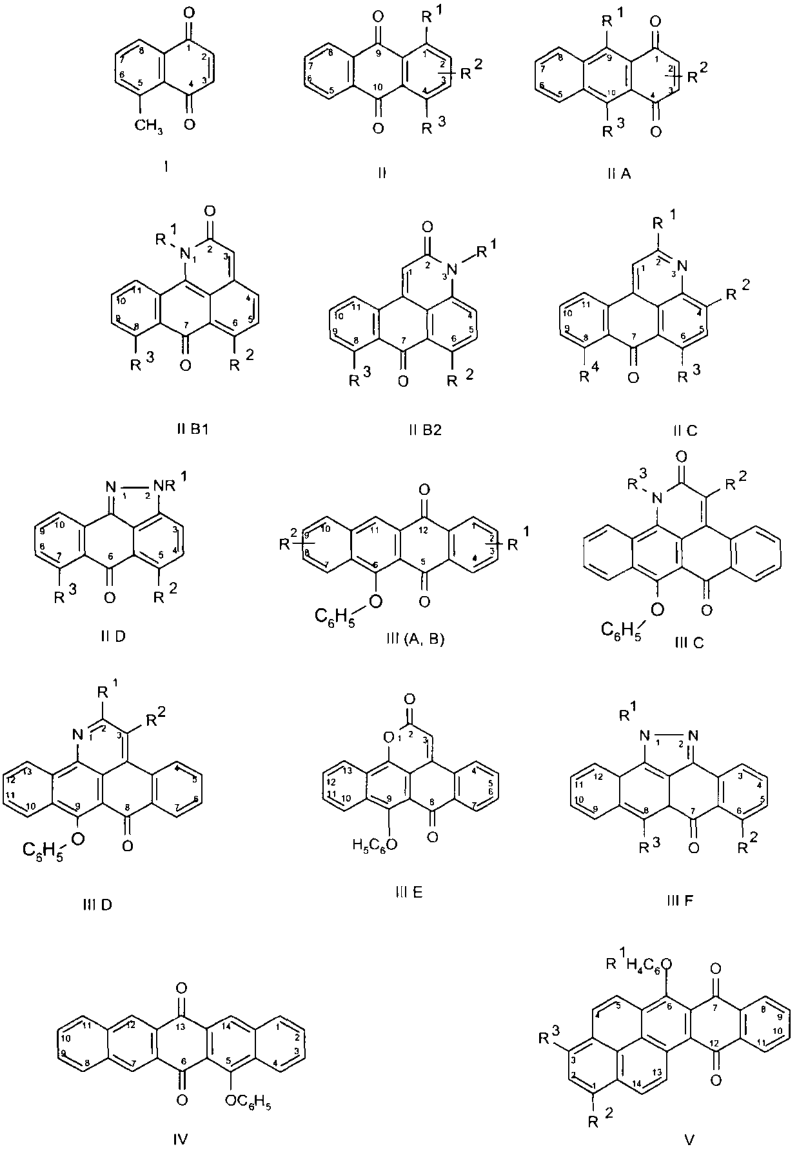
Scheme 1

V. A. Barachevsky • Photochemistry Center, Russian Academy of Sciences, Moscow, Russia.

Organic Photochromic and Thermochromic Compounds, Vol. 1, edited by John C. Crano and Robert Guglielmetti, Plenum Press, New York, 1999.

7.2. SYNTHESIS OF PHOTOCHROMIC QUINONES

At present, a number of photochromic quinones have been synthesized, including derivatives of naphthoquinone (I), substituted anthraquinones (II, IIA–IID) and naphthacenequinones (IIIA—IIIF), pentacenequinones (IV), and phthaloylpyrenes (V) (Figure 7.1). The family of photochromic anthraquinones involves



I II II A

II B1 II B2 II C

II D III (A, B) III C

III D III E III F

IV V

Figure 7.1. Structures of photochromic quinones.

derivatives of 9,10- and 1,4-anthraquinones (II, IIA) and anthrapyridones of two types (IIB1, IIB2), anthrapyridines (IIC) and pyrazolanthrones (IID). Photochromic naphthacenequinones fall into several types of compounds, namely, aryloxynaphthacenequinones with 11-phenoxy (IIIA) and 6-phenoxy (IIIB) substituents, naphthacenepyridones (IIIC), naphthacenepyridines (IIID), pyrone (IIIE), and pyrazolnaphthacenones (IIIF).

7.2.1. Methylnaphthoquinone[11]

5-Methyl- 1,4-naphthoquinone (I) was obtained by the Diels–Alder addition of piperylene to *p*-benzoquinone.[11]

7.2.2. Derivatives of Anthraquinone[2,4,12–42]

1-Methylanthraquinone (II) was synthesized by fusing *o*-(*o*-toluene)benzoic acid and poly-phosphoric acid and cooling the mixture with the addition of some water.[30]

1-Arylcyanomethyl-9,10-anthraquinones (II) were obtained by the interaction of the corresponding anthraquinone derivatives with phenylacetonitrile and pentafluorophenylacetonitrile in dimethyl sulfoxide (DMSO) in the presence of a base.[36]

2-,4-,5- and 8-Monoxy-1-aryl-9,10-anthraquinones (II) were synthesized by the condensation of corresponding halide anthraquinones with phenols.[19]

1-Aryloxy-2,4-dioxyanthraquinones (II) were produced by the rearrangement of 1,4-dioxy-2-aryloxy-anthraquinone.[19]

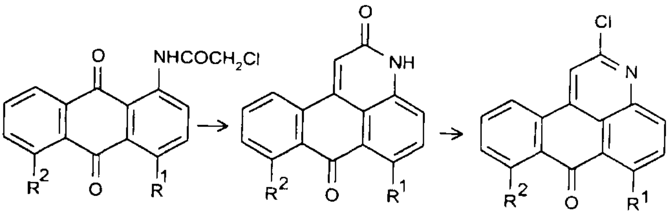
Amino- and methoxy-substituted derivatives of 1-acyloxy-9,10-anthraquinone (II) were obtained by acylation of the corresponding 1-hydroxyanthraquinones using acetic anhydride and acetyl chloride in the presence of pyridine.[28]

The synthesis of the series of 2,4,5-amino-substituted derivatives of 1-phenoxyanthraquinone (II) was accomplished by an exchange of chlorine or bromine atoms upon heating the corresponding 1-chloro- or 1-bromoanthraquinones in a phenol–phenoxide solution as well as by alkylation of 1-aminomethyl- or dimethylanthraquinones using methyliodide.[14]

1-(1-Naphthoxy)anthraquinone (II) was obtained by the Ullmann condensation of 1-bromoanthraquinone with the corresponding potassium naphtholate.[32] 1-Bromoanthraquinone was prepared by the Sandmeyer reaction from 1-aminoanthraquinone.

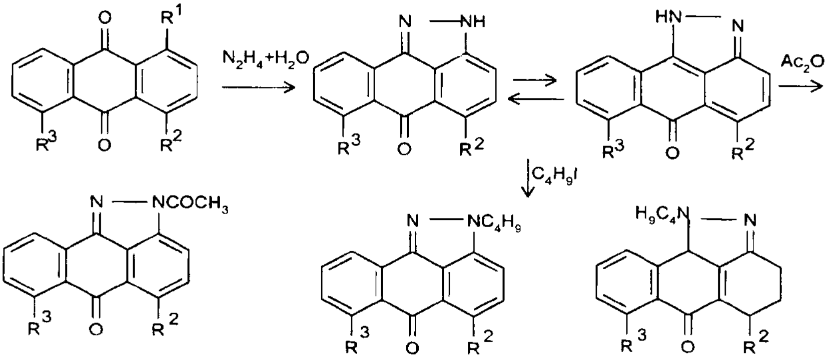
Photochromic anthrapyridones (IIB1, IIB2) were produced by cyclization of 1-chloracetylamino-4-(or -5)-phenoxyanthraquinones with the subsequent reductive elimination of the pyridine group from the products obtained in pyridine (Scheme 2).[38] Photochromic chloro derivatives of pyridines (IIC) were synthesized by the interaction of the resultant photochromic anthrapyridines with phosphorous chloroxide.[38]

Photochromic pyrazolanthrones (IID) were obtained by the interaction of 1,4- and 1,5-dichloro- and diphenoxyanthraquinones with hydrazinehydrate in pyridine (Scheme 3).[40–42)] Acetyl derivatives of pyrazolanthrones were synthesized by a brief



Scheme 2

heating of pyrazolanthrones in acetic anhydride. Butyl derivatives were formed by the treatment of pyrazolanthrones with butyl iodide in dimethylformamide.



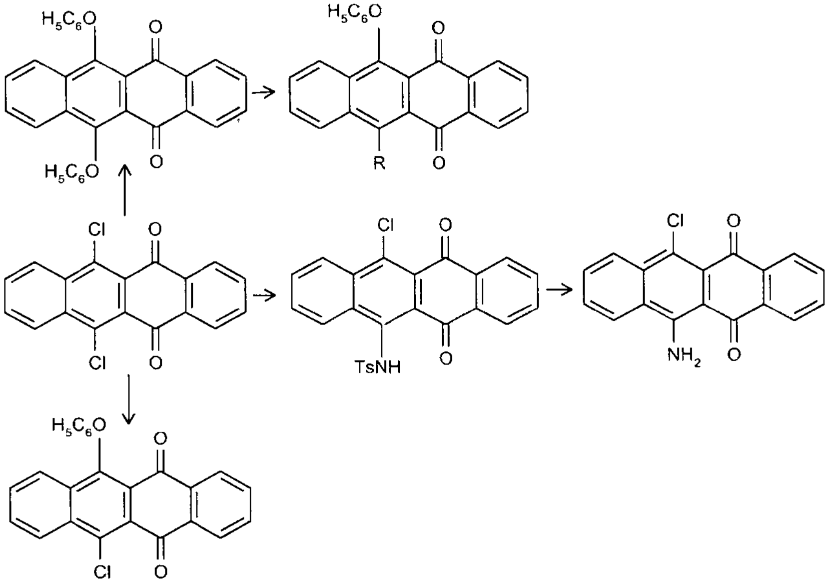
Scheme 3

7.2.3. Derivatives of Naphthacenequinone[3,37,39,40,42–55]

The basic methods for the synthesis of 5,12-naphthacenequinone are reactions involving the oxidation of naphthacene and its derivatives as well as cyclization reactions, with reactions of intramolecular acylation and diene synthesis being of particular interest.[7]

A number of photochromic phenoxynaphthacenequinones were obtained using the initially synthesized 6-substituted 11-phenoxynaphthacene-5,12-quinones (IIIA) (Scheme 4).[46] 6,11-Dichloro-naphthacenequinone was the initial compound for the synthesis of these 6-chloro-11-phenoxynaphthacenequinone compounds. 6-Chloro-11-tosylaminonaphthacene-5,12-quinone was obtained by interaction with phenoxide potassium in DMSO and *p*-toluenesulfamide in nitrobenzene, respectively. The latter compound was hydrolyzed in sulfuric acid to form 6-chloro-11-aminonaphthacene-5,12-quinone. The treatment of 6-chloro-11-phenoxynaphthacene-5,12-quinone and 6-chloro-11-aminonaphtacene-5,12-quinone with potassium phenoxide gave rise to 6-tosylamino- and 6-amino-11-phenoxynaphthacene-5,12-quinones

(IIIA). The latter compounds were used for the synthesis of 6-acetyl- and 6-nitro-substituted 11-phenoxynaphthacene-5,12-quinone by acetylation with acetic anhydride in the presence of catalytic content of sulfuric acid and by oxidation with peroxyacetic acid, respectively.



Scheme 4

6-Methyl, 6,6-dimethyl, and 6-phenylamino derivatives of phenoxynaphthacene-5,12-quinone (IIIA) were produced by the interaction of 6,11-diphenoxynaphthacene-5,12-quinones with the corresponding amines.[46]

Acetylation of 6-methylamino-11-phenoxynaphthacene-5,12-quinone by acetic anhydride in the presence of a catalytic quantity of sulfuric acid and 6-oxy-11-phenoxynaphthacene-5,12-quinone in the presence of pyridine yields *N*-acetyl-,6-methylamino- and 6-acetoxy-11-phenoxynaphthacene-5,12-quinones (IIIA).[46]

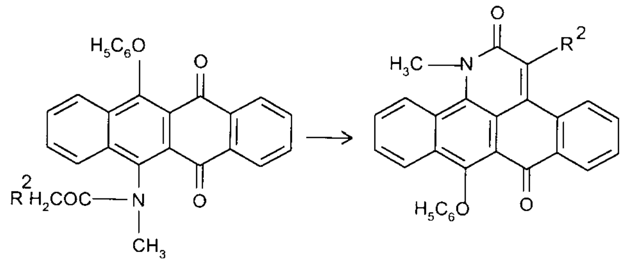
6-Oxy-11-phenoxynaphthacene-5,12-quinone (IIIA) was separated after the interaction of 6,12-diphenoxynaphthacene-5,11-quinone with piperidine or secondary amines.[46]

11-Aryloxy-derivatives of 6-amino-11-phenoxynaphthacene-5,12-quinones (IIIA) were synthesized by heating 6-amino-11-chloro-5,12-naphthacenequinone in a phenol–phenoxide melt of a suitably substituted phenol or by interaction with a corresponding substituted potassium phenoxide in DMSO in the presence of cuprous (I) chloride.[52]

6-Chloro-5,12-naphthacenequinone was used for the synthesis of 6-[4(2-(4-hydroxyphenyl)-isopropyl]- and 6-[4-(potassium sulfophenylazo)phenoxy]-5,12-naphthocenequinones (IIIB)[55] as well as other derivatives of 11-phenoxynaphthacene-5,12-quinone.[53]

Acrylate and styrene polymers as well as polysiloxanes with 11-phenoxy-naphthacene-5,12-quinone side groups (IIIB) were synthesized using the reaction of the active ester copolymers with 6-[(tyrosinebutylester)*o*-yl]-5,12-naphthacenequinone.[53]

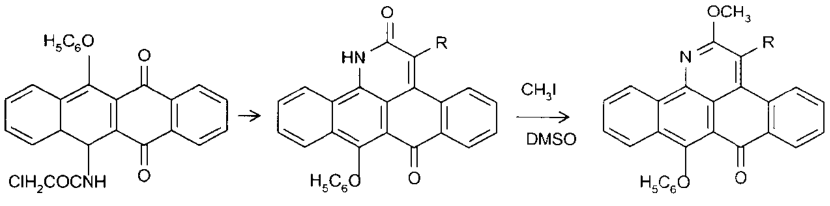
9-Phenoxy-3-chloro-naphthacenepyridone (IIIC, R^2 = Cl, $R^3 = CH_3$) was prepared by cyclization of chloracetylaminoanthraquinone in pyridine (Scheme 5).[37] Cyclization of *N*-chloracetyl-6-methylamino-11-phenoxy-naphthacene-5,12-quinone during heating in phenol yields 3,9-diphenoxy-naphthacenepyridone (IIIC, R^2 = phenoxy, $R^3 = CH_3$). Heating *N*-acetyl-6 methylamino-11-chloro- or *N*-acetyl-6-methylamino-11-phenoxy-5,12-naphthacenequinone in phenol in the presence of sodium carbonate proved to be a convenient method for the synthesis of 9-phenoxy-naphthacenepyridone.



Scheme 5

9-Phenoxy-substituted 2*H*, 8*H*-naphtha [1,2,3-de]-benz[*h*]-2,8-quinolinedione (IIIC, R^2 = hydrogen, $R^3 = CH_3$) was synthesized by cyclization of *N*-chloro-acetyl-6-aminonaphthacenequinone in pyridine to the corresponding naphthacenepyridonyl-3-pyridinium chloride, with the subsequent reductive elimination of the pyridinium residue.[39] The 3-acetyl derivative was obtained by the interaction of 6-amino-11-chloro-5,12,naphthacenequinone with acetic anhydride in phenol in the presence of anhydrous sodium carbonate.[39]

Methylation of naphthacenepyridones by methyl iodide in DMSO was used for preparation of 2-methoxynaphthacenepyridines (IIID).[39]



Scheme 6

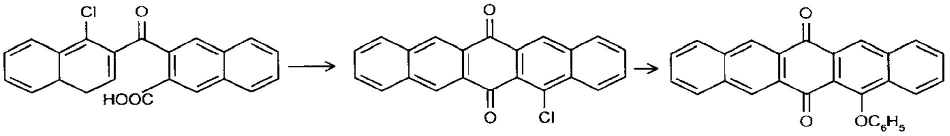
9-Phenoxynaphthaceno[12,11[*bc*]-2,8-pyrandione (IIIE) was obtained from 6-phenoxy-5,11-naphthacenequinone (Scheme 6), which was synthesized from

6-phenoxy-5,12-naphthacenequinone with acetic anhydride in pyridine using a photochemical method.[48]

Derivatives of phenoxypyrazolonaphthacenone (IIIF) was synthesized using 6,11-dichloro- and 6,11-diphenoxy-5,12-naphthacenequinone according to known methods.[42,56]

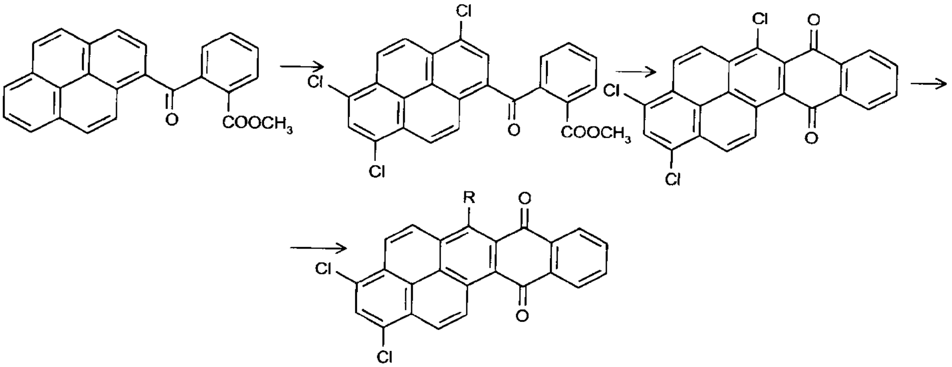
7.2.4. Phenoxypentacenequinone and Derivatives of Phthaloylpyrene

6-Phenoxy-5,13-pentacenequinone (IV) was obtained by the replacement of chlorine atoms with phenoxy groups in 5-chloro-6,13-pentacenequinone in a phenol-phenoxide melt (Scheme 7).[57] 5-Chloro-6,13-pentacenequinone was synthesized by cyclization of 2-(1-chloro-2-naphthoyl)-3 naphthoic acid, which was prepared by acylation of α-naphthol with anhydrous naphthalene-2,3-dicarboxylic acid and by the subsequent treatment of the resultant 2-(1-oxy-2-naphthoyl)-3 naphthoic acid with phosphorus pentachloride.



Scheme 7

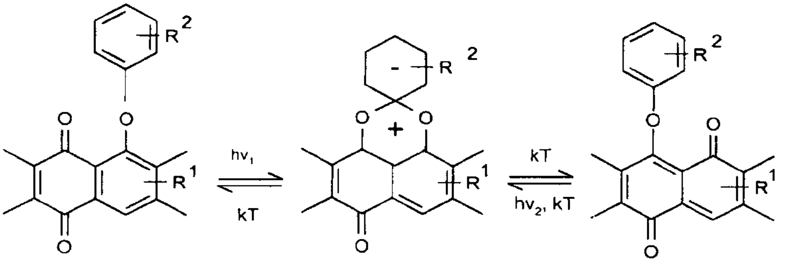
Photochromic 1,3-dichloro-6-phenoxy-7,12-phthaloylpyrene (V) was obtained by the interaction of the trichloro derivative with molten phenol containing caustic potassium hydroxide (Scheme 8).[58] The treatment of 1,6,8-tichloro-2,3,-phthaloylpyrene with different substituted phenols yielded a number of phenoxy derivatives with different substituents on the phenyl group.[59]



Scheme 8

7.3. MECHANISM OF PHOTOCHROMIC TRANSFORMATIONS IN QUINONES

Photochromism of quinones is caused by the reversible photoisomerization of the para quinone structure to the ana quinone structure as a result of photo- and thermoinduced intramolecular substitution according to the associative mechanism with participation of the δ-complex (Scheme 9).[5]

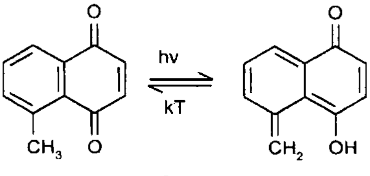


Scheme 9

In addition to the photoinduced transfer of the phenyl group, photoinduced migration of an acyl group or a hydrogen atom is rendered possible in photochromic quinones. The mechanism of the photochromic transformation of quinones depends on the structure of the initial compounds.

7.3.1. Photochromism of Naphthoquinone

Photochromic transformations of 1,4-naphthoquinone were discovered after the introduction of a methyl substituent in the peri position for suppression of its photochemical reactivity toward intermolecular hydrogen abstraction.[11] The mechanism of photochromism is based on reversible photoenolization (Scheme 10) .[11]



Scheme 10

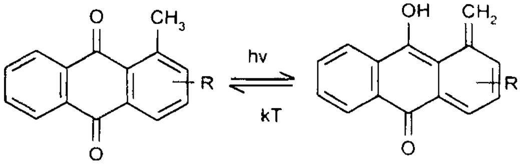
The suggested structure of the photoinduced form of naphtoquinone methide was confirmed by identification of this compound at 77 K, the coincidence of experimental and calculated Pariser-Parr-Pople self-consistent field chemical ionization (PPP SCF CI) spectral characteristics, and the sharp change in the rate of the dark relaxation from the photoinduced state to the initial form (by four orders of magnitude) upon passage from hydrocarbon to aprotic hydrogen-bond acceptor solvents.[11]

7.3.2. Photochromism of Anthraquinones

The well-known photochromic transformations of anthraquinones are closely associated with the photoinduced migration of hydrogen, acyl, or aryl groups. Although photochromism of these compounds fits the reaction shown in Scheme 9, the processes of photochromic transformation exhibit some features related to the nature of the photoreactive state and details of the mechanism of the photochromic transformations.

7.3.2.1. Alkylanthraquinones

As in the case of 5-methyl-1,4-naphthoquinone, photochromic transformations of 1-alkylanthraquinone derivatives represent a thermally reversible photoenolization which was first demonstrated for 1-methyl-9,10-anthraquinone (II, $R^1 = CH_3$, $R^2 = R^3 = H$) (Scheme 11).[16]

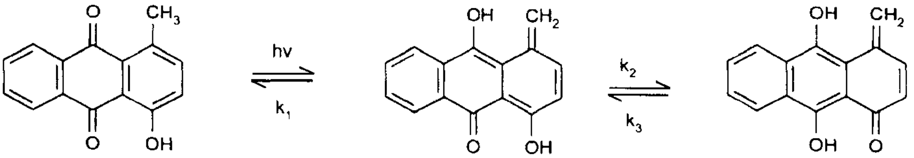


Scheme 11

The derivatives of 1-methyl-9,10-anthraquinone exhibit photochromism in an ethanol matrix at 77 K. The recovery of the initial structure was found to occur at ambient temperature.[16,18,26]

One can see from Table 7.1 that a compound in which two hydrogen atoms in the methyl group are replaced by two phenyl groups showed no photochromism.[26]

In the case of 1-methyl-4-oxy-9,10-anthraquinone (II, $R^1 = CH_3$, $R^2 = H$, $R^3 = OH$), the photoinduced transfer of a hydrogen atom from a methyl group to oxygen occurs together with the thermal transfer of a proton from the OH group to the second oxygen (Scheme 12).[8,9,18,26] The related photoinduced transformations were observed for the derivatives of 1-alkyl and 1-benzylanthraquinones.[8,9,23,26]



Scheme 12

Compounds with substituted methyl groups were characterized by complex kinetics of thermal relaxation from the photoinduced form to the initial form because of the production of two photoinduced isomers with different (by an order of magnitude) lifetimes.[26,30]

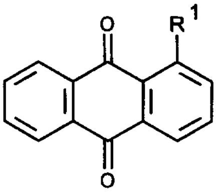
The study of photochromic transformations of 1-methylanthraquinone and its deuterium analog by means of laser photolysis over a wide temperature range[30] showed that photoinduced hydrogen migration occurs in the single (S*) as well as triplet (T) states. These states are of the $n\pi^*$-nature. In the case of hydrogen migration involving the T ($n\pi^*$) state, the main product of photoreaction is T-excited quinone methide. Therefore, this process is an adiabatic photochemical hydrogen migration. According to the quantum-chemical calculations, the T state is a $\sigma\pi$ biradical with the unfolded CH_2 fkagment.[30]

The rate constant of the S* → T transition is equal to $k = 1 \times 10^{11}\ s^{-1}$ and the rate constants for the hydrogen atom transfer are $k = 3 \times 10^{10}\ s^{-1}$ for the nondeuterated compound and $k = 1 \times 10^{10}\ s^{-1}$ for its deuterated analog.[30]

7.3.2.2. Acyloxyanthraquinones

Photochromic transformations of compounds of this type were identified during irradiation of 1-acetoxy-9,10-anthraquinone (II, $R^1 = OCOCH_3$, $R^2 = R^3 = H$)

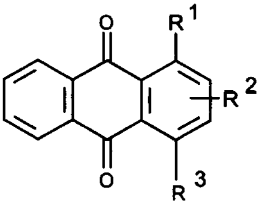
Table 7. 1. Spectro-Kinetic Characteristics of Initial (IF) and Photoinduced Form (PF) of 1-Substituted Methyl-9-10-Anthraquinone[17,18,26,36] (Type II)



	λ_{max} (log ε) toluene–THF at 77 K[a]		φ_B λ_{exc} = 334 nm	τ (μs) ethanol at 290 K (f)		ΔE (kJ/mol)	
R^1	IF	PF		τ_1	τ_2	ΔE_1	ΔE_2
CH_3	376(3.74), 340(3.78)	581(3.97)	0.20 0.22[b] 0.21[d]	152±5 167[c]	—	45.2±0.4	—
$CH(CH_3)_2$	335	598	0.11[b]	—	2800±20	—	552±0.4
CH_2CH_3	337	586	0.15[b]	294±200	2500±20	41.0±1.0	538±12
$CHPh_2$	341	—	—	—	—	—	—
CH_2Ph	341	635	—	36±3	—	—	—
$CHCH_3Ph$	339	621	—	17±1	170±10	—	—
$CH_2C_6F_5$	338	588	—	18±1	169±10	—	—
CHC_6H_5CN	330	635	—	1 × 10^7	—	—	—
CHC_6H_5CN	327	631	—	—	—	—	—

[a] THF-tetrahydrofuran.
[b] 313 nm.
[c] Isopropanol, 290 K.
[d] 436 nm.
[e] At 300 K
[f] τ = Lifetime (time for decrease of optical density to 1 /e x initial value) τ_1 and τ_2 are lifetimes for two rotational isomers.

Table 7.1. (continued)

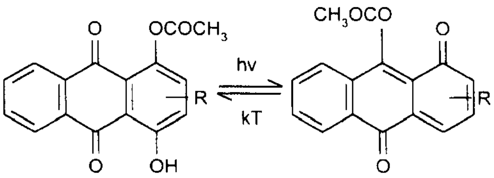


R^1	R^2	R^3	λ_{max} (log ε) toluene–THF at 77 K[a]		φ_B $\lambda_{exc.}$ = 334 nm	τ (μs) ethanol at 290 K
			IF	PF		
CHC_6H_5CN	H	OCH_3	388	610	—	4.76×10^8
CHC_6H_5CN	H	Cl	339	636	—	9.1×10^6
CHC_6H_5CN	H	NO_2	335	632	—	16.7×10^7
CH_3	H	OCH_3	396 (3.83)[e]		0.19	220[c]
			405 (3.88)	595 (3.41)		—
CH_3	H	Piperidine	530 (3.56)[e]		0.0014	—
			525 (3.54)	617 (3.77)	0.0001[b]	—
CH_3	H	OH	415 (3.73)[e]		0.023	1.32×10^8
			417 (3.73)	478 (3.72)	0.003[d]	—
CH_3	3-CH_3	OH	420 (3.84)[e]		0.0025	—
			418 (3.81)	472 (3.72)	0.0003[b]	
CH_3	H	Cl	345 (3.63)[e]		0.01	95[c]
			348 (3.68)	578 (3.86)		—
CHC_6H_5CN	2-OCH_3	H	371	622	—	—
CH_3	3-Cyclohexene-l-yl	H	373 (3.73)	595 (3.84)	0.017	120[c]
			389 (3.68)		0.001[d]	—
CH_3	3-(2-Nitrocyclohexene)-l-yl	H	340 (3.81)[e]		0.07	263[c]
			344 (3.84)	588 (3.90)		—
CH_3	3-Cyclohexyl	H	339 (3.74)[e]		0.2	86[c]
			340 (3.78)	588 (3.97)		—

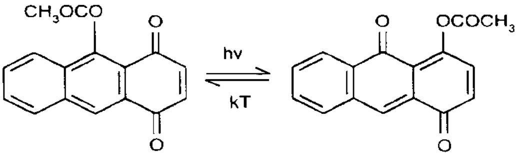
[a] THF-tetrahydrofuran.
[b] 313 nm.
[c] Isopropanol, 290 K.
[d] 436 nm.
[e] At 300 K

(Scheme 13) and 9-acetoxy-1,4-anthraquinone (IIA, $R^1 = OCOCH_3$, $R^2 = R^3 = H$) (Scheme 14) in a glassy matrix at 77 K.[19,21,34] It was found that photochromic transformations occurred only in acetoxyanthraquinones with electron-donating substituents (amino and methoxy groups) and also in unsubstituted 9-acetoxy-1,4-anthraquinone. However, unsubstituted I-acetoxy-9,10-anthraquinone and its derivatives with the substituents in 2-,4-,5- and 8-positions did not exhibit photochromism (Table 7.2).[21,28,34]

The photoinduced migration of the acetyl group occurs adiabatically with the participation of the T state.[28,34] The quantum chemical calculations showed that the



Scheme 13

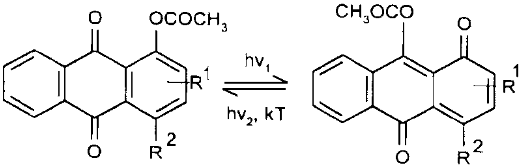


Scheme 14

photochromic compounds of this type in the para quinone form have a lower excited ππ* or nπ*state.[34] If this state correlates with the lower excited ππ* or nπ* state of the photoinduced form, migration of the acetyl group will be effective. Otherwise, the molecules will react with solute molecules, resulting in the formation of products of irreversible photochemical reactions.

7.3.2.3. Aryloxyanthraquinones

It has been found[11,13,15,19,50] that photochromic transformations of aryloxyanthraquinones depend on the position and the electron character of substituents in the anthraquinone cycle (Scheme 15). The structure of the photoinduced form was supported by the results of an IR spectral study.[4]

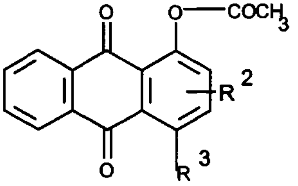


Scheme 15

Tables 7.3 and 7.4 show that unsubstituted and most of the substituted 1-phenoxy-9,10-anthraquinones exhibit photochromic properties. The majority of compounds with mono- and dialkylamino substituents shows no photochromic transformations but undergoes irreversible photochemical conversion.[5,8] The photochromism is also absent in the case of 1-phenoxy-8-hydroxy-anthraquinone. It is suggested[31] that, unlike 1-naphthoxyanthraquinone,[32] the structural isomer of 1-phenoxy-anthraquinone arises from the rotameric isomer.

In the case of 1-phenoxy-4-acetoxy anthraquinone (II, $R^1 = OC_6H_5$, $R^2 = OCOCH_3$), the photoinduced migrations of phenyl and acetyl groups occur simultaneously (Scheme 16).[19] The study of photochromic transformations of this compound by the laser photolysis method[22] showed that the processes include the phototransfer of either phenyl or acetyl groups as well as subsequent thermal transfer of either acetyl or phenyl groups, respectively.

Table 7.2. Spectra-Kinetic Characteristics of Derivatives of 1-Acetoxy-9,10-Anthraquinone (Type II) and 9-Acetoxy- 1,4-Anthraquinone (Type IIA)[21,28,34]

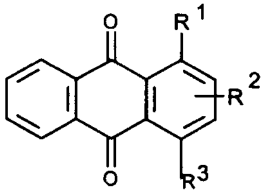


II

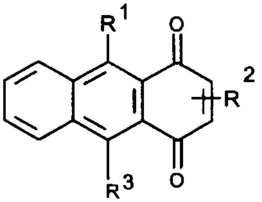
		λ_{max} (nm) (log ε) ethanol at 77 K		τ (μs) toluene at 290 K	*k* (s^{-1}) at 290 K		φ, ethanol at 77 K
R^2	R^3	IF	PF		Toluene	Isopropanol	
H	H	330 (3.77)	—	—	—	—	—
2-OCH_3	H	374 (3.80)	526 (4.04) 520[a]	4.04	5.6×10^5 2.5×10^{5b}	2.9×10^5 4.7×10^{5c}	0.45
2-$OCOCH_3$	H	331 (3.78)	—	—	—	—	—
2-$N(CH_3)_2$	H	463 (3.70)	683 680[a]	16.0	6.2×10^4 6.2×10^{4b}	9.1×10^4 9.1×10^{4c}	0.015
2-$NHCOCH_3$	H	378	512sh, 546, 586sh	—	—	—	—
2-Piperidine	H	445	654	—	—	—	—
H	OCH_3	402 (3.78)	510 (3.48) 500[a]	3.5	2.9×10^5	3.1×10^5 3.11×10^{5c}	0.37
H	$OCOCH_3$	340 (3.77)	—	—	—	—	—
H	$NHCOCH_3$	410	—	—	—	—	—
H	NHC_6H_{11}	527 (3.90)	—	—	—	—	—
H	$NHCH_3$	525	—	—	—	—	—
3-Piperidine	H	489	—	—	—	—	—
5-OH	H	340 (3.77)	—	—	—	—	—
5-$OCOCH_3$	H	342 (3.76)	—	—	—	—	—
8-OH	H	340 (3.72)	—	—	—	—	—
8-$OCOCH_3$	H	338 (3.78)	—	—	—	—	—

(*continued*)

Table 7.2. (continued)



II



IIA

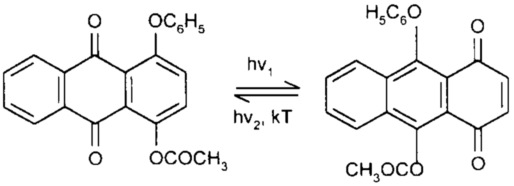
			λ_{max} (nm) (log ε) ethanol at 77 K		τ (μs) toluene at	k (s^{-1}) at 290 K		φ ethanol
R^1	R^2	R^3	IF	PF	290 K	Toluene	Isopropanol	at 77 K
9-$OCOCH_3$(IIA)	H	H	410 (3.72)	486 460[a]	325	3.1×10^3 3.1×10^3[b]	5.0×10^3 5.0×10^3[c]	1.2
9-$OCOCH_3$(IIA)	H	Cl	406	461 460[a]	161	—	—	—
9-OPh (IIA)	H	$OCOCH_3$	410 (3.72)	470 Toluene	330 Toluene	3×10^3	—	0.4 Toluene
H	H	$OCOCH_3$	—	468 460[a]	—	—	—	—
1 -$OCOOC_2H_5$	2-OCH_3	H	330 (3.68)	526,566sh	—	3.1×10^3[b] 6.5×10^5[d]	—	—
1 -OCOOPh	2-OCH_3	H	335,365	520, 560sh	—	5.0×10^4[b]	—	1.0[d]
1 -OCO-furan	2-OCH_3	H	333,366	519, 560sh	—	4.3×10^4[b]	—	—
1 -OC–PhN$(CH_3)_2$	2-OCH_3	H	327,370sh	—	—	4.3×10^3[b]	—	—
1 -OCO–N$(C_2H_5)_2$	2-OCH_3	H	337, 377	526, 562	—	2.9[b] 2.9[d]	—	0.05[d]
1 -OCO–$NPhCH_3$	2-OCH_3	H	337, 377	527, 560	—	—	—	—
1 -OCO–NPhOH	2-OCH_3	H	337, 362	526, 560	—	—	—	—

[a] 285 K.

[b] Benzene.

[c] Ethanol.

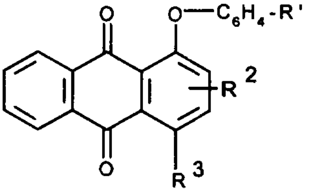
[d] Toluene, taken from Ref. 42.



Scheme 16

A similar mechanism of photochromic transformation is suggested for 1-phenoxy-4-hydroxy-9,10-anthraquinone.[19] The only difference is that the photochromic transformations can be observed at 77 K because they occur with high rate and with a very low activation energy.

Table 7.3. Spectral Characteristics of Amino-Substituted 1-Phenoxy-9,10-Anthraquinones (type II)[5,13–15,19,29,32]



			λ_{max} (nm) (lg ε)			
			IF		PF	
R^1	R^2	R^3	Benzene, heptane[a]	Polyvinyl alcohol + polystyrene	Benzene, heptane[a]	Polyvinyl alcohol + polystyrene
1	2	3	4	5	6	7
H	H	H	364	380 (3.59)	480	477 (3.68)
H	2-NH_2	H	415 (3.70) 415 (3.70)[a]	—	616[b]	—
m-CH_3	2-NH_2	H	402 (3.69)[a]	—	587 (3.81)[b]	—
p-$C(CH_3)_3$	2-NH_2	H	404 (3.73)[a]	—	587 (3.87) b	—
H	2-$NHCH_3$	H	438 (3.81) 424 (3.78)[a]	—	648[b] 615 (3.94)[a]	—
m-CH_3	2-$NHCH_3$	H	424 (3.72)[a]	—	615 (3.93)[a b]	—
p-$C(CH_3)_3$	2-$NHCH_3$	H	423 (3.86)[a]	—	616 (3.94)[a b]	—
p-$C(CH)_3$	2-$NHCOCH_3$	H	373	373 (3.72)	543	543 (3.98)
H	2-$NHCOC_6H_5$	H	376 (3.85)	—	552[b]	—
p-$C(CH_3)_3$	2-$NHCOC_6H_5$	H	—	373 (4.08)	—	556 (4.08)
p-$C(CH_3)_3$	2-NHC_2H_5	H	426 (3.90)[a]	—	628 (4.03)[a b]	—
H	2-$N(CH_3)_2$	H	448 (3.70)	—	665[b]	—
p-$C(CH_3)_3$	2-$N(CH_3)_2$	H	448. 430[a]	—	665	—
p-$C(CH_3)_3$	2-$NHCH_2C_6H_5$	H	427 (3.89)[a]	—	621 (4.02)[a]	—
p-$C(CH_3)_3$	2-$N(C_2H_5)_2$	H	468[a]	—	[c]	
p-$C(CH_3)_3$	2-$NHCOCF_3$	H	354	354 (3.72)	527	527 (3.94)
p-$C(CH_3)_3$	2-$NHCOC_6F_5$	H	—	369 (3.79)	—	541 (3.93)
p-$C(CH_3)_3$	3-NH_2	H	415 (3.64)	—	434 (3.88)[b]	—
p-$C(CH_3)_3$	3-$NHCH_3$	H	438 (3.64)	—	442 (3.81)[b]	—
p-$C(CH_3)_3$	3-$N(CH_3)_2$	H	459 (3.74)	—	443 (3.89)[b]	—
p-$C(CH_3)_3$	3-$NHSO_2HC_6H_4CH_3$	H	380 (3.66)	—	466 (3.81)	—
H	H	NH_2	473 (3.86)	—	510sh, 543, 586	—
p-$C(CH_3)_3$	H	NH_2	478 (3.86)	—	581	—
p-$C(CH_3)_3$	H	$NHCOC_6H_5$	445 (3.86)	—	541 (4.11)	—
H	H	$N(CH_3)_2$	511 (3.71)	—	[c]	—
H	5-NH_2	H	466 (3.81)	—	582	—
p-$C(CH_3)_3$	5-NH_2	H	466 (3.76)	—	575	—

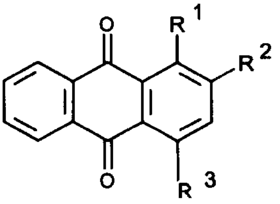
(*continued*)

Table 7.3. (continued)

1	2	3	4	5	6	7
H	5-$NHCH_3$	H	505 (3.88)	—	[c]	—
p-$C(CH_3)_3$	5-$NHCH_3$	H	504 (3.80)	—	[c]	—
H	5-$NHCOCH_3$	H	419	—	508	—
p-$C(CH_3)_3$	5-$NHCOCH_3$	H	415 (3.86)	—	502 (4.04), 523 (4.02)	—
H	5-$NHCOC_6H_5$	H	419 (3.87)	—	508 (3.47), 532 (3.95)	—
p-$C(CH_3)_3$	5-$NHCOC_6H_5$	H	418 (3.84)	—	506 (3.97), 532 (3.95)	—
H	5-$N(CH_3)_2$	H	502 (3.72)	—	[c]	—
p-$C(CH_3)_3$	8-NH_2	H	472 (3.75)	—	[c]	—
p-$C(CH_3)_3$	8-$NHCH_3$	H	510 (3.79)		[c]	—
H	2-OH	H	369 (3.74)	—	387 (3.82), 532 (3.83)	—
H	H	OH	430 (3.75)	—	464 (3.73)	—
p-$C(CH_3)_3$	H	OH	432 (3.76)	—	468 (3.75)	—
H	H	OCH_3	386 (3.72)	—	486 (4.03)	—
H	H	$OCOCH_3$	373 (3.53)	—	397 (3.51)	—
p-$(CH_3)_3$	H	$OCOCH_3$	376 (3.60)	—	400 (3.59)	—
H	5-$OCOCH_3$	$OCOCH_3$	334 (3.79)	—	470 (3.85)	—
H	2-OH	OH	424 (3.75)	—	475 (3.85)[b]	—
p-$C(CH_3)_3$	2-OH	OH	427 (3.81)	—	479 (3.91)[b]	—
p-$C(CH_3)_3$	2-OCH_3	OH	395 (3.88)	395 (3.88)	—	525 (3.98)
R_1 = NPX[d]	H	H	370	—	468 (4.06)	—
p-$C(CH_3)_3$	2-$NHCOCH(CH_3)_2$	H	—	375 (3.75)	—	546 (3.92)
p-$C(CH_3)_3$	2-$NHCOC_6H_4NO_2$-p	H	371 (3.93)	371 (3.93)	546 (4.04)	546 (4.04)
p-$C(CH_3)_3$	2-NHCOC $(CH_3) = CH_2$	H	—	372 (3.82)	—	541 (3.82)
p-$C(CH_3)_3$	8-$NHCOCH_3$	H	416 (3.84)	—	556 (3.56)[b]	—
p-$C(CH_3)_3$	8-$NHCOC_6H_5$	H	421 (3.88)	—	566 (3.53)[b]	—
p-$C(CH_3)_3$	2-OH	H	3.69 (3.74)	—	389 (3.82), 532 (3.83)	—
p-$C(CH_3)_3$	2-OCH_3	H	374 (3.68)	—	506 (3.64)	—
p-$C(CH_3)_3$	2-$OCOCH_3$	H	326 (3.65)	—	483 (3.79)	—
p-$C(CH_3)_3$	H	OCH_3	390 (3.74)	—	490 (3.90)	—
H	H	OC_6H_5	384	—	434	—
H	5-OH	H	373 (3.71)	—	477 (3.79)[b]	—
H	5-OCH_3	H	375 (3.75)	—	479	—
H	5-OC_6H_5	H	370	—	480	—
H	8-OH	H	415 (3.89)	—	[c]	—
H	8-$OCOCH_3$	H	351 (3.60)	—	475 (3.64)	—
H	8-OC_6H_5	H	374	—	494	—

[a] Solution in heptene.
[b] Irreversible reaction.
[c] Nonphotochromic compound.
[d] NPX = Naphthoxy.

Table 7.4. Spectral Characteristics of Phenoxyanthraquinones (Type II)[38]



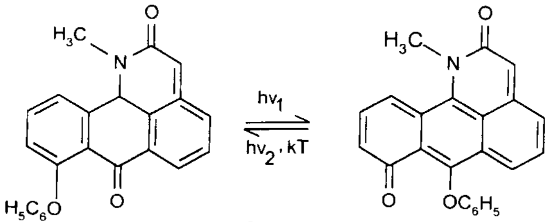
			$\lambda_{max.}$ (nm) (log ε) benzene at 290 K	
R^1	R^2	R^3	IF	PF
$NHCOCH_2Cl$	OC_6H_5	H	419 (3.85)	527
$NHCOCH_2Cl$	H	OC_6H_5	402 (3.90)	510
$NHCOCH_2CH_3$	H	OC_6H_5	366 (4.01)	[a]

[a] Nonphotochromic compound.

The important disadvantage of photochromic aryloxyanthraquinones is their photodegradation as a result of the interaction of photoproducts with a trace amount of water. This is a consequence of the unusually high reactivity of ana anthraquinones with respect to nucleophilic reagents.

7.3.2.4. Anthrapyridones and Anthrapyridines

Photochromic transformations that are similar to these of the above anthraquinones are also characteristic for anthrapyridones[37–39] and anthrapyridines.[37,39] The character of spectral changes (Table 7.5) and the similarity of photochromic transformations to the conversion processes for the acyl derivatives of 1-phenoxy-4-aminoanthraquinone suggest an analogous mechanism for 6-phenoxy-*N*-methylanthrapyridone (IIB1) (Scheme 17).[37] Anthrapyridones of another type (IIB2) show similar photochromic properties.[38]



Scheme 17

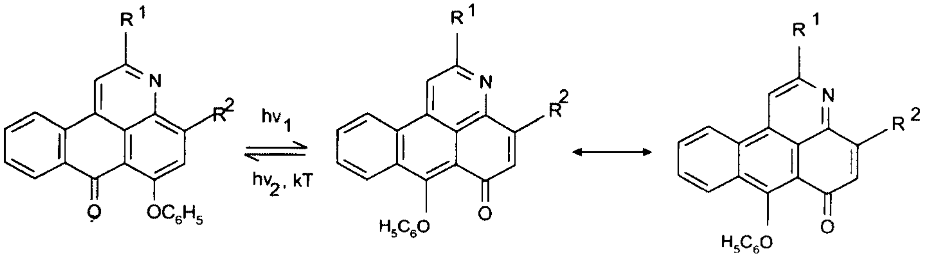
The character and reversibility of the spectral changes of IIC anthrapyridines (Table 7.6)[37,39] suggest a similar photochromism caused by the photoinduced arylotropy (Scheme 18).

Table 7.5. Spectral Characteristics of Photochromic Anthrapyridones (Type IIB_1 and IIB_2)[37–39]

			$\lambda_{max.}$ (nm) (log ε) toluene at 290 K	
R^1	R^2	R^3	IF	PF
CH_3	OC_6H_5	H	415 (3.85), 434 (3.85)	531,572 (B_1)
H	OC_6H_5	H	418 (3.73)	557 (B_2)
H	H	OC_6H_5	367(4.04)	507 (B_2)

Table 7.6. Spectral Characteristics of Photochromic Anthrapyridines (Type IIC)[37,39]

				$\lambda_{max.}$ (nm) (log ε) toluene at 290 K	
R^1	R^2	R^3	R^4	IF	PF
Cl	H	OC_6H_5	H	384 (4.01)	422
Cl	H	H	OC_6H_5	384 (4.07)	532
OCH_3	CH_3	OC_6H_5	H	396 (4.02)	424



Scheme 18

Anthrapyridine (IIC, $R^1 = OCH_3$, $R^2 = CH_3$) manifests photochromic transformations in chloroform and ethanol, in contrast to the phenoxy derivatives of anthrapyridone.[39] This difference is associated with effective photoinduced phototropic transformations of anthraquinones in methanol to the lactime form (Scheme 18), which is rapidly isomerized to the initial compound.

Photochromism of 2-chloro-6-phenoxy- and 2-chloro-8-phenoxyanthrapyridines indicates that the presence of the fixed quinone structure is not needed for the existence of the photoinduced arylotropy of these compounds.[38]

7.3.2.5. Pyrazoloanthrones

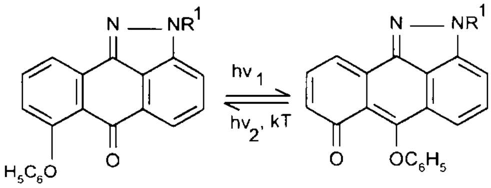
The phenomenon of photodinduced arylotropy is extended to periphenoxy derivatives of pyrazoloanthrones that have the quinone-imine structure (Scheme 19).[41,42]

Table 7.7. Spectral Characteristics of Pyrazolanthrones (Type IID)[41,42]

			λ_{max} (nm) (log ε) toluene at 290 K	
R^1	R^2	R^3	IF	PF
H	H	OC_6H_5	337 (3.42), 400 (4.03).	561
H	OC_6H_5	H	345 (3.78), 398 (3.88)	[b]
$COCH_3$	H	OC_6H_5	346sh (3.89), 368sh (4.15), 382 (4.19)	526
$COCH_3$	OC_6H_5	H	345 (3.93), 365sh (4.02), 382 (4.12)	409, 440[a]
C_4H_9	OC_6H_5	H	346 (3.86), 405 (4.04), 424 (4.06)	459[a]
C_4H_9	H	OC_6H_5	341 (3.60), 402sh (4.13), 420 (4.16)	577

[a] Irreversible reaction.
[b] Nonphotochromic compound.

Among the synthesized pyrazoloanthrones, the compounds with phenoxy groups in 5 - and 7-positions are light-sensitive compounds, but photochromic transformations are observed for 7-phenoxy derivatives of pyrazoloanthrone only (Table 7.7).

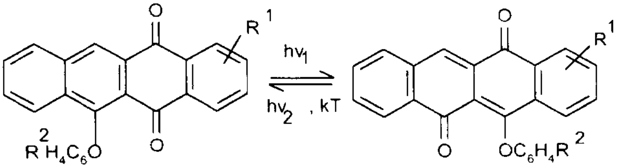


Scheme 19

7.3.3. Photochromism of Naphthacenequinones

7.3.3.1. Aryloxynaphthacenequinones

Unlike phenoxyanthraquinones, the photochromism of phenoxynaphthacenequinones is characterized by a long lifetime of the photoinduced ana form. This property allows one to perform a more detailed study of the mechanism of the photochromic transformations (Scheme 20).[5]



Scheme 20

One can see from Tables 7.8 and 7.9 that among these compounds, 11-hydroxy and 11-acetoxy derivatives of phenoxynaphthacenequinone do not exhibit photo-

Table 7.8. Spectral Characteristics of Phenoxynaphthacenequinones [Type IIIA (11-phenoxy-), $R^2 =$ H][46]

	λ_{max} (nm), (lg ε), toluene at 290 K	
R^1	IF	PF
H	400 (3.78)	480 (4.23)
6-Cl	398 (3.74)	444 (4.20), 472 (4.21)
6-NH$_2$	389 (3.55), 468 (3.99)	474 (4.05), 503 (4.24), 538 (4.17)
6-NHCH$_3$	402 (3.73), 502 (4.09)	524 (4.15), 559 (4.07)
6-N(CH$_3$)$_2$	408 (3.78), 465 (3.60)	[a]
6-NHC$_6$H$_5$	404 (3.84), 496 (3.95)	525 (3.94), 558 (3.86)
6-NHTs	422 (3.77)	509
6-NHCOCH$_3$	429 (3.87)	504 (4.20)
6-N(CH$_3$)COCH$_3$	396 (3.85)	448 (4.19), 476 (4.20)
6-NHSO$_3$C$_7$H$_7$	422	509
6-NO$_2$	394 (3.70)	453 (4.15), 479 (4.13)
6-OH	443 (4.00)	[a]
6-OCH$_3$	400 (3.82)	447 (4.16), 469 (4.16)
6-OC$_6$H$_5$	404	472
6-OCOCH$_3$	396 (3.89)	[a]

[a] Nonphotochromic compound, Ts = tosyl.

Table 7.9. Spectral Characteristics of Phenoxynaphthacenequinones [Type IIIA(11-phenoxy-), IIIB (6-phenoxy-)][43,52]

		λ_{max}(nm) (log ε), toluene at 290 K		
R^1	R^2	IF	PF	Type
H	*p*-NHC$_6$H$_5$	396 (3.81)	476 (4.26)	(B)
H	*p*-OH	400 (3.72)	480 (4.23)	(B)
H	*p*-OCH$_3$	400 (3.76)	480 (4.20)	(B)
H	2,4,6-(CH$_3$)$_3$	410 (3.83)	498 (4.40)	(B)
H	*p*-COCH$_3$	400 (3.78)	480 (4.26)	(B)
H	*p*-NO$_2$	395 (3.78)	480 (4.20)	(B)
H	C(CH$_3$)$_2$C$_6$H$_5$OH	291 (4.33), 396 (3.80)(DMSO)	276 (4.33), 453 (4.21), 482 (4.21) (DMSO)	(B)
H	N=N-C$_6$H$_5$SO$_3$K	293 (4.38), 352 (4.38) (DMSO)	481 (4.13) (DMSO)	(B)
6-NH$_2$	H	389 (3.55), 468 (3.99)	541	(A)
6-NH$_2$	*p*-CH$_3$	392 (3.66), 475 (4.08)	543	(A)
6-NH$_2$	*p*-C$_2$H$_5$	392 (3.66), 475 (4.08)	543	(A)
6-NH$_2$	*p*-OCH$_3$	393 (3.65), 475 (4.09)	543	(A)
6-NH$_2$	*o*-CH$_3$	392 (3.61), 475 (4.05)	543	(A)
6-NH$_2$	*p*-NHC$_6$H$_5$	392 (3.69), 473 (4.07)	543	(A)
6-NH$_2$	*p*-HO	392 (3.58), 473 (4.01)	543	(A)
6-NH$_2$	*m*-Cl	390 (3.59), 471 (4.07)	541	(A)
6-NH$_2$	*p*-NO$_2$	391 (3.63), 472 (3.98)	543	(A)
6-NH$_2$	α-naphthyl	385 (3.62), 475 (4.15)	[a]	(A)

[a] Nonphotochromic compound.

chromism.[26] The lack of photochromism for these compounds is explained by the similarity of the absorption spectra for initial and photoinduced forms due to thermal migration of the proton and acetyl groups. [8]

Similar to 1-phenoxyanthraquinones, photochromism is absent in 6-dimethylamino and 6-phenylamino derivatives of 11-phenoxy-5,l2-naphthacenequinone. [26] Photochromic properties are absent for 11-phenoxyphenol-6-amino-5,12-naphthacenequinone because of steric hindrances to forming the transient spirocomplex (see Scheme 9) during photochromic transformation of this compound.

To determine the photoinduced structure, the orange crystals that were formed after irradiation of benzene solutions of 6-phenoxy-5,12-naphthacenequinone were used.[46] It turned out that the elemental composition of the photoinduced form coincided with the ana-quinone composition. In addition, the interaction of 6-phenoxy-5,12-naphthacenequinone with ammonia and aniline in benzene resulted in the formation of compounds that were identified as derivatives of ana-naphthacenequinone by the counter synthesis. The ana structure of the photoinduced form was supported by the similarity of the absorption spectrum of the ana form to the spectra of unsubstituted and 5-bromo derivatives of 6,12-naphthacenequinone[46] as well as by the analysis of the IR spectra of initial and photoinduced forms of 6-phenoxy-5,l2-naphthacenequinone. [4]

Photochromic transformations from the para- to ana-quinone structure of these compounds occur through intermediate photoproducts in the triplet state.[51] The experimental evidence of the influence of oxygen in solution and the viscosity of solvents on the lifetime of these photoproducts supports this statement. It was found[50] that both initial and photoinduced forms have lower triplet levels of the $n\pi^*$-type.

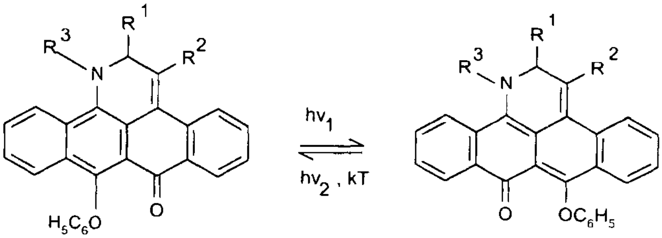
Closer examination of the mechanism of photochromic transformations in phenoxynaphthacenequinones by pica- (25 ps) and nanosecond (8 ns) photoexcitation showed that photoisomerization of these compounds, as in photochromic anthraquinones, is an adiabatic reaction that proceeds through the triplet state of the initial form [54]:

$$\mathrm{A} \xrightarrow{h\nu} \underset{380\ \mathrm{nm}}{\mathrm{A(S_1{}^*)}} \xrightarrow{k_1 = 1.2 \times 10^{10}\ \mathrm{s^{-1}}} \underset{500\ \mathrm{nm}}{\mathrm{A(T)}} \xrightarrow{k_2 = 1.8 \times 10^{8}\ \mathrm{s^{-1}}} \underset{400,\ 460\ \mathrm{nm}}{\mathrm{B(T)}} \xrightarrow{k_3 = 1.6 \times 10^{5}\ \mathrm{s^{-1}}} \underset{490\ \mathrm{nm}}{\mathrm{B}}$$

Based on this mechanism, the distinctions observed between the T–T absorption spectra of the intermediate product and nonphotochromic para-naphthacenequinone[51] with a similar structure were explained by the T–T absorption of the photoinduced ana form of this compound, which is observed after the excitation of a photochromic solution by the laser pulse with a width of 25 ns. However, according to other laser photolysis data for compounds of this type, the intermediate product is a σ -spirocomplex,[60] which was assumed earlier.[5,51]

7.3.3.2. Naphthacenepyridones and Naphthacenepyridines

Photochromism resulting from photoinduced reversible arylotropy (para-ana phototransformations) was observed for the quinonemethide analog of phenoxy-naphthacenequinone (Scheme 21).[37,39]

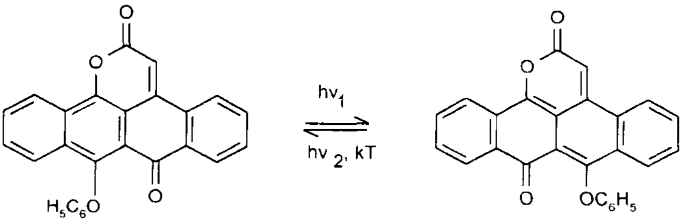


Scheme 21

The proposed mechanism of the photochromic transformations was supported by the character of the spectral changes (Table 7-10) and similarity of the photochromic transformations for these compounds to 11-phenoxy-6-aminonaphthacenequinone.

7.3.3.3. Pyrone

Reversibility of the spectral changes under irradiation and the photostability of the compound without the phenoxy substituent suggested a photochromic para-ana-quinone transformation of 9-phenoxy-pyrone (9-phenoxynaphthacene [12,11-*bc*]-2,8-pyrandione) (Table 7.10, Scheme 22).[48]



Scheme 22

7.3.3.4. Pyrazolonaphthacenones

Photochromic transformations of 8-phenoxy derivatives of pyrazolonaphthacenones[56,57] were similar to phototransformations of the above-described photochromic pyrazoloanthrones (Scheme 23) (Table 7.11). Photochromism of these compounds depends on the character of a substituent in the heterocyclic fragment.

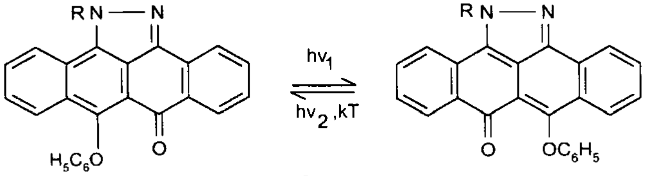
Table 7.10. Spectral Characteristics of Photochromic Naphthacenepyridones (Type IIIC), Naphthacenepyridines (Type III D),[37,39,48] and Pyrone (IIIE)[48]

			λ_{max} (nm) (log ε) toluene at 290 K		
R^1	R^2	R^3	IF	PF	Type
—	H	CH_3	436 (3.84), 461 (3.82)	513, 544	(C)
—	OC_6H_5	CH_3	434 (3.97), 455 (3.98)	505 sh, 542	(C)
—	C_6H_5NCl	CH_3	453sh (3.98), 472 (4.04) (ethanol)	485, 513	(C)
—	Cl	CH_3	440 (3.94), 460 (3.93)	505, 537	(C)
—	H	H	425 (3.90), 452 (3.81)	500	(C)
—	$COCH_3$	H	433 (3.92), 454 (3.82)	520	(C)
OCH_3	H	—	400 (3.98), 422 (4.29)	443	(D)
OCH_3	$COCH_3$	—	425 (3.16)	440	(D)
—	—	—	425 (3.92), 448 (3.86)	494, 532	(E)

Table 7.11. Spectral Characteristics of Pyrazolonaphthacenones (Type IIIF)[56,57]

			λ_{max} (nm) (log ε) toluene at 290 K	
R^1	R^2	R^3	IF	PF
H	H	OC_6H_5	361sh (4.01), 380 (4.07), 400 (4.07)	450[a]
$COCH_3$	H	OC_6H_5	361sh (4.01), 380 (4.07), 400 (4.07)	455
C_4H_9	H	OC_6H_5	409sh (3.97), 428 (4.01) (chloroform)	447

[a] Irreversible reaction.

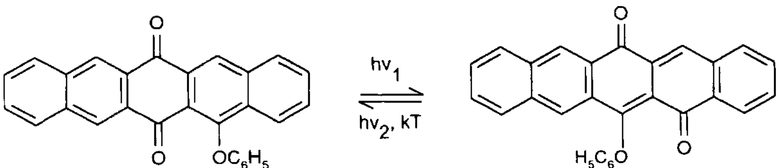


Scheme 23

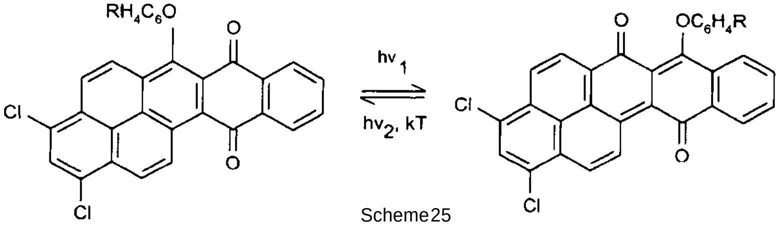
7.3.4. Photochromism of Phenoxypentacenequinone and Derivatives of Phthaloylpyrene

5-Phenoxy-6, 13-pentacenequinone[57] exhibits reversible photoinduced para-ana-quinone transformations (Scheme 24).

It turned out that formerly synthesized[58] 1,3-dichloro-6-phenoxy-7,12-phthaloylpyrene exhibited photochromic transformations in aprotic solvents (Scheme



Scheme 24



Scheme 25

25).[59] As for phenoxyanthraquinones and phenoxynaphthacenequinones, the intensity of the valence vibrations of the carbonyl group in IR spectra decreased and a new band appeared in the low-frequency region.[59]

The structural similarity of derivatives of phenoxynaphthacenequinone and phenoxyphthaloylpyrene and the photoinduced changes of absorption (Table 7.12) and IR spectra suggest an identical mechanism for photochromic transformations.

Analysis of experimental and theoretical data on quinone photochromism shows that their photochromic transformations are caused by photoinduced para-ana-quinone reconstruction of molecules. Photochromic changes involve triplet states of the initial and photoinduced forms and, probably, the intermediate σ-spirocomplex.

Table 7.12. Spectral Characteristics of Phenoxyphthaloylpyrenes (Type V)[59]

		λ_{max} (nm) (log ε) toluene at 290 K	
R^1	$R^2 = R^3$	IF	PF
H	H	476	604, 652
2-Cl	Cl	480	608, 658
2-CH_3	Cl	480	610, 662
2-OCH_3	Cl	484	610, 662
2,4,6-$(CH_3)_3$	Cl	494	615, 664
4-Br	Cl	480	612, 662
4-OC_2H_5	Cl	483	612, 662
4-$OC_6H_4NH_2$	Cl	480	610, 660
4-NO_2	Cl	480	610, 666

7.4. PHOTOCHROMIC BEHAVIOR OF QUINONES

7.4.1. Spectral Characteristics

Absorption spectra of the initial and photoinduced forms of 5-methyl-1,4-naphthaquinone are presented in Figure 7.2.[11] The experimental data are in good agreement with the prediction of quantum-chemical calculations.[11] Flash photolysis studies showed the dependence of the location of the absorption band maximum of the photoinduced form on the nature of the solvent.[11] A photoinduced absorption band with λ_{max}= 550 nm in nonpolar solvents shows a red shift in polar solvents (λ_{max} = 580 nm).

Photoinduced forms of all derivatives of 1-methyl-9,10-anthraquinones studied (Table 7.1) exhibited a long-wavelength absorption band located, as a rule, in the 580–600 nm range.[17,18,26,36] Compounds with phenyl groups in 1-alkyl-substituted and 4-piperidino-1-methyl-9,10-anthraquinone (Figure 7.3) were characterized by a red shift of the absorption band (617–635 nm).[26,36] The absorption band of the photoinduced form of 4-oxy-derivatives of 1-methyl-9,10-anthraquinone was shifted to the blue region to 472–478 nm.

The spectral characteristics of acyloxyquinones (Figure 7.4, Table 7.2) indicated that the positions of the absorption bands of both initial and photoinduced forms of derivatives of 1-acetoxy-9,10-anthraquinone depended on the nature of the substituents in the anthraquinone cycle. Photoinduced forms of 9-acetoxy-1,4-anthraquinones showed the shortest wavelength absorption bands.

The spectral characteristics of anthraquinones with migrating oxy groups of different types are virtually identical.[25,28]

All substituted phenoxyanthraquinones synthesized were characterized by photoinduced absorption bands that were red shifted by 5–150 nm compared with the unsubstituted phenoxyanthraquinones (Table 7.3, Figure 7.5). As a rule, the

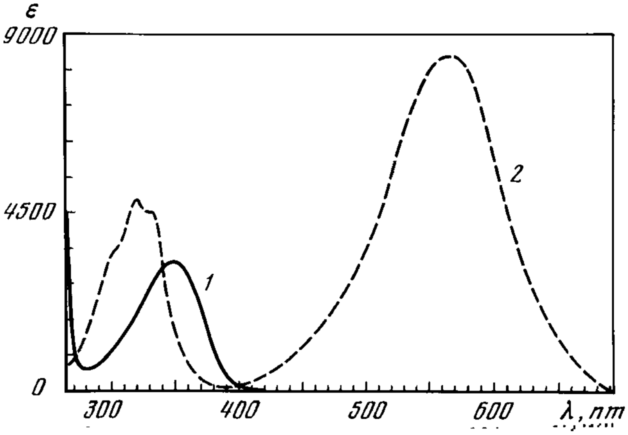


Figure 7.2. Absorption spectra of 5-methyl-1,4-naphthaquinone in ethanol–methanol glass at 77 K[11] before (1) and after (2) UV irradiation.

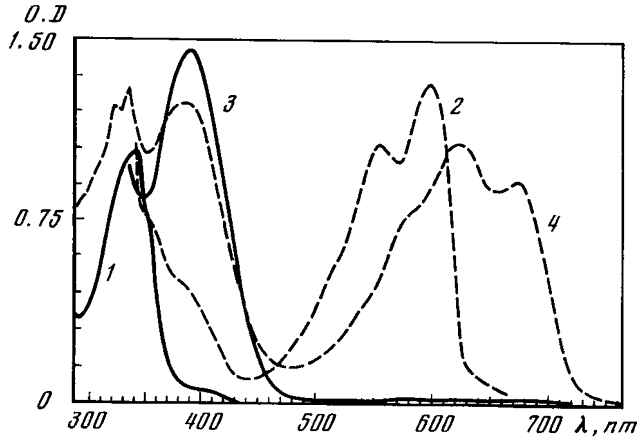


Figure 7.3. Absorption spectra of 1-methylanthraquinone in ethanol matrix at 77 K (C = 4.6 × 10^{-4} mol/liter) (1, 2)[16] and 1-phenylcyanomethyl-4-methoxy-9,10-anthraquinone in *tert*-butanol (C = 2.25 × 10^{-4} mol/liter) without oxygen at 290 K (3, 4)[36] before (1, 3) and after (2, 4) UV irradiation.

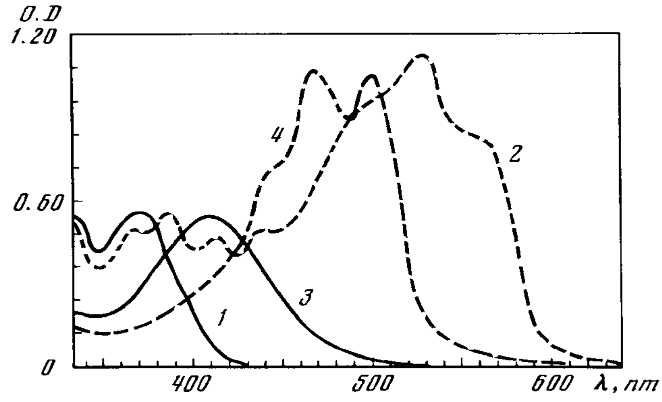


Figure 7.4. Absorption spectra of 1-acetoxy-2-methoxy-9,10-anthraquinone (1, 2)[28] and 9-acetoxy- 1,4-anthraquinone in ethanol at 77 K (3, 4)[34] before (1, 3) and after (2, 4) UV irradiation.

absorption bands of the initial form were also shifted to the visible spectral region. One can see from Table 7.3 that a number of derivatives, especially with hydroxyl and acetyl substituents in the 4-position, were characterized by a blue shift of the photoinduced absorption bands. Replacement of the phenoxy group by a naphthoxy group did not change the spectral characteristics of the initial and photoinduced forms.[32]

The spectral characteristics of 1-chloro-acetylamino-4-phenoxy- and 1-chloro-acetylamino-5phenoxyanthraquinones (Table 7.4) were similar to those of 5-amino derivatives of 1-phenoxyanthraquinone (Table 7.3).

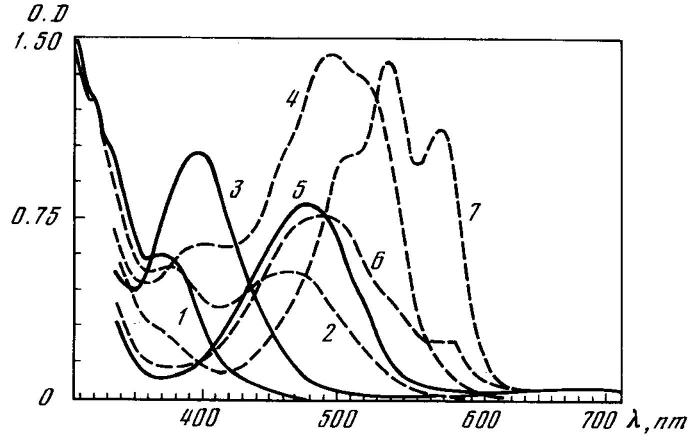


Figure 7.5. Absorption spectra of 1-(1-naphthoxy)-anthraquinone in benzene (C = 2×10^{-4} mol/liter) (1, 2),[32] 1-phenoxy-4-methoxyanthraquinone in benzene (C = 1×10^{-4} mol/liter) (3, 4)[19] and 1-phenoxy-4-aminoanthraquinone (5-7)[15] before (1, 3, 5) and after (2, 4, 6) UV irradiation as well as absorption spectrum of the ana form for 1-phenoxy-4-aminoanthraquinone (7).

The spectral characteristics of photochromic anthrapyridones (Table 7.5) and anthrapyridines (Table 7.6) depended on the compound structure.[38] The photoinduced forms of 6-phenoxy derivatives of anthrapyridone and 2-methoxy-4-methyl-6-phenoxyanthrapyridine were distinct. The absorption band of the latter compound is shifted to the blue (Figure 7.6) The reason is that the photoinduced ana form of this compound exists largely in the form of quinoneimines.[38,39] Spectral characteristics of photochromic pyrazoloanthrones (Figure 7.7) also depended on the compound structure.[41,42] Table 7.7 shows that 7-phenoxy derivatives of pyrazolan-

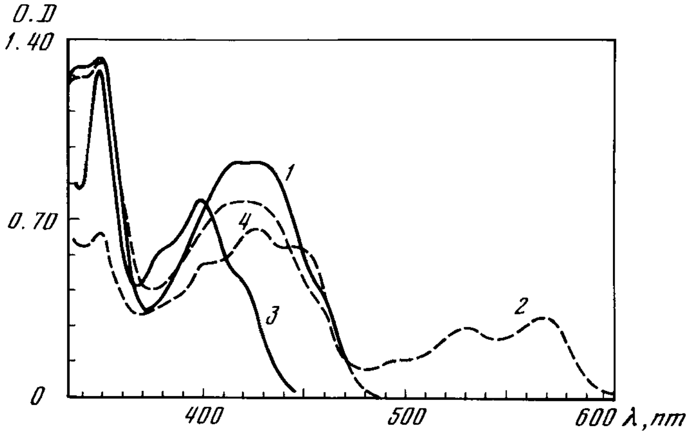


Figure 7.6. Absorption spectra of 6-phenoxy-*N*-methylanthrapyridone in toluene (C = 1.53×10^{-4} mol/liter) (1, 2)[37] and 2-methoxy-4-methyl-6-phenoxyanthrapyridine in toluene (C = 4.36×10^{-5} mol/liter) (3, 4)[39] before (1,3) and after (2, 4) UV irradiation.

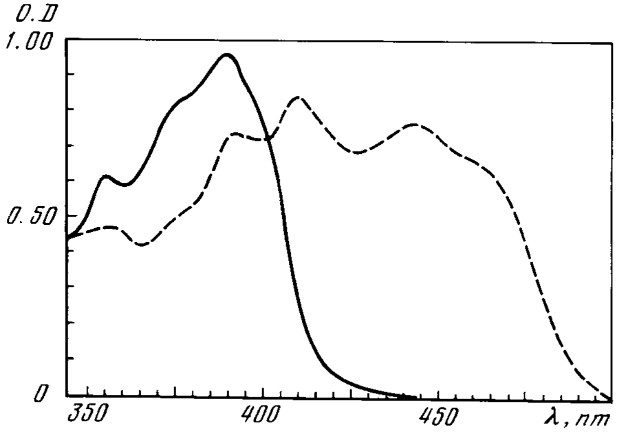


Figure 7.7. Absorption spectra of 2-acetyl-5 phenoxypyrazoloanthrone in toluene (C = 7.338 × 10^{-5} mol/liter)[41] before (1) and after (2) irradiation.

throne were characterized by longer wavelength absorption bands of the photoinduced ana form compared with 5-phenoxy derivatives of this compound.

Unsubstituted phenoxynaphthacenequinone is characterized by the absorption bands of the paraquinoid form in the UV spectral region and the ana form in the visible spectral range (Figure 7.8).

One can see from Table 7.8 that there was a distinct dependence of the maxima of the initial and photoinduced forms on the nature of the substituent in the naphthacenequinone ring. Note that the absorption spectra of 11-phenoxynaphthacene-5,12-quinones and nonphotochromic para-quinone without the phenoxy group were quite similar.[46] The linear correlation (r = 0.992) between the position of the

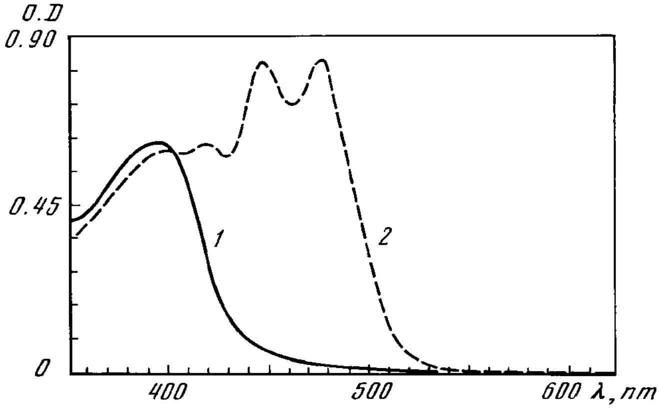


Figure 7.8. Absorption spectra of 6-phenoxy-5,12-naphthacenequinone in toluene (C = 1.02 × 10^{-4} mol/liter)[43] before (1) and after (2) irradiation (λ_{exc} = 405 nm).

maxima of the long-wavelength absorption bands of para- and ana-quinones was found by the method of proportional response.[46]

The positions of the absorption bands of the initial and photoinduced forms did not change for phenoxynaphthacenequinones that are bonded to acrylic, styrene, and siloxane polymer chains.[53]

Table 7.9 shows that the positions of the long-wavelength absorption bands were virtually independent of the substituent nature in the phenyl ring of the phenoxy group for the photochromic compounds without and with 6-amino substituents in a naphthacenequinone nucleus.[43,52] However, the introduction of 6-amino substituents resulted in the shift of the absorption bands of the initial and photoinduced forms to the visible spectral range (Table 7.9) and their substantial overlapping (Figure 7.9).

The luminescence observed was associated with the photodegradation products rather than with the photoinduced ana form.[54] The luminescence spectrum coincided with the luminescence spectrum of 11-hydroxy-5,12-naphthacenequinone.[50]

The spectral characteristics of photochromic naphthacenepyridones in solution (Table 7.10, Figure 7.10) were similar to those for acyl derivatives of 1-phenoxy-4-aminoanthraquinone and 11-phenoxy-6-aminonaphthacenequinone.[37]

Note that the shape of the absorption spectra of phenoxynaphthacenepyridones depended on the solvent, which is assignable to the lactame–lactime tautomerism.[39] In this case, the equilibrium position depended on the solvent nature. Polar solvents shifted the equilibrium to the lactime form.

The absorption bands of the photoinduced ana form of phenoxynaphthacene-pyridines were shifted to the blue compared with the corresponding absorption bands of phenoxynaphthacenepyridones. This was explained by the fact that these compounds have the quinone-imine form.[39]

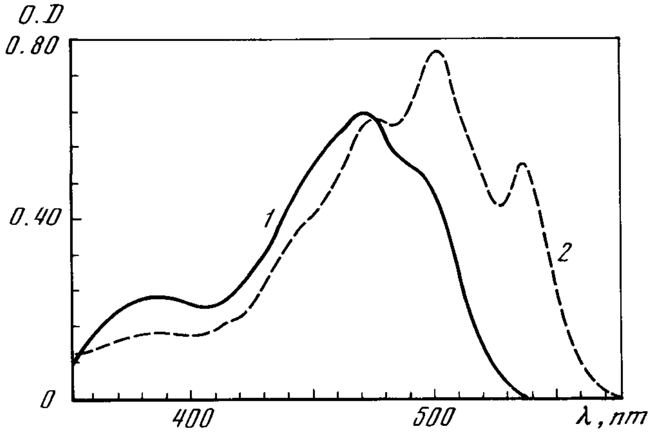


Figure 7.9. Absorption spectra of 6-amino-11-(4-methylphenoxy)-5, 12-naphthacenequinone in toluene ($C = 5.28 \times 10^{-5}$ mol/liter)[52] before (1) and after (2) UV irradiation.

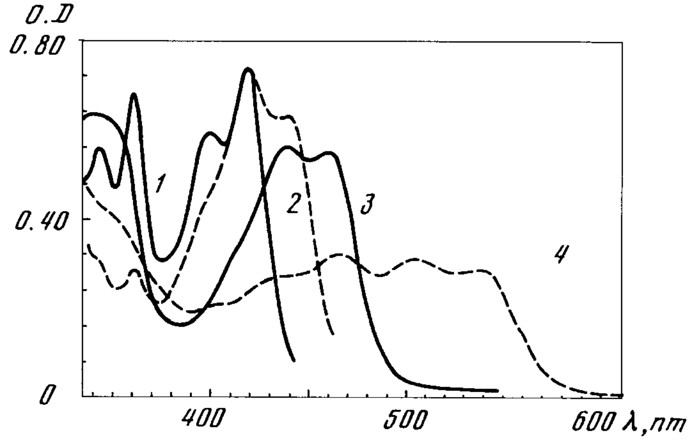


Figure 7.10. Absorption spectra of 2-methoxy-9-phenoxy 2*H*, 8*H*-naphtha [1,. 2, 3-*dc*[benz][*h*]-8-quinoline in toluene (C = 4.66 × 10^{-5} mol/liter) (1, 2)[39] and 2*H*, 8*H*-1-methyl-3-chloro-9 phenoxy-naphthaceno [12, 11-*bc*] pyridine-2,8-dione in toluene (C = 6.59 × 10^{-5} mol/liter) (3, 4)[37] before (1, 3) and after (2, 4) UV irradiation.

The absorption spectra of the initial and photoinduced forms of 9-phenoxynaphthaceno[12,11- *bc*]-2,8-pyrandione (Table 7.10, Figure 7.11) were similar to those of phenoxynaphthacenepyridones.[48]

Phenoxy derivatives of pyrazolonaphthacenone were characterized by the photoinduced absorption band with a maximum at 450 mm (Figure 7.12,[56] Table 7.11), which was unchanged for substituted derivatives.

Absorption bands of the initial and photoinduced forms of 6-phenoxy-5,13-pentacenequinone (Figure 7.13) were slightly shifted (by 10 nm) to the red compared with 11-phenoxy-5,12-naphthacenequinone.[57]

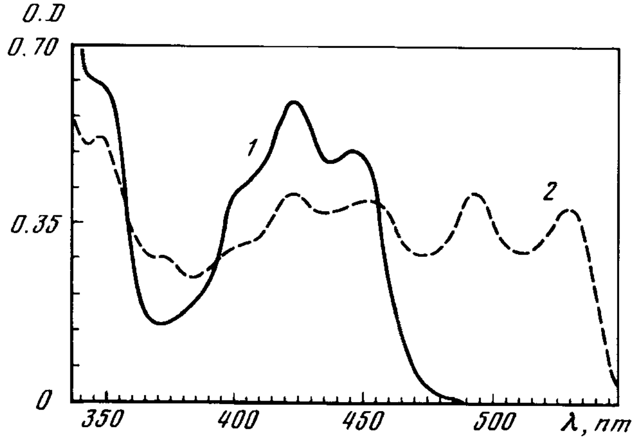


Figure 7.11. Absorption spectra of 9-phenoxynaphthacenopyrone in toluene (C = 6.97 × 10^{-5} mol/liter)[7] before (1) and after (2) UV irradiation.

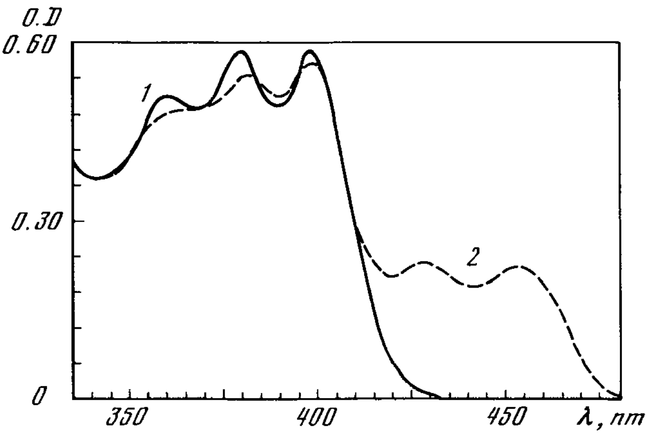


Figure 7.12. Absorption spectra of 1-acetyl-8-phenoxypyrazolonaphthacenone in toluene (C = 5.77 × 10^{-5} mol/liter)[56] before (1) and after (2) UV irradiation.

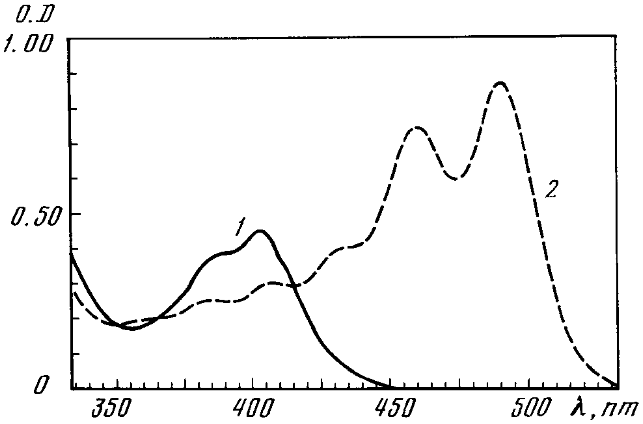


Figure 7.13. Absorption spectra of 5-phenoxy-6,13-pentacenequinone in toluene (C = 1 × 10^{-4} mol/liter)[57] before (1) and after (2) UV irradiation.

In the case of the phthaloylpyrene derivatives, a greater bathochromic shift of both absorption bands was observed (Figure 7.14, Table 7.12). This shift was caused by the formation of pyrenquinone methide.[59]

Analysis of the spectral characteristics of photochromic quinones showed that the absorption band of the photoinduced form strongly depended on the compound structure. The substituents in the quinone nucleus most strongly affected the spectral characteristics of the photoinduced form.

In relation to the perspective of application of photochromic quinones in optical recording media, the spectral characteristics of the photoinduced form for phenox-

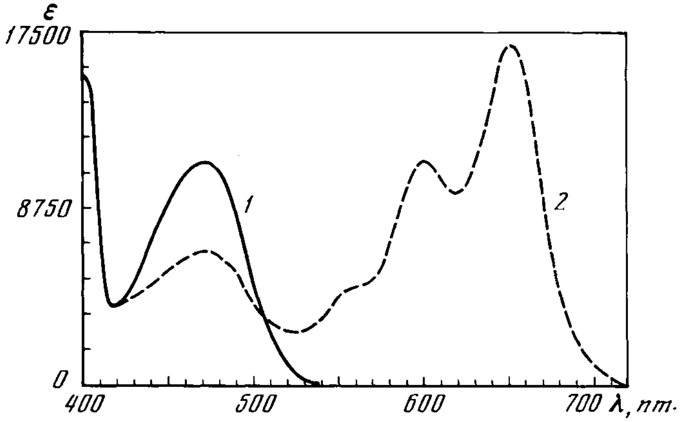


Figure 7.14. Absorption spectra of 1,3-dichloro-6-phenoxy-7,12-phthaloylpyrene in chlorobenzene[59] before (1) and after (2) irradiation.

yphthaloylpyrenes have attracted considerable interest. These compounds are characterized by the longest wavelength absorption bands of the photoinduced form. This fact indicates the possibility of using semiconductor lasers to record optical information via photochromic media based on photochromic phthaloylpyrenes.

7.4.2. Kinetic Characteristics

7.4.2.1. Methylnaphthoquinone

Quantum yields of the product of photoenolization (4-hydroxy-5-methylidene-1(5*H*)-naphthalenone) approached $\varphi = 1.0$ for all solvents.[11]

The thermal bleaching rate of the photoinduced form of 5-methyl-1,4-naphthaquinone depended on the solvent polarity (Table 7.13).[11] It was assumed[11] that an

Table 7.13. Lifetime of Photoinduced 4-Hydroxy-5-Methylidene-1(5*H*)-Naphthalenone in Various Solvents[41]

Aprotic solvents	τ (s)	Protic solvents	τ (s)
Cyclohexane	8×10^{-6}	Ethanol abs.	8×10^{-4}
Benzene	4×10^{-5}	Acetonitrile + 1% water	8×10^{-4}
Diethyl ether	2×10^{-3}	Acetonitrile + 30% water	1.3×10^{-3}
Acetonitrile	3×10^{-3}	Acetic acid	2.6×10^{-5}
Tetrahydrofuran	7×10^{-3}		
Dimethyl sulfoxide	1.1×10^{-2}		
Hexamethyl phosphoric acid triamide, deaerated	9×10^{-2}		

increase in the lifetime of the photoinduced form by several orders of magnitude when passing from a hydrocarbon solvent to a solvent that forms a hydrogen bond with solute molecules was caused by solvation of the enolic proton.

7.4.2.2 Derivatives of Anthraquinone

One can see from Table 7.1 that the quantum yield of photolysis of alkyl-substituted anthraquinones only slightly depended on the replacement of the methyl group by the ethyl or isopropyl group.[26] However, it decreased drastically after the introduction of electron-donor substituents in 3- or 4-positions of the anthraquinone ring.[17] Quantum yields of phototransformations of 1-arylcyanomethyl-9,10-anthraquinones were found to be substantially lower (by two orders of magnitude) than for 1-methylanthraquinone.[36]

The lifetime of the photoinduced form for a number of these compounds lay in the microsecond range except for those of 1-arylcyanomethyl-9,10-anthraquinones[36] and 1-methyl-4-oxy-9,10-anthraquinone.[17] The lifetime of the photoinduced form for these compounds amounted to several minutes. The enhanced stability of the photoinduced form of 1-phenylcyanomethyl-4-methoxy-9,10-anthraquinone was responsible for a number of irreversible photochemical transformations of this compound.

The substituents in the anthraquinone ring affected the rate constant of thermal bleaching of derivatives of 1-methylphenoxyanthraquinone (Table 7.1).[17,18,26] The substituents that increased the π-electron density on the hydrogen atom of the methide group decreased the lifetime of the photoinduced form (Table 7.1).[18,26] The introduction of methoxy and piperidine substituents stabilized the photoinduced form (Table 7.1).

Studies of the dependence of the lifetime of the photoinduced form on the type of substituent in the 1-position of the anthraquinone ring showed that some photochromic derivatives yielded two photoproducts. The kinetics of their thermal bleaching were characterized by two exponentials (Table 7.1). The lifetimes of these photoproducts differed by an order of magnitude. These results were explained by the formation of two rotational isomers under irradiation that were characterized by virtually coincident absorption spectra.[26] The difference in the lifetimes of the photoinduced forms in compounds with substituents $R^1 = CH_3$ and $R^1 = CH_2CH_3$ (for the short-lived isomer) was caused by the electronic effect of the methyl group. This group displaces the π-electron density from the carbon atom to the molecular π system, resulting in an increase in the thermal resistance of the photoinduced form. The coincidence of lifetimes of photoinduced forms in compounds with substituents $R^1 = CH(CH_3)_2$ and $R^1 = CH_2CH_3$ (for the long-lived isomer) (Table 7.1) indicated the effect of steric factors on the rate of thermal bleaching. The activation energies of thermal reaction were identical within the accuracy of the measurement (Table 7.1). The 20-fold difference in the lifetimes of the photoinduced forms in compounds with substituents $R^1 = CH_3$ and $R^1 = CH_2CH_3$ (for the long-lived isomer) was mainly caused by the difference in the activation energies. This means that thermal

Table 7.14. Kinetic Characteristics of 1-Methyl-4-Oxy-9,10-Anthraquinone in Different Solvents[18]

Solvent	k (s^{-1}) photocoloration	*k* (298 K (s^{-1}) thermal bleaching	*E* (kcal/mol)
Isopropanol	5.1×10^{10}	1.8×10^{-2}	17.1 ± 0.5
Isobutanol	7.4×10^{10}	2.5×10^{-2}	17.1 ± 0.5
Acetone	3.7×10^{10}	3.7×10^{-2}	16.4 ± 0.5
Pyridine	6.2×10^{8}	8.6×10^{-2}	13.5 ± 0.5
Ethylacetate	1.6×10^{9}	9.8×10^{-2}	14.0 ± 0.5
Benzene	9.6×10^{8}	5.45	11.4 ± 0.5
Heptane	2.9×10^{8}	10.5	10.1 ± 0.5

migration of the hydrogen atom is affected by the steric hindrance rather than by the preexponential factors.[26]

The rate constant of thermal bleaching of derivatives of 1-methylanthraquinone depended on the nature of the solvent. Table 7.14[18] shows that it decreased by several orders or magnitude as the proton-donor ability increased.

Quantum yields of photoproduction of ana-quinones of acetoxy-substituted anthraquinones with amino substituents in the anthraquinone ring as well as with an acetyl group proved to be the lowest (Table 7.2)[28,42] As in the case of photochromic alkylanthraquinones, the reverse photoreaction, from ana-quinone to para-quinone for derivatives of acetoxyanthraquinone, proved to be impossible.[21] The transition from ana-quinone to para-quinone occurred during freezing out of a sample owing to thermal bleaching.

The kinetics of reverse dark migration of the acetyl group after pulse photoexcitation of solutions at 290 K was described by a first-order equation. The rate constant and activation energy were virtually independent of the type of solvent (Table 7.2).[33,42] However, these parameters depended on the compound's structure.[28] One can see from Table 7.2 that the rate constants for 1-acetoxy-9,10- and 9-acetoxy-1,4-anthraquinones were substantially different. The substituents in the anthraquinone ring have less of an effect. The difference observed between the rate constants was due to the difference in reaction enthalpies for photochromic derivatives 9,10- and 1,4-anthraquinones.[28]

The structure of the migratory group substantially affected the rate of the acetyl group migration (Table 7.2).[28,33] The introduction of electron-donor substituents in the migratory group resulted in a decrease in the rate constant of thermal bleaching. Replacing the methyl group by a diethylamino group resulted in a decrease in the rate constant by five orders of magnitude.[28]

Note that the introduction of electron-donor substituents in the migratory group led to a strong decrease not only in the rate of the thermal reaction but also in the rate of the photochemical processes of the acyl group migration.[33]

Unlike derivatives of acetoanthraquinone, 1-phenoxy-4-acetoxy-9,10-anthraquinone exhibited photochromic transformations under irradiation that was absorbed both by the initial form and photoinduced forms.[22] This effect was caused by the photoinduced transfer of phenyl and acetyl groups sequentially. It has been found that migration of the phenyl group in 1-phenoxy-4-acetoxy-9,10-anthraquinone under irradiation was followed by thermal migration of the acetyl group. In the case of 9-phenoxy-10 acetoxy-1,4-anthraquinone at the first stage, the photoinduced transfer of the acetyl group was observed. The phenyl group migrated during the second thermal stage.

The study of the efficiency of photochromic transformations for a series of aryloxy-substituted anthraquinones in polymer matrices showed that the quantum yields of phototransformations in a polymer were large and somewhat dependent on the compound's structure (Table 7.15).[29]

The efficiency of photocoloration of these compounds was found to be characterized by a small temperature dependence. The activation energy for this process depended on the compound's structure and varied from 0.5 to 8.82 kcal/mol (Table 7.15).[29]

The efficiency of the photocoloring process for 1-phenoxy-4-aminoanthraquinones in solution decreased as the electron-donor ability of substituents increased.[14]

A comparison of the quantum yields of the photoinduced form for 1-phenoxy- and 1-naphthoxy-9,10-anthraquinones[31,32] showed that the value of the quantum yield for the second compound ($\varphi = 0.05$) was smaller than that for the first compound by a factor of 4. It was suggested that this distinct effect is related to the influence of the steric factor on the photoinduced process of the aryl group transfer.

Data on the lifetime of the photoinduced form for aryloxyanthraquinones are very scarce, which is probably explained by the high efficiency of the irreversible chemical transformations of the ana form.

The rate constant of the dark bleaching resulting from the thermal migration of the aryl group and the activation energy depended on the structure of the photochromic compounds.

All photochromic anthrapyridones and anthrapyridines were characterized by a reversible change of their spectra under UV and visible light, but the kinetic processes have not been investigated. Kinetic data are lacking at present.

Table 7.15. Kinetic Characteristics for Processes of Photocoloration and Thermal Bleaching of 1-Aryloxyanthraquinones ($R^1 = OC_6H_4R', R^3 = H$) in Polymeric Matrix at 290 K (Type II)[27]

R^1	R^2	φ_B $\lambda_{exc} = 365$ nm	E_{ph} (kcal/mol) photocoloration	$k \times 10^3$ (s^{-1})	E_a (kcal/mol) thermal bleaching
H	H	0.67	6.74	0.45	11.99
t-C(CH$_3$)$_3$	2-NHCOCH$_3$	0.21	8.82	0.011	20.49
t-C(CH$_3$)$_3$	2-NHCOCH(CH$_3$)$_2$	0.67	2.01	0.015	21.32
t-C(CH$_3$)$_3$	2-NHCOC$_6$H$_5$	0.53	4.73	0.025	29.11
t-C(CH$_3$)$_3$	2-NHCOC$_6$H$_4$NO$_2$-p	0.74	2.19	0.064	18.04
t-C(CH$_3$)$_3$	2-NHCOC$_6$H$_5$	0.54	0.50	0.020	25.23
t-C(CH$_3$)$_3$	2-NHCOCF$_3$	0.28	8.66	0.24	19.93
t-C(CH$_3$)$_3$	2-NHCOC$_6$H$_5$	0.54	0.72	0.026	29.0

As in the case of the photochromic quinones discussed earlier, the kinetics of the photochromic transformations for phenoxypyrazoloanthrones were determined by the irradiation intensity that activated the initial or photoinduced form.[41,42]

7.4.2.3. Derivatives of Naphthacenequinone

A comparative study of the efficiency of the photochromic transformations for a series of 6-acetyl-amino-11-naphthacene-5,12-quinones (Table 7.8) showed that, as for 4 derivatives of 1-phenoxyanthraquinone, the light sensitivity of these compounds decreased with the increasing electron-donor capacity of substituents.[46]

The presence of the electron-donor substituents in the migration group of 11-aryloxy derivatives of 6-amino-5,12-naphthacenequinone was favorable for photochromic transformations.[52] Aryloxynaphthacenequinones with electron-acceptor substituents in the phenoxy group were photoisomerized less efficiently.

Table 7.16[55] shows that the introduction of bulky substituents in the migratory group resulted in a decrease in the efficiency of the transformation from a para to an ana form under UV light. This efficiency is particularly low for the compound that manifested the additional reversible cis-trans photoisomerization of a substituent.[55] Note that the latter compound was characterized by the greatest value of the light sensitivity for transition of this compound from the photoinduced form to the initial form under the action of visible light.

A comparative study of the photochromic transformations for 6-phenoxy-5,12-naphthacenequinone in toluene and polymer matrix showed that the value of the quantum yields was unchanged with a polymer binder in place of toluene.[61] Quantum yields for direct and back photoreactions were equal to $\varphi_B = 0.3$ and $\varphi_A = 0.005$ under UV light and $\varphi_A = 0.005$ under visible irradiation.

The insertion of phenoxynaphthacenequinone in the polymeric chains led to an effective decrease in the rate of photochromic transformation.[53] The phototransformation rate of this compound in polymers depended on the polymer nature as follows: polysiloxane > poly(methyl methacrylate) > polystyrene. This rate was affected moderately by changing the concentration of the photochromic compounds, but it increased with the length of the chain in poly(methyl methacrylate) and

Table 7.16. Rate Constants for Photoconversion of Phenoxynaphthacenequinones (Type III B, R^1 = H) in DMSO (λ_{exc} = 365 nm)[55]

	k (min^{-1})	
R^2	para-ana	ana-para
H	0.73	0.15
$-C(CH_3)_2C_6H_4OH$	0.27	0.06
$-N=N-C_6H_4SO_3K$	0.05	0.26

decreased with increasing chain length in polysiloxane. The glass transition temperature played a key part in the photochromic transformations.

Quantum yields of phototransformations of phenoxy-substituted naphthacenequinones depended on the nature of the solvent.[59] One can see from Table 7.7 that the replacement of benzene by ethanol led to a decrease in the quantum yield of the ana form. At the same time, the quantum yield of the photodegradation of the ana form increased.

Studies of polymolecular films based on phenoxynaphthacenequinones[62] showed that the efficiency of photochromic transformation depends on the compound structure and the technique of producing Langmuir–Blodgett films. The best photochromism was observed for the polymolecular layers based on 6-phenoxy-5,12-naphthacenequinone with an amphiphilic substituent in the migratory group. The elimination of this group from 11-amino-6-phenoxy-5,12-naphthacenequinone decreased the efficiency of the photochromic transformations. The interaction between molecules of amino-substituted phenoxynaphthacenequinone and stearic acid in polymolecular films led to the same effect. The intermolecular interaction of the photochromic molecules in polymolecular layers reduced the light sensitivity to a great extent.

The dark relaxation processes from the photoinduced state to the initial form are characterized by a very low rate, for example, $k < 1 \times 10^{-8}$ s^{-1} and $E_a = 30$ kcal/mol for 6-phenoxy-5,12-naphthacenequinone in toluene at 298 K.[61] This thermodynamic characteristic is typical for the photochromic derivatives of naphthacenequinone, pentacenequinone, and phthaloylpyrene.

The photocoloring efficiency for *NH*-naphthacenepyridones in chloroform was comparable to the photochromism efficiency for the 9-phenoxy derivatives of N-methyl-substituted naphthacenepyridines.[37] Unlike the latter compounds, *NH*-naphthacenepyridones lost their photochromic properties in ethanol. This difference was due to the high efficiency of the photoinduced prototropic transformations of these compounds to the lactime form in ethanol.

The photochromism of phenoxypyrone is similar to the photochromic transformations for phenoxynaphthacenequinones.[48]

The presence of electron-acceptor substituents in the heterocyclic fragment of photochromic phenoxypyrazolnaphthacenones was favorable for the photoarylotropic rearrangement.[56]

The efficiencies of the photochromic transformations for phenoxypentacenequinone and the derivatives of phenoxyphthaloylpyrene match the photocoloring and photobleaching efficiencies for the phenoxy derivatives of naphthacenequinone.[57]

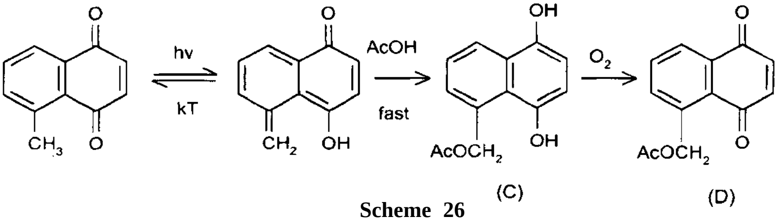
An analysis of the kinetic characteristics of photochromic quinones showed that the photochromic transformations of methylnaphthoquinone, alkyl- and acyloxyanthraquinones in solution at room temperature were observed in the microsecond range. As a consequence, these compounds may be of theoretical interest in the future. The photochromic aryloxyanthraquinones are characterized by a lifetime of the photoinduced form that reaches several minutes in solution and several hours in polymer films at room temperature, which makes them acceptable for a number of applications. In this regard, of special interest are photochromic naphthacenequinones, which are characterized by the thermally stable photoinduced form. The additional increase in the lifetime of the photoinduced form for these photochromic compounds was achieved by use of proton-donor solvents, polymers, or polymolecular layers. This property of the photoinduced form raises the possibility of its application in light-sensitive recording media for optical memory systems.

Studies of the efficiency of quinone photochromism showed that the introduction of electron-donor substituents in the quinone cycle as well as the bulky substituents in the migratory group reduced the efficiency of the photoinduced para- ana-quinone rearrangement. At the same time, the introduction of electron-donor substituents in the migratory phenoxy group was favorable for photochromic transformations. On the contrary, the introduction of electron-acceptor substituents decreased the efficiency of the phototransformations. These experimental data agree well with the known concept of the photochromic transformations of these compounds as reversible intramolecular photoinduced substitutions.

7.4.3. Fatigue

7.4.3.1. Methylnaphthaquinone

5-Methyl-1,4-naphthaquinone in glacial acetic acid under irradiation gave products of an irreversible photochemical reaction, namely, 5-(acetoxymethyl-1,4-naphthalenediol) (C) and 5-(acetoxymethyl-1,4-naphthaquinone) (D) (Scheme 26).[11]



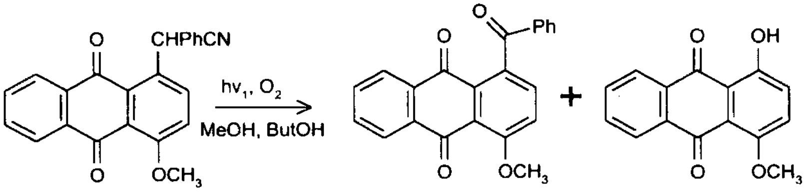
Scheme 26

7.4.3.2. Derivatives of Anthraquinone

Photochromism of 1-alkylanthraquinones (which is different from 1-methylanthraquinone) in ethanol at 77 K was complicated by secondary photochemical reactions that generated a new product.[26] This product was formed very inefficiently at room temperature owing to the short lifetime of the photoinduced form of this photochromic compound.

The specially synthesized 1-arylcyanomethyl-9,10-anthraquinones with a long lifetime for the photoinduced form showed photodegradation in alcohols as well.[36] It was found that despite the variable lifetime of the photoinduced form of the different compounds of this type, the dark reaction of its interaction with alcohol dominated over the hydrogen atom transfer, which was due to the photochromic process. The efficiency of the photochromic transformations depended on the nature of the alcohol.[36] It was higher for isopropyl alcohol and *tert*-butyl alcohol than for methanol and ethanol because of the steric hindrance between molecules of the photoinduced form and solvent in the former compounds.

The rate constants of the dark transformation of the compounds with the long lifetime depended on the oxygen concentration in solution.[36] The interaction of the photochromic molecules with oxygen resulted in the formation of the irreversible photoproducts of 4-methoxy- and 1-oxy-4-methoxyanthraquinone (Scheme 27).



Scheme 27

Thus, the dark transformations of the photoinduced form of 1-arylcyanomethyl-9,10-anthraquinone included not only the reversible photochromic transfer of the hydrogen atom but the irreversible interaction of the photoinduced form with alcohols and dissolved oxygen.

The photolysis of non-photochromic 1-acetoxy-9,10-anthraquinone in alcohols resulted in a photochemical reaction of hydrogen atom removal from solvent.[21] This reaction is typical for 9,10-anthraquinones. The absorption spectrum that was observed after a flash pulse was similar to the absorption spectrum of the anthrasemiquinone radical. The lifetime of this radical depended on the oxygen concentration in solution.

Photochromic 1-acetoxy-2-piperidino- and 1-acetoxy-2-dimethylamino-9,10-anthraquinone also manifested photodegradation.[28] The mechanism of these irreversible photochemical transformations includes intermediate 1,10-anthraquinone, which exhibited the photochemical transformations well known for anthraquinones with dialkylamino substituents adjacent to the carbonyl group.

The original photoproduct of these reactions has a hydrated oxazolic ring formed by the interaction of the carbonyl group with the neighboring N-alkylated amino group.[28] This photoproduct was transformed into anthra[2,1-*d*]oxazoline derivatives, which form following oxidative cleavage.

Irreversible photochemical transformations were observed for photochromic phenyl-containing 1-carbamoyloxy-2-methoxy-9,10-anthraquinones.[25] The formation of photoproducts depended strongly on the water concentration in organic solutions.

Among aryloxyanthraquinones, amino derivatives of 1-phenoxyanthraquinone were characterized by low resistance to the occurrence of irreversible photochemical transformations.[12,14] The photoinduced ana-quinones were subject to photodegradation. The corresponding 1-oxy-2-aminoanthraquinones were identified via the photodegradation products.[12–14] The interaction of the photoproducts with nucleophilic reactants led to a change in the phenoxy group with the water residue, ammonia, primary aliphatic, or aromatic amines and thus to formation of oxyalkylaminoanthraquinones.[13]

Decomposition of the photochromic compounds can occur because of the interaction between molecules of the photoinduced form and alcohols. This phenomenon is a consequence of the deficiency of the electron density on the carbon atom in the 9-position of the ana form for aryloxyanthraquinones.[27] The reaction of nucleophilic 1,4-addition of alcohol molecules with molecules of 9-aryloxy-1,10-anthraquinones depended on the nature of the substituent.[27] The introduction of electron-acceptor substituents enhanced and the electron-donor substituents reduced the rate constant. The electron-donor substituents contributed to the stability of the photoinduced 1,10-anthraquinones. This conclusion was supported by the data on the interaction between derivatives of 9-aryloxy-1, 10-anthraquinone, and aliphatic and aromatic amines.[35]

Among photochromic 1-aryloxyanthraquinones with an unsubstituted and substituted oxy group, as with a substituent in the anthraquinone nucleus, partial destruction was observed for 1-phenoxy-5-oxy- and 1-phenoxy-8-acetoxyanthraquinones.[19] In addition, 2,4-dioxy derivatives of 1-phenoxyanthraquinone also exhibited irreversible photochemical transformation. As for aminoaryloxyanthraquinones, oxy- or 9-imino compounds are produced by reaction with water or ammonia, respectively.

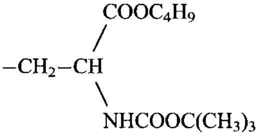
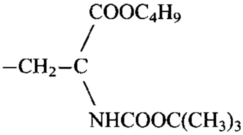
2-Methoxy-4-methyl-6-phenoxytanthrapyridines in chloroform also exhibited irreversible photochemical transformations.[39] A similar irreversible photoconversion for 6-phenoxypyridones was observed in toluene. [37]

Photochromism of 7-phenoxypyrazolanthrones was complicated due to dearylation of the photoinduced form to the corresponding 7-hydroxy derivatives.[41]

7.4.3.3. Derivatives of Naphthacenequinone

Phenoxynaphthacenequinones differ favorably from other photochromic quinones owing to their stability to irreversible phototransformations.[10] The photochromic systems based on these compounds preserved their properties after 500 cycles of coloring and bleaching. However, their photodegradation was observed during long irradiation.[54] The results obtained showed that the photodegradation rate depended on the nature of the solvent. The quantum yields of photodecomposition of the phenoxynaphthacenequinones studied were greater in alcohol than in benzene (Table 7.17). Experimental data[54] suggest that the processes of photodegradation and photochromic transformation occurred simultaneously. The photodecomposition in pure alcohol was a chain reaction, as is evidenced by the change in absorption of the solution after irradiation.[54] Irreversible phototransformation of photochromic compounds was associated with hydrogen abstraction from alcohol molecules by molecules of photochromic compounds in the triplet state. The estimates showed that the rate constants of hydrogen abstraction were equal to $k = 9.3 \text{ x } 10^4 \text{ mol}^{-1}$

Table 7.17. Quantum Yields for Ana Form (φ_B) and Irreversible Photodecomposition (φ_c) of Phenoxynaphthacenequinone Compounds (Type IIIB, R^1 = H) in the Presence of Oxygen (λ_{exe} = 366 nm)[59]

R^2	Solvent	φ_B	φ_c
H	Benzene	0.6±0.1	0.00014
H	*i*-PrOH	0.5±0.1	0.0035±0.0005
 $-CH_2-CH(COOC_4H_9)(NHCOOC(CH_3)_3)$	Benzene	0.6±0.1	0.00034±0.0001
 $-CH_2-C(COOC_4H_9)(NHCOOC(CH_3)_3)$	*i*-PrOH	0.4±0.1	0.0026±0.0001

s^{-1} for the ana form and $k = 1.3 \times 10^8$ mol^{-1} s^{-1} for the para form[54] which is specific to the $\pi\pi^*$- and $n\pi^*$ triplet state, respectively.

The loss of the photochromic properties of phenoxynaphthacenequinone in dimethylformamide was caused by the interaction between photochromic molecules and impurities.

It was found[39] that photochromic transformations of phenoxynaphthacenepyridones in chloroform were accompanied by the destruction of the photoinduced form. Photochromic phenoxypyrazolonaphthacenones also exhibited fatigue.[56]

Analysis of the available data on photodegradation of photochromic quinones suggests that this class of photochromic organic compounds, like other organic photochromes, exhibits fatigue.

Photochromic anthraquinones are characterized by very rapid photodecomposition because of the large reactivity of the 9-position in these molecules. Photodestruction gave rise to oxy derivatives of anthraquinone. The concentration of these irreversible photoproducts depended on the water content in solvent or the nature of the solvent.

Phenoxynaphthacenequinones were more stable to irreversible phototransformations than other photochromic quinones. The efficiency of their photodegradation increased in alcohols.

7.5. APPLICATIONS OF PHOTOCHROMIC QUINONES

An analysis of the properties of photochromic quinones shows that the main potential field of their applications is a light-sensitive medium for recording, multiplying, storing, and processing optical information.

7.5.1. Recording and Multiplication of Images

Studies of polymeric films based on some phenoxyanthraquinones showed that the value of their light sensitivity depended on the structure of the photochromic compound and that the wavelength of the activating irradiation was in the range of 1.5-10.0 cm²/J.[29] Photochromic films were characterized by maximum light sensitivity to UV irradiation at 365 nm. This result correlated with data for quantum yields of the ana form measured using the activation irradiation at different wavelengths. An optimum value of the light sensitivity for a film was achieved at a concentration of photochromic compound in the film equal to 4 wt% and a film thickness of 40 µm. The light sensitivity of the photochromic films to visible irradiation was one order of magnitude below that to UV light.[59]

The contrast coefficient varied between 0.5 and 1.5, depending on the compound structure.[29]

The number of cycles for rewriting images on the same site of a film with photochromic anthraquinones amounted to 10.[29]

Films based on photochromic anthraquinones may be used as intermediate carriers of optical information. Owing to the low light sensitivity of these films to visible irradiation, it is possible to produce more than 100 prints on photographic paper using a standard enlarger.[29]

7.5.2. Optical Memory

Photochromic films based on phenoxynaphthacenequinone were characterized by high stability to irreversible phototransformations, in contrast to recording media with photochromic phenoxyanthraquinones. The above films allowed more than 500 cycles of rewriting of optical information at the same site of the light-sensitive layer. In addition, they were characterized by an extremely low rate of thermal relaxation from ana-quinoid into para-quinoid form. This means that the lifetime of the photoinduced form in a polymer film in darkness was equal to many years.

Whatever the nature of the polymeric matrix, the sensitivity of photochromic films based on phenoxynaphthacenequinones reached 10 cm²/J to UV irradiation and 1 cm²/J to visible irradiation. These values were measured for the photoinduced change of optical density at the maximum of the absorption band of the photoinduced form.[61]

Photochromic films based on phenoxynaphthacenequinones were used for hologram recording using a helium-cadmium laser (441.6 nm) with a maximum diffraction efficiency up to 1%.[63] These media allow the nondestructive readout of recorded information beyond the absorption band of the photoinduced form by a helium-neon laser (632.8 nm). The nondestructive readout is possible because of the photoinduced change in the index of refraction at this wavelength during the hologram recording.

Photochromic films of this type are suitable for recording polarization holograms because of the Veigert effect and oriented photodichroism.[63]

Polymers with photochromic phenoxynaphthacenequinone side groups were also used for recording holograms.[49]

Studies of photochromism of phenoxynaphthacenequinones in polymolecular layers[62,63] suggested the possibility of the development of reversible optical memory on optical disks for operative recording and processing optical information.

Information storage in polymeric media based on phenoxynaphthacenequinones was permanent at room temperature. This property suggests that these media may be suitable for use as materials for 3D optical memory.[63–66] In this connection, photofluorochromic quinones providing large two-photon cross sections, high fluorescence quantum yields for the photoinduced form, and relatively low ones for the initial form are of chief interest.[67,68]

7.5.3. Gradation Masking

Photochromic films based on 1-(*p*-*tert*-butylphenoxy)-2-benzoyl-aminoanthraquinone were suitable for gradation masking of negative images during photoprinting.[69] The useful maximum effective density of masking was equal to $D_{\text{ef. max}} = 1.1$. The photographic latitude was varied through $L = 1–2$ range. The contrast coefficient exceeded 1.0. Based on real parameters of existing photochromic materials, a mask was manufactured with the use of the initial part of the characteristic curve. In this case, the maximum density of the mask should not exceed the value at which the effective gradient of the photochromic film with respect to the photochromic medium becomes equal to unity.

7.6. CONCLUSION

In the past 25 years, considerable progress has been made in studies of the photochromism of quinones. Various photochromic naphtha-, anthra-, naphthacene-, pentacenequinones, and phthaloylpyrenes were synthesized. The mechanism of photochromic transformations in these compounds has been established. The basis for photochromism of quinones is the reversible photoinduced para-ana quinoid rearrangement. The influence of the compound structure and the carrier nature on spectral and kinetic characteristics and fatigue has been ascertained. Finally, the possibility of the application of photochromic polymeric and polymolecular layers as light-sensitive recording media has been demonstrated. The phenoxy derivatives of naphthacenequinone are the most acceptable for practical application because they are characterized by two thermodynamically stable states and exhibit appropriate light sensitivity and fatigue.

The success of future searches for photochromic compounds feasible for applications will be determined by the progress in studying the relationship between the structure of these compounds and their properties.

7.7. EXAMPLES OF SYNTHESIS OF PHOTOCHROMIC QUINONES

7.7.1. 1-Phenoxy-2,4-dioxy and 1-(p-*tert*-butyl)phenoxy-2,4-dioxyanthraquinones[19]

2-Phenoxy-1,4-dioxy (I)- or 2-(*p*)-*ter*t-butyl)phenoxy-1,4-dioxy (II)-anthraquinones (0.01 mol) and KOH (0.02 mol) in DMSO (10 mol) were heated at 130°C for 10 h. Yield: 36; 35%; mp, respectively: 196–198°C (I) and 109–111°C (II).

IR for (II), $\nu_{\text{max.}} = 1635, 1680, 2965\ \text{cm}^{-1}$.

7.7.2 6-Phenoxy-5,12-naphthacenequinone[3]

Phenol (45 g), potassium hydroxide (1.4 g) and 6-chloro-5,12-naphthacenequinone (5 g) were mixed at 165–170°C for 1 h. The reaction mixture was cooled up to 120°C and poured in 10% KOH (300 ml), filtered off, washed with hot water, dried and crystallized from benzene. Yield: 4.8 g (81%); mp: 220–220.5°C.

7.7.3. 6-Phenoxy-5,12-pentacenequinone[57]

2-(1-chloro-2-naphthoyl)-3-naphthoic acid (1 g), boric acid (1 g), and sulfuric acid (5 ml) were mixed at 105–110°C for 3 h. The cooled mass was poured onto ice, filtered, and dried. Yield: 0.56 g (59%) of 5-chloro-6,13-pentacenequinone. This material was used without further purification in the next step.

5-Chloro-6,13-pentacenequinone (3.12 g) was mixed at 150°C in a mixture of phenol (30 g) and KOH (0.75 g) for 2 h. The cooled mass was processed by 3% solution of KOH and hot water. Yield: 3.22 g (83.5%) of 5-phenoxy-6,13-pentacenequinone. This material was used without further purification in the next step.

5-Phenoxy-6,13-pentacenequinone (0.1 g) in nonaqueous benzene was exposed to UV light (313 nm) for 5 h. Benzene (100 ml) was distilled off the exposed solution in vacuum. The residual solution was filtered through a layer of silica gel. 5-Phenoxy-6,13-pentacenequinone was washed out by benzene. The layer of silica gel with 6-phenoxy-5,12-pentacenequinone was washed by acetone, which was evaporated. Yield: 0.07 g (70%). It was isomerized into 5-phenoxy-6,13-pentacenequinone during determination of the melting point.

7.7.4. 1,3-Dichloro-6-phenoxy-7,12-phthaloylpyrene[59]

Benzoyl chloride (8.6 ml) and 4 drops of concentrated H_2SO_4 were added to the solution of 1,6,8-trichlor-3-*o*-carbomethoxybenzoylpyrene (5.73 g) in nitrobenzene (170 ml) at 100°C. This mixture was heated to 180°C and stirred for 40 min. The cooled solution was filtered and washed by methanol. Yield: 4.32 g (80.7%) of 1,6,8-trichloro-2,3-phthaloylpyrene; mp: 339–340°C. This material was used without further purification in the next step.

This compound (1 g) was added to melted phenol (8 g) with KOH (0.26 g) at 60°C. The mixture was stirred at 165–170°C for 3 h. The cooled solution was diluted by methanol, filtered, and washed by methanol and hot water. Yield: 1.07 g (95%); mp: 258–260°C. After crystallization from chlorobenzene, orange crystals, were obtained 272–273°C.

7.8. REFERENCES

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8

Perimidinespirocyclohexadienones

VLADIMIR I. MINKIN, VITALY N. KOMISSAROV,
AND VLADIMIR A. KHARLANOV

8.1. INTRODUCTION

Valence and prototropic tautomeric reactions are among the most important mechanisms that govern transformations of a broad variety of photochromic organic systems.[1,2] Until recently, no examples of photochromic compounds have been reported whose photochromic behavior was due to a combination of these two tautomeric reactions. Such a combination, which is characteristic of ring-chain tautomerism[3] has been implemented in the photochromic and thermochromic rearrangements of a novel type of heterocyclic photochromes, derivatives of 2,3-dihydro-2-spiro-4'-(2',6'-di-*ter*t-butylcyclohexadien-2',5'-one)perimidine **1a** and its analogs.[4] The occurrence of a proton transfer step is in accord with the fact that the *N,N'*-dimethyl derivative of **1a** exhibits no photochromic properties.

When UV irradiated, an octane solution of **1** (R = H, Alk) changes its color from yellowish to deep blue. The initial spectrum is slowly restored at room temperature (the effective lifetime of the colored form at room temperature is about 10^4 s). No concentration dependence of the rate of the dark reaction was observed, which agrees with the intramolecular nature of the reaction. Figure 8.1 portrays the evolution of the absorption spectrum of a perimidinespirocyclohexadienone **1** (R = Me) during UV irradiation of its hexane solution (Scheme 1).

The mechanism of the photochromic reaction involves cleavage of a C–N bond in the first singlet excited state of **1a** followed by the conformational rearrangement of the thus formed zwitterionic (biradical) intermediate **2** that precedes the final step of the intramolecular proton transfer (Scheme 2).

Vladimir I. Minkin, Vitaly N. Komissarov and Vladimir A. Kharlanov • Institute of Physical and Organic Chemistry, Rostov University. 344090 Rostov on Don. Russia

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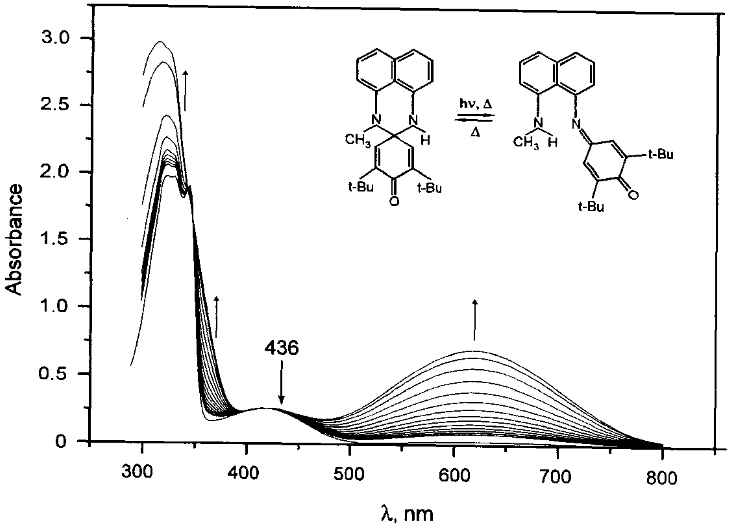
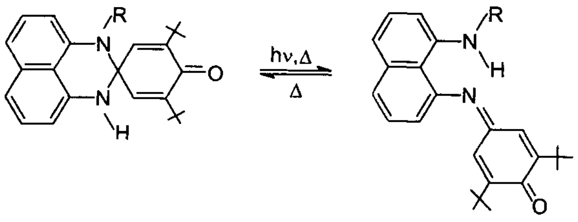


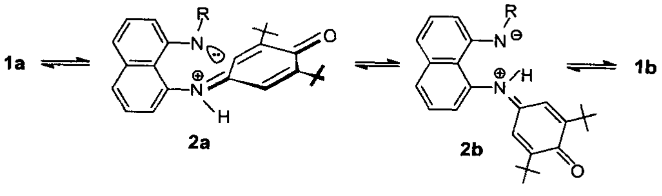
Figure 8.1. Changes of the UV/VIS absorption spectrum of compound **1a** (R = Me) on irradiation of its hexane solution (containing 2% of triethylamine) at the longest wavelength band with time interval of 5 min (295 K).



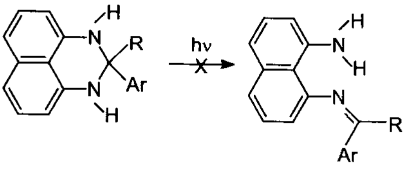
1a **1b**

Scheme 1

Attempts to extend the photochromic rearrangements featured in Scheme 1 to the nonspirocyclic Type **3** compounds structurally similar to **1** failed, which suggests a direct relationship between the photochromism of the latter compounds and the



Scheme 2



3a **3b**

Scheme 3

presence in their molecules of a spiroannellated cyclohexadien-2,5-one fragment (Scheme 3).

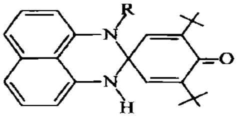
It has therefore been concluded that any further modification of the photochromic compound **1** should be associated with structural variations in its 2,3-dihydroperimidine moiety. In the course of subsequent studies, the spirocyclohexadienones belonging to structural types **1-9** have been found to display photo- and thermochromic properties.

8.2. SYNTHESIS AND REACTIONS

Coupling carbonyl compounds with aromatic amines bearing amino, hydroxy, or thiol groups in *o*-positions is known to be a general method for the synthesis of 1,3-benzazoles, with the intermediate formation of the respective 2,3-dihydro derivatives. No heterocyclization occurs, however, in the reaction of *o*-phenylenediamines or *o*-aminophenols with *p*-quinones. In these cases, the reaction stops at the stage of formation of the deeply colored quinoneimine **10**[5] which is similar to that obtained by the previously studied reaction of a variety of *p*-substituted anilines with derivatives of *p*-benzoquinone.[6] Compounds **10** do not undergo cyclization under heating or irradiation of its solution (Scheme 4).

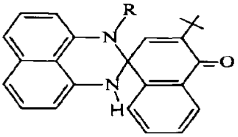
In contrast to *o*-phenylenediamines, 1,8,naphthylenediamine and most of its derivatives react with 2,6-di-*tert*-butyl-1,4-benzoquinone to give perimidinespirocyclohexadienone **11** (Scheme 5).[4,6–8] The reaction occurs readily under noncatalytic conditions when refluxing propanol or toluene solutions of the components. By contrast, catalysis of the reaction with strong proton acids (e.g., *p*-toluenesulfonic acid) is necessary for the preparation of 2,3-dihydro-2-spiro[4(4*H*)-2-*tert*-butyl-l-naphthalenone]perimidine **4** when 2,6-di-*tert*-butyl-1,4-benzoquinone is replaced in this reaction by 2-*tert*-butyl-1,4-naphthoquinone.[9]

The molecular structures of perimidinespirocyclohexadienones **1a** (R = Me) and **4** (R, R', R" = H) as determined by an X-ray diffraction study,[7] are shown in Figures 8.2 and 8.3, respectively. The heterocyclic and cyclopentadienone fragments in these compounds are virtually orthogonal. The dihedral angles between the N(1)C(1)N(2) and C(2)C(1)C(6) planes were found to be equal to 87.8° in **1a** (R = Me) and 87.3° in **4**. An important structural peculiarity is significant folding of the six-membered diazaheterocyclic ring along the N(1)-N(2) axis. Both nitrogen atoms in each of the compounds are approximately sp^3-hybridized, with the lone



R = H, Alk

1



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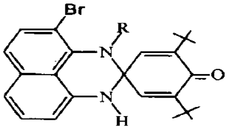

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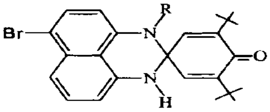

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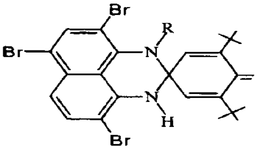

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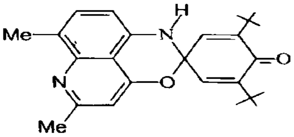

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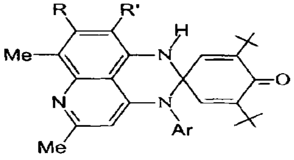

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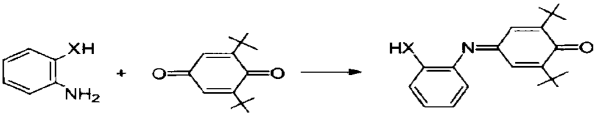
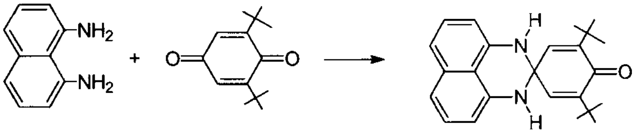


Scheme 4

10. X = O, NR



Scheme 5 **11**

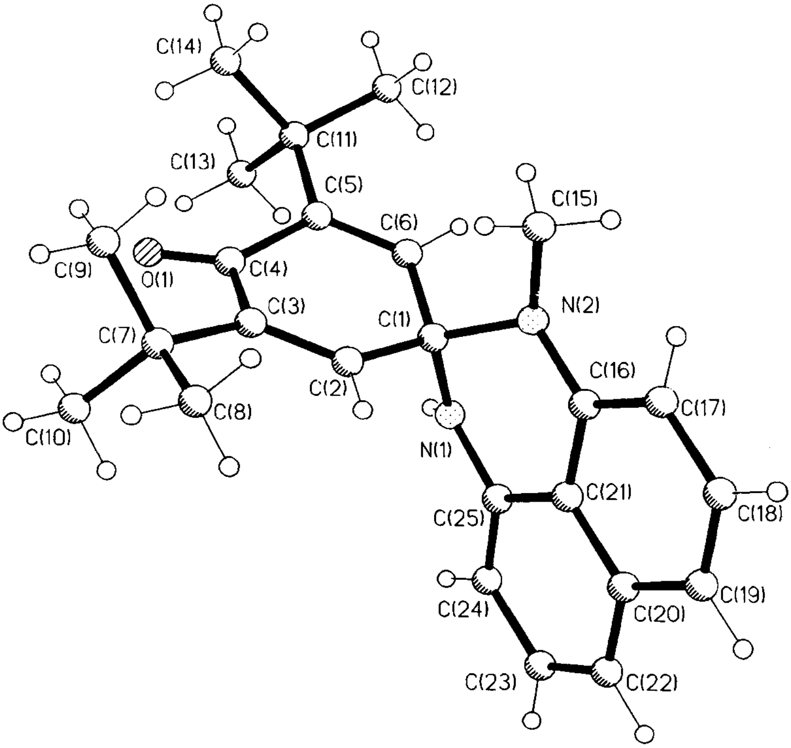


Figure 8.2. X-ray structure of **1a** (R = Me).[7] (Reproduced with the permission of the Russian Academy of Science.)

electron pair being cis-positioned. Also acoplanar are the cyclohexadienone rings that possess boat conformations. Some of the geometric parameters of the compounds **1a** (R = H) and **11** (R = H) are listed in Table 8.1.

The different courses of the reactions of *o*-phenylenediamines and 1,8-diaminonaphthalenes with quinones cannot be assigned to different terms for thermodynamic control. The spirocyclic isomers are most probably energy-preferable forms for both Type **10** and **11** compounds.* The cyclization step is definitely kinetically

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* According to the semiempirical Parametric Model 3 (PM3) calculation,[10] the energy difference between the ring-opened and ring-closed tautomers is equal to 12.1 and 7.6 kcal/mol for 2,3-dihydroperimidine-spirocyclohexadienone and 2,3dihydrobenzimidazolespirocyclohexadienone, respectively, the cyclic structure being energy favorable.

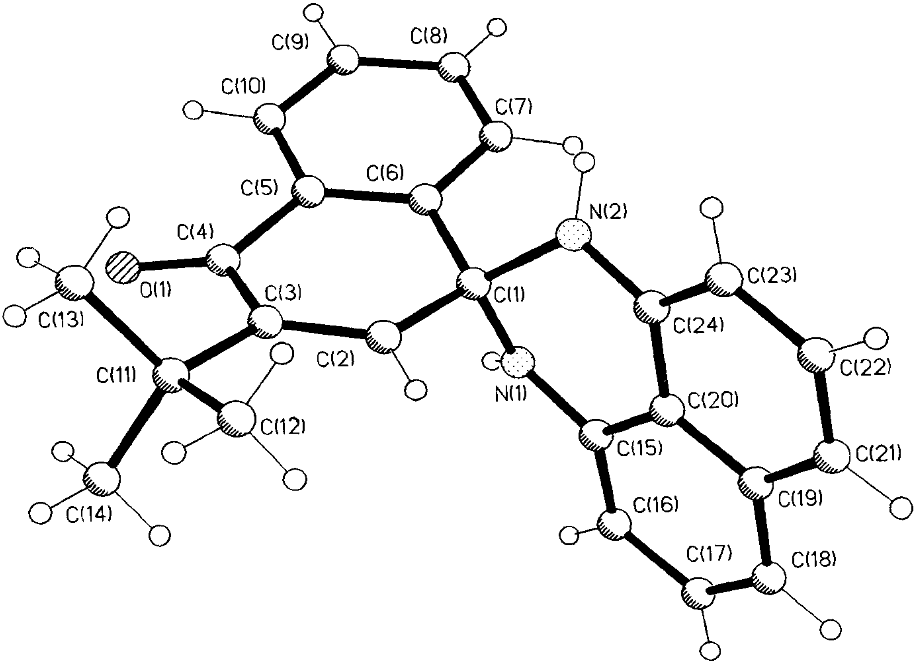


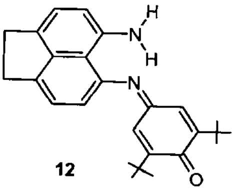
Figure 8.3. X-ray structure of **4** (R, R', R" = H).[7] (Reproduced with the permission of the Russian Academy of Science.)

Table 8.1. Geometric Characteristics of Spiroperimidines **1a** (R = CH_3) and **11** (R = H) according to X-ray Diffraction Data[7] [a]

Parameter	**1a** (R = Me)	**11**
C(1)–N(1),pm	148.0	150.7
C(1)–N(2),pm	145.8	146.5
C(25)–N(1),pm	138.2	—
C(16)–N(2),pm	139.4	—
C(15)–N(1),pm	—	138.7
C(24)–N(2),pm	—	139.8
N(1)–N(2) folding, deg.	41.6°	40.4°
C(2)–C(6) folding, deg.	10.8°	9.7°
C(3)–C(5) folding, deg.	21.3°	15.7°

[a] The labeling scheme is given in Figures 8.2 and 8.3.

controlled, i.e., it depends on energy requirements for the occurrence of the type **1b** → **2b** → **2a** interconversion. Even tiny structural variations strongly affect the condensation reaction. Thus, when 5,6-diaminoacenaphthene was coupled with 2,6-di-*tert*-butyl-1, 4-benzoquinone under the same conditions at which 1,8-diamino-



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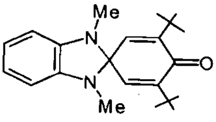

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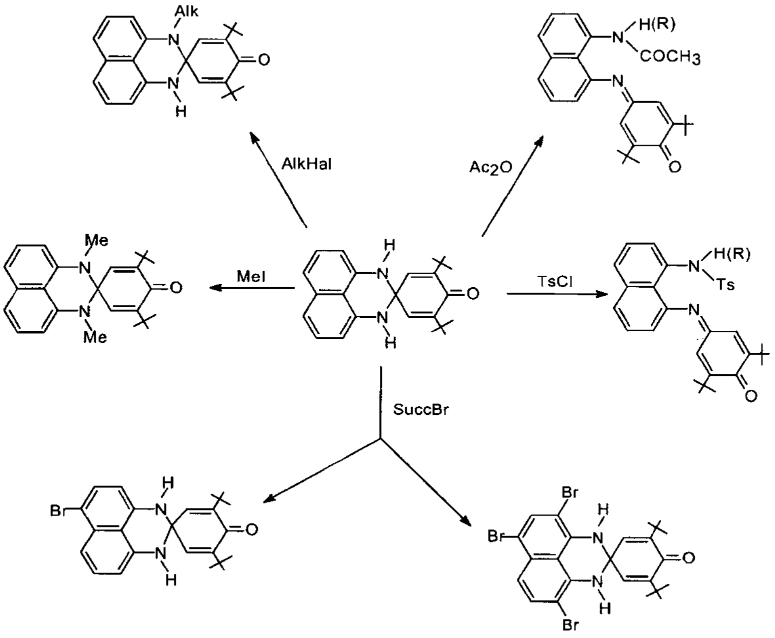
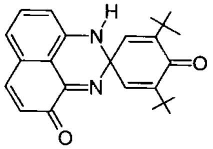
naphthalenes afford spiran **11**, the only product of the reaction was the ring-opened tautomer **12**[7]. At the same time, condensation of this quinone with *N*-*N*′-dimethyl-phenylenediamine gives rise to the spiran **13**, which is photochemically inert.

Scheme 6 describes the most important reactions of the perimidinespirocyclohexadienone **1**. A treatment of **1** (R = H) in dimethylsulfoxide (DMSO) solution with methyl iodide in the presence of potassium carbonate affords the *N*-methyl derivative **1a** (R = Me), whereas use of an excessive amount of methyl iodide in this reaction leads to the *N*,*N*′-dimethyl derivative of the ring-closed tautomer.[4,7] By contrast, acylation of **1a** by acetic anhydride or its tosylation by treatment with *p*-toluenesulfonyl chloride results in the formation of the respective derivatives of the ring-opened tautomeric form **1b**.

The structure of the latter compound has been determined by X-ray diffraction study.[11] Bromination of **1a** with an equivalent amount of *N*-bromosuccinimide



Scheme 6



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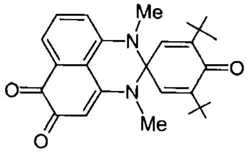

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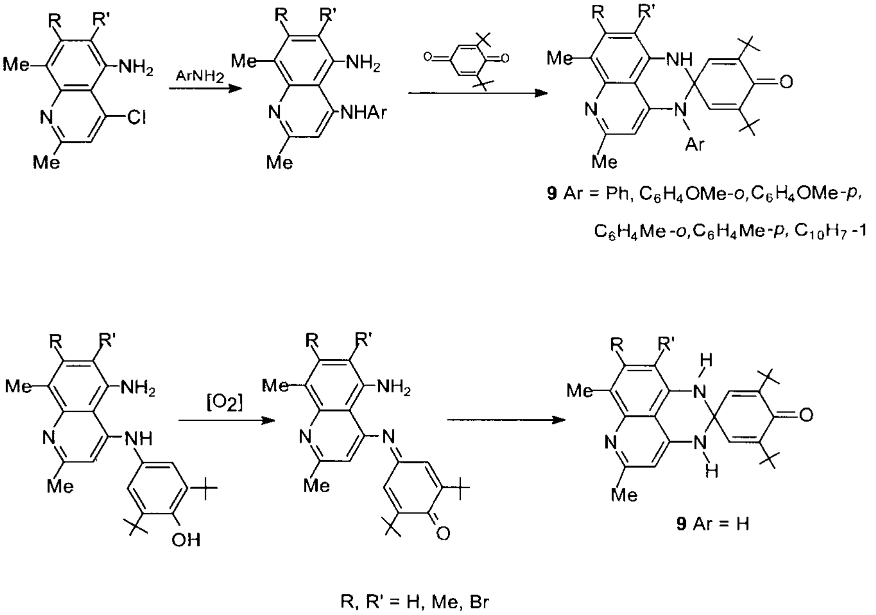
(SuccBr) in CCl_4 affords the 4-bromoderivative **5**, whereas its 6-bromo isomer **6** is prepared through direct coupling of 4-bromo-1,8-diaminonaphthalene with 2,6-di-*ter*t-butyl-1,4-benzoquinone. When three equivalents of *N*-bromosuccinimide were used in the reaction with **1a**, the tribromo derivative **7** was prepared in good yield. Another way to **7** is the condensation of 2,4,7-tribromo-1,8-diaminonaphthalene with 2,6-di-*ter*t-butyl-1,4-benzoquinone.[8]

On prolonged passing of air through ethanol or acetonitrile solutions of **1** (R = H) in a quartz photoreactor with an immersed mercury lamp, 2',3'-dihydro-2'-spiro-4-(2,6-di-*ter*t-butylcyclohexadien-2,5-one)perimidin-4'-one **14** was isolated as the main product of the photooxidation reaction. With the *N,N'*-dimethyl derivative of **1**, photooxidation results in the formation of the perimidinedione **15**.[12]

The first representative of a new group of photo- and thermochromic compounds in which the naphthalene fragment in spiroperimidine (**1**) is changed to a quinoline moiety has been obtained by coupling 2,6-di-*ter*t-butyl-1,4-benzo-



Scheme 7

quinone with 5-amino-4-chloro-2,8-dimethylquinoline. The reaction includes a step of nucleophilic substitution of an active chlorine atom in the quinoline ring, which is followed by cyclization resulting in the formation of 6,8-dimethyl-2,3-dihydropyrido-[2,3,4-*h,i*]benzo[*d*]-1,3-oxazine-2-spiro-4' -(2' ,6'-di-*ter*t-butylcyclohexa-2' ,5' ,-dien-1'-one), **8**.[13] Such a reaction is specific with quinones. Other carbonyl-containing compounds (e.g., aromatic and heterocyclic aldehydes) do not react with 4-chloroquinoline to give benzoxazine derivatives.

Two methods have been developed for the preparation of derivatives of another heterocyclic system congeneric to **1**, cyclohexa-2,5-dienonequinazolidine **9**. 4-Chloro-5-aminoquinolines susceptible to ready displacement of the chlorine atom in their molecules by an arylamino group were used as the starting material in both of the approaches.[14,15] These are illustrated in Scheme 7.

8.3. SPECTRAL AND PHOTOCHROMIC PROPERTIES

As seen from Figure 8.1, UV irradiation of a solution of the perimidinespirocyclohexadienone **1a** leads to its rapid coloration due to the appearance of a long-wave absorption band ($\lambda_{max} \simeq 600$ nm) assigned to the ring-opened isomer **1b**. Upon extinguishing UV irradiation, the decoloration process which restores the initial spectrum occurs slowly at room temperature. Photochromic perimidinespirocyclohexadienone **1** possesses high fatigue resistance properties. The photocoloration-thermal decoloration cycles can be repeated several dozen times without noticeable loss in intensity of the longest wavelength absorption of the spirocyclic isomer **1a**. Under continuous illumination of a polystyrene film of compound **1a** (R = Me, Et) with a light intensity of 10^{15} photons at their λ_{max}, the time required to reduce the absorbance in the long wavelength absorption band of the colored isomer **1b** to half is 130–150 h. Similar photochromic transformations are also characteristic of all other derivatives **5–7** and heteroanalogs (**8, 9**) of **1a**, as well as of perimidinespiro-4*H*-naphthalenone **4**. The photochromic behavior of the latter is illustrated by the spectral pattern shown in Figure 8.4

Owing to the orthogonality of the two spiroannellated halves of perimidinespirocyclohexadienones (see Figures 8.2 and 8.3), their absorption spectra may, in a first approximation, be considered as the superposition of the spectra of these fragments. Thus, the spectra of compound **1a** contain absorption bands at 234, 333, and 352 nm (octane) whose positions and intensities correspond well to those of a model compound **16**. The absorption band at 269 nm (appearing as a shoulder) originates, as follows from the comparison with the spectrum of **17**, from an electronic transition localized in the cyclohexadienone moiety.[4,7] A low-intensity ($\varepsilon \simeq 1500$–2000 1 x M^{-1} cm^{-1}) long-wavelength absorption band in the region of 390–440 nm that is inherent in perimidinespirocyclohexadienones **1, 4–9** (see Figures 8.1 and 8.4) and nonexistent in the spectra of any of their mutually orthogonal fragments should be associated with an electronic transition that manifests significant spiroconjugation between the heterocyclic and cyclohexadi-

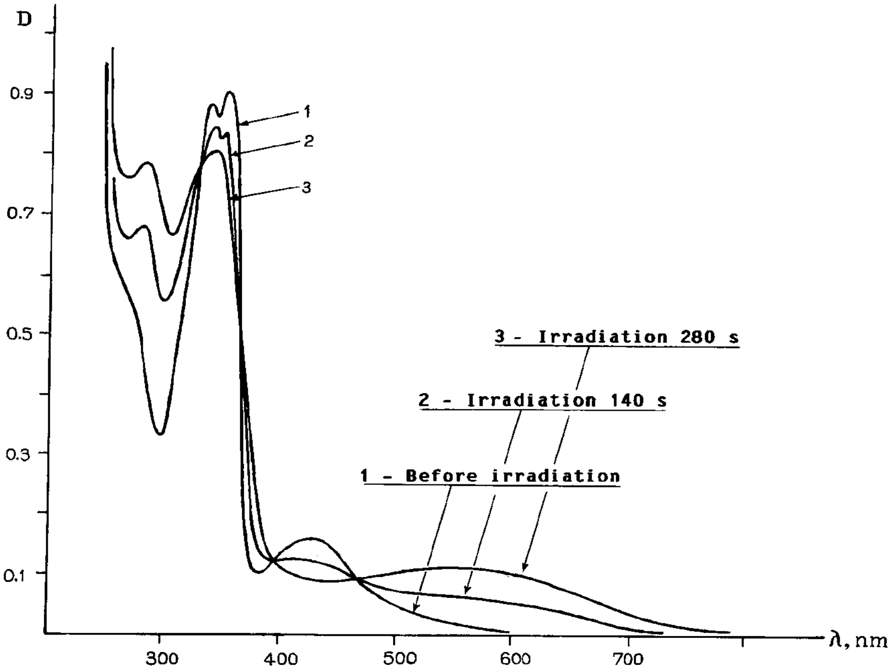
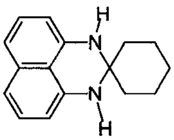


Figure 8.4. Photochromic behavior of perimidinespironaphthalenone **4** (R, R' R" = H) in ethanol solution, c=-6 x 10^{-4} (298 K). Irradiation by filtered light (405 nm) of high-pressure mercury lamp.[9] Effective lifetime, τ, of the colored photoisomer after the light is extinguished is equal to 11.5 h.

enone moieties of **1, 4–9**. Such an effect has been thoroughly studied in the spiropyran series of spiroconjugated molecules and reported to exert a negligible influence on their spectral properties.[16,17] Therefore, the incomplete additivity of the absorption spectra of perimidinespirocyclohexadienones **1, 4–9** should be regarded as their distinctive feature. The new electronic state that causes an appearance of the longest-wave absorption band strongly affects the spectral properties and photochemical behavior of these compounds. In contrast to the model compounds **16** and **17**, compounds **1, 4–9** exhibit no fluorescence or phosphorescence in solution or in crystal form.



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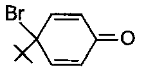

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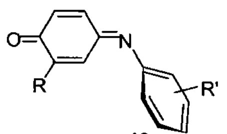

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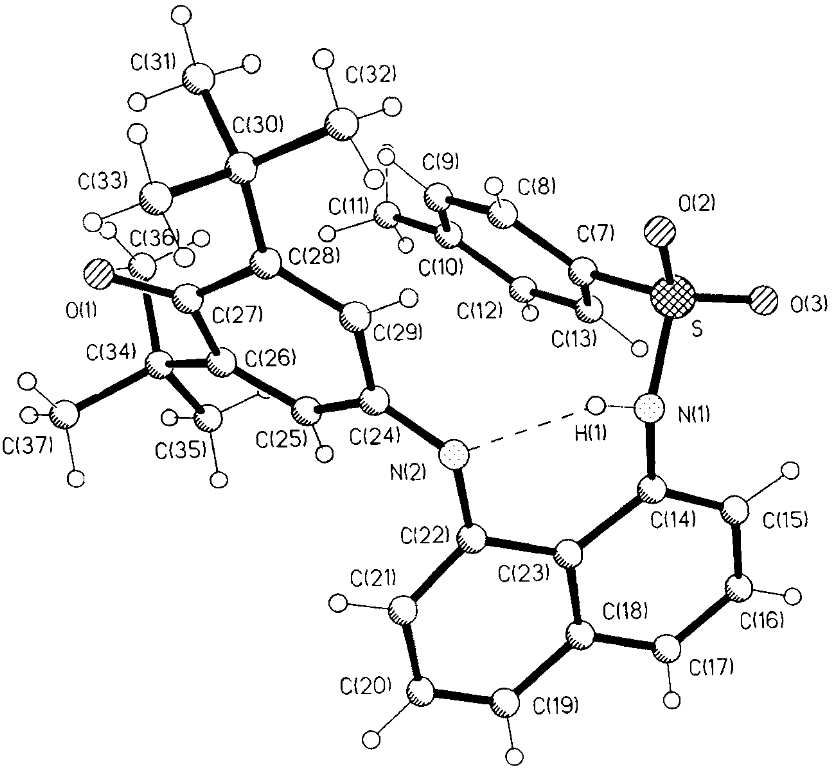


Figure 8.5. X-ray structure of 2,6,-di-*tert*-butylquinone-4-*N*-(8'-tosylaminonaphtyl-1')-imine.[11]

The nature of the colored isomers of photochromic perimidinespirocyclohexadienones has been unambiguously proven through comparison of their UV/VIS absorption spectra with those of *N*-acetyl (λ_{max} = 536 nm, lg ε = 4.3, octane) and *N*-tosyl (λ_{max} = 504 nm, lg ε = 3.8, hexane) derivatives of **1** obtained in their stable ring-opened forms (see Scheme 2 and Figure 8.5) as well as through comparison with the spectrum (Figure 8.6) of the acenaphtylene derivative **12**, which also possesses the quinoneimine structure.[18]

Table 8.2 contains data on positions and intensities of the longest wavelength absorption bands of the ring-opened photoisomers of perimidinespirocyclohexadienone **1** and its analogs **4–9**. It is noteworthy that although the absorption maxima of these bands lie in the range of 560–630 nm, the tails of the bands usually extend to 800–900 nm, i.e., to the near-IR spectral region. An analogous spectral pattern is also characteristic of the type **18** indoaniline dyes[19] whose structure and therefore nature of the electronic transitions are similar to those of quinoneimine **1b**. According to intermediate neglect of differential overlap/(INDO/S) calculations,[20] an essential role is played by charge transfer from the imino nitrogen lone electron pair to the lowest unoccupied molecular orbital (MO) of the molecule. The greater the acoplanarity of the molecule, the longer the absorption wavelength. As is the

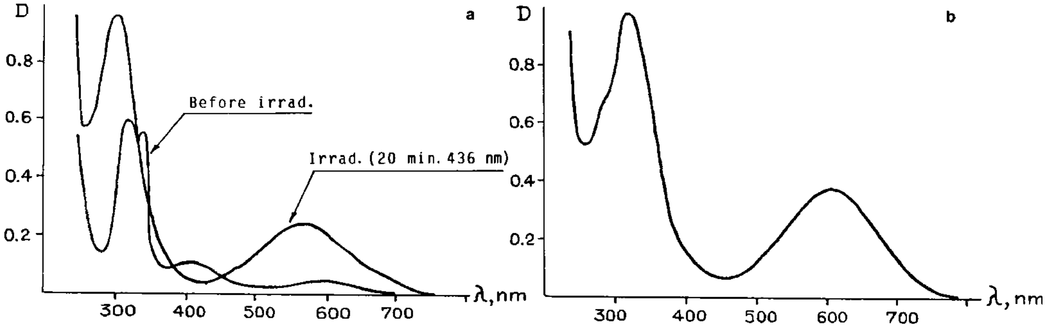


Figure 8.6. Absorption spectra of perimidinespirocyclohexadienones in octane solution: (a) **1** (R = H) (c = 2 x 10^{-4} M) before and after irradiation at the long-wavelength band of the spirocyclic isomer **1a** (b) Compound **12** stable in the quinoneimine form (c= 1 x 10^{-4} M).[18]

case of indoaniline dyes **18**, relatively small extinction coefficients are characteristic of the photoisomers of **1**, which is in agreement with the close structural similarity of molecules **18** and **1b**.

The data currently available on the rates and quantum efficiency of the photocoloration reactions **1a** → **1b** of perimidinespirocyclohexadienones and their analogs are rather scarce. The values of the quantum yield for the photoconversion of compound **1a** under excitation at its long-wavelength absorption band were determined with the use of the Aberchrome™ 540 actinometer. These are given in Table 8.3.

The values of Φ measured for solutions in octane are close to those typical of many spiropyrans[17,21] and fulgides.[22] It is noteworthy that in acetonitrile solution, the quantum efficiency of the photocoloration reaction is substantially lower. No significant photobleaching was observed, while thermal bleaching was found to be very slow (see Section 8.4). Triplet quenchers tend to slow down but do not inhibit the photocoloration reaction. This observation indicates that the main channel of the light-initiated ring-opening reaction relates to the first excited singlet state of the spirocyclic structure **1a**.

Compounds **1, 4–9** exhibit photochromism not only in solution and polymeric films, but also in solid vacuum-deposited thin films, which property is known to be of particular importance for materials used in erasable optical disks, optical memory media, and light-triggered molecular switching devices.[19, 23] By evaporation under a pressure of about 10^{-5} torr at 250–450°C at a rate of 3–30 Ås^{-1}, stable amorphous films of perimidinespirocyclohexadienones and their analogs were deposited on fused quartz or KBr substrates. When exposed to UV light, they showed reversible spectral changes similar to those portrayed by Figures 8.1 and 8.4. Figure 8.6 features the photochromic properties of perimidinespirocyclohexadienone **1** (R = H and R = Me) as displayed by their thin solid vacuum-deposited films.

Relative rates of photocoloration ("colorabilities"[24]) have been determined as slopes of the $D(t) - t$ absorbance curve obtained by measurement of the rate of

Table 8.2. Position and Extinction Coefficients of the Longest-wavelength Absorption Band of Type **1b** Photoisomers of Perimidinespirocyclohexadienones and their Analogs **4–9**[4, 7, 13–15]

Compound	λ_{max} (nm)	ε, 1 x M^{-1} x cm^{-1}	Solvent
1 (R = H)	584	5300	Octane
1 (R = Me)	620	4700	Octane
1 (R = Me)	602	3900	Acetonitrile
1 (R = Et)	626	4400	Octane
1 (R = Et)	602	3700	Acetonitrile
1 (R = Pr)	630	4600	Octane
1 (R = *i*-Pr)	607	4200	Acetonitrile
1 (R = *t*-Bu)	630	4200	Octane
1 (R = CH_2Ph)	611	4300	Octane
1 (R = CH_2Ph)	595	3900	Acetonitrile
4 (R',R'' = H)	571	4400	Octane
4 (R',R'' = $CH_2)_2$	616	4600	Octane
5 (R = H)	584	4600	Octane
6 (R = H)	569	3400	Octane
7 (R = H)	557	2100	Octane
8	580	4900	Toluene
9 (R,R' = H, Ar = $C_{10}H_7$)	556	6700	Toluene
9 (R,R' = H, Ar = C_6H_4Me-*o*)	535	3100	Ethanol
9 (R,R' = H, Ar = C_6H_4Me-*p*)	560	7000	Octane
9 (R,R' = H, Ar = C_6H_4Me-*o*)	559	6500	Octane
9 (R,R', Ar = H)	552	4300	Octane
9 (R, Ar = H, R' = Me)	597	1700	Benzene
9 (R = Me, R', Ar = H)	560	6700	Benzene
12	614	4700	Octane

Table 8.3. Quantum Yields (Φ, mole x $einstein^{-1}$) of the Photochromic Reaction **1a** → **1b**[a]

R	Octane	Acetonitrile	Polystyrene
Me	0.24	0.06	0.12
Et	0.42	0.06	0.19
Pr	0.38	0.05	0.13
CH_2Ph	0.26	0.06	0.08

[a] Irradiation at 365 nm, intensity of illumination 1.02 x 10^{16}photons/s.

evolution of intensity of the long-wavelength absorption band upon irradiation of thin solid films by the light of a high-pressure mercury lamp at 365 nm. The homogeneity of the films under study was tested by scanning their interference patterns along two orthogonal coordinates with the use of a polarization microscope. Only those films were selected that fully absorbed the UV light at 365 nm. Figure 8.7 shows the absorption time curves for the perimidinespirocyclohexadienone **1a** (R = H and R = Me) in comparison with those obtained in identical conditions for

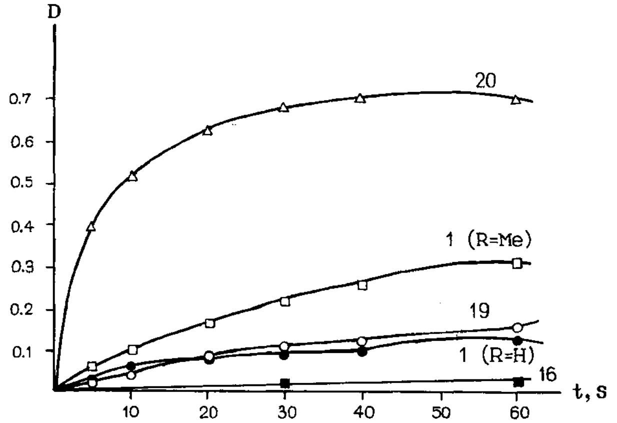
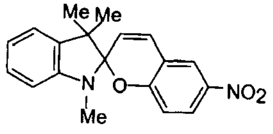


Figure 8.7. Changes in optical densities of vacuum-deposited thin solid films of compounds **1a** (R = H), and **1a** (R = Me), spiropyrans **19, 20,** and a model compound **16** (photochemically inert) measured at the absorption maxima of the long-wavelength absorption band of the photocolored isomers as a function of time of irradiation (high-pressure mercury lamp DRSH-250, 365 nm). Relative colorabilities of the compounds, A_{rel}, were calculated to be equal to **19** (6-NO_2BIPS) = 1; **1** (R = H) = 0.9; **1** (R = Me) = 3.2; **20** = 2.1.



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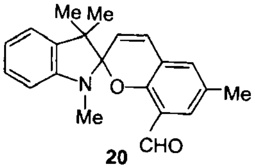

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two representative spiropyrans. One can see that the colorability of compounds **1** in the solid state is of comparable value to that of the standard,[17] 6-nitro-1',3',3'-trimethylspiro[2H-1]lbenzopyran-2,2'-indoline (6-NO_2-BIPS), **19**, and even the indolinespiropyrans bearing an 8-formyl group in their 2*H*-chromene ring (e.g., **20** that showed highest colorabilities in vacuum-deposited solid films.[25] However, in solid polystyrene or poly(methyl methacrylate) films, the colorabilities of perimidinespirocyclohexadienones **1** are one to two orders of magnitude lower than those of spiropyrans.

8.4. THERMAL DECOLORATION REACTION

A peculiar feature of the photochromic behavior of perimidinespirocyclohexadienones and their structural analogs is an extremely slow thermal bleaching of the colored quinoneimine photoisomer **1b** caused by its conversion to the ring-closed form **1a**. The effective lifetimes of the colored isomers formed upon UV irradiation of solutions of perimidinespirocyclohexadienones in nonpolar solvents at room

Table 8.4. Effective Lifetimes (hours) of the Photocolored Isomers of Perimidinespirocyclohexadienone 1b (and the Derivatives **6**, **7**) at 298 K[a]

$$\mathbf{1a} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{1b}$$

Compound	Octane	Octane + Et_3N (40 :1)	Ethanol	Thin solid film
1 (R = H)	49	145	—	3.3
1 (R = Me)	0.2	21	—	5.2
1 (R = *i*-Bu)	15	122	1.5	—
6 (R = H)	77	96	—	—
7 (R = H)	0.9	1800	1.4	—

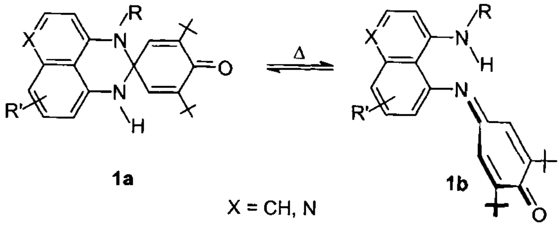
[a] Lifetimes measured by the rate of establishment of their thermal equilibrium with **1a** after irradiation of solutions of the latter by the light at the maximum of the long-wavelength absorption of **1a**: $\tau = 1/(k_{-1}-k_1)$.[18]

temperature range up to several days. The slowness of the **1b** → **1a** decoloration reaction is determined mostly by inclusion of the Z–E configurational isomerization step **2b** → **2a** (Scheme 2), which is associated with the high-energy barrier process of internal rotation about the $C{=}N^+$ bond in **2b**. An alternative mechanism of the Z ⇄ E isomerization through the planar inversion of the dicoordinate nitrogen atom in the quinoneimine **1b** also requires surmounting a considerable activation barrier. Typically, the magnitudes of the energy barriers for the two above-mentioned stereoisomerizations fall into the range of 15–25 kcal/mol.[26,27]

Further retardation of thermal fading of the colored photoisomers is accomplished when strong bases (triethylamine, morpholine, or hydroxide ion) are added to their solutions. This effect[18] has its origin in the formation of a strong intermolecular hydrogen bond of an N–H with the external nucleophile, which impedes the intramolecular proton transfer at the **1b** → **2b** stage of the ring-closing reaction (Scheme 2). Table 8.4 contains an excerpt of the kinetic data available on thermal fading of the quinoneimine photoisomers of perimidinespirocyclohexadienones.

8.5. THERMO- AND SOLVATOCHROMISM

In a solid film, most of the perimidinespirocyclohexadienones and their derivatives are stable in the **1a** ring-closed form. Upon dissolution in nonpolar solvents, (e.g., hydrocarbons or tetrachloromethane), an equilibrium is gradually established between **1a** and the deeply colored **1b** quinoneimine isomeric form, whose appearance is detected from the characteristic long-wavelength absorption band in the region of 560–630 nm. Some of the perimidinespirocyclohexadienones that exist in a solid as purely spirocyclic compounds, such as **4** (R',R"=$-CH_2CH_2-$), **8**, **9**, fully convert to the quinoneimine form when dissolved



Scheme 8

in octane.[8, 13, 15] At the same time, the compound **9** (R = R' = H) represented in crystal by its quinoneimine form, exists in an ethanol solution as an equilibrium mixture of both ring-closed and ring-opened isomers. The position of the **1a** $\rightleftharpoons$**1 b** equilibrium depends strongly on the solvent in use and temperature of the solution, which defines, respectively, solvato- and thermochromic properties of perimidine-spirocyclohexadienones (Scheme 8). In proton donor and polar solvents (alcohols, acetonitrile, dimethylformamide), the equilibrium is shifted to the spirocyclic form, spirocyclic isomers of compounds **1** and **6** being the only isomers present in such solutions.[4,7]

Thermodynamic parameters of thermal equilibria of a number of **1** perimidine-spirocyclohexadienones (X = CH, N) have been determined by use of a dynamic ^{1}H NMR spectroscopy technique. Owing to the acoplanarity of the quinoneimine **1b**,[20] which is a general structural characteristic inherent in *N*-arylimines,[28] the tertiary butyl groups in these compounds are diastereotopic and are seen in the ^{1}H NMR spectrum as two distinct signals. By contrast, protons of both tertiary butyl groups in the spirocyclic isomer **1a**, which possesses a symmetry plane, form a common 18-proton signal. By measuring the redistribution of the intensities of these signals with changing temperature of the solutions, thermodynamic parameters of the **1a**$\rightleftharpoons$**1b** equilibrium have been determined for a number of perimidinespirocyclohexadienones. A typical pattern of the temperature evolution of the ^{1}H NMR spectra is exemplified by Figure 8.8 for the case of perimidinespirocyclohexadienone **1** (R = CH_2Ph, X = CH).

The time during which the thermal equilibrium between the interconverting isomers of perimidinespirocyclohexadienones is established is particularly long for the type **9** quinazoline compounds. The thermodynamic and activation parameters have been determined[15] for this equilibrium with the use of dynamic ^{1}H NMR spectroscopy. These are listed in Table 8.5. No concentration dependence of thermodynamic or kinetic parameters relevant to the thermal equilibria under consideration has been observed (in the concentration range of 10^{-3}–10^{-5} M), which is in agreement with the intramolecular character of these transformations (Scheme 9).

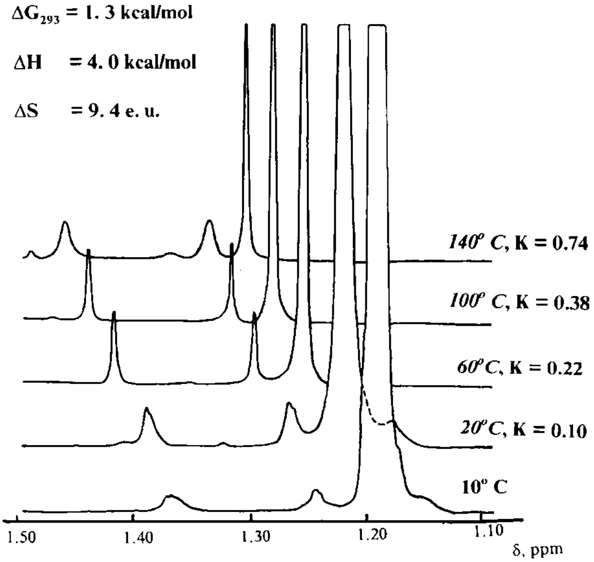
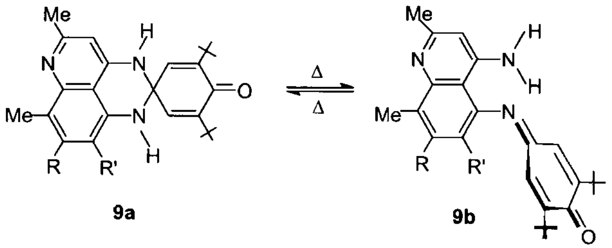


Figure 8.8. Temperature evolution of the 300-MHz ^{1}H NMR spectrum and thermodynamic parameters of the **1a** $\rightleftharpoons$ **1b** equilibrium of the perimidinespirocyclohexadienone **1** (R = CH_2 Ph, X = CH) in nitrobenzene-d_5 solution. The signal at 1.18 ppm belongs to equivalent *tert*-butyl groups of **1a**, whereas signals at 1.24 and 1.37 ppm originate from the protons of diastereotopic *tert*-butyl groups of the quinoneimine isomer **1b**.

Table 8.5. Thermodynamic and Activation Parameters of the Equilibrium **9a**$\rightleftharpoons$**9b** in Nitrobenzene-d_5 Solution

Compound	K_{293} = [**9b**]/[**9a**]	Δ*G*# (kcal/mol)
R = R' = H	0.37	22.5 (423 K)
R = Me, R' = H	0.64	24.0 (453)
R = H, R' = Me	0.06	—

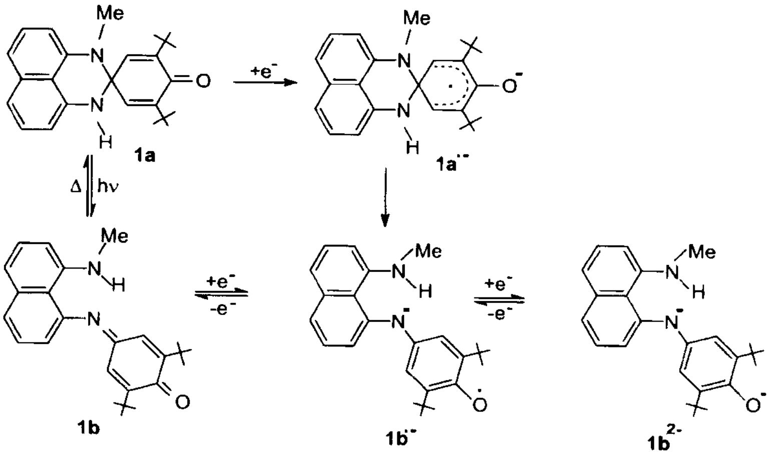


Scheme 9

8.6. INTEGRATED PHOTOCHROMIC AND ELECTROCHROMIC PROPERTIES

The photoinitiated rearrangement of **1a** to **1b** results in the establishment of conjugation between the two lateral moieties of a perimidinespirocyclohexadienone molecule, which causes drastic changes in the electrochemical properties of the interconverting isomers. This makes possible light-triggered switching of redox and electronic conduction properties of solutions of **1**. By use of cyclic voltammetry, it was found[29] that the initial spirocyclic isomer **1a** requires a very high negative potential (E_p^r = – 2150 mV vs. ferrocene) for its irreversible two-electron reduction to the dianion. The reduction proceeds as a multistep process consisting of electrochemical and chemical substeps. The latter process is due to the valence isomerization occurring at the radical anion stage, **1a**$^{\cdot-}$ → **1b**$^{\cdot-}$. The acceptor capability of the compound is raised to the extent that the redox potential for dianion formation of the quinoneimine form becomes more positive than E_p^r, so that **1b**$^{\cdot-}$ is immediately reduced further to **1b**$^{2-}$ at the existing electrode potential. After the potential scan is reversed, two distinctly separated voltammetric signals appear that correspond to the oxidation of **1b**$^{2-}$ via **1b**$^{\cdot-}$ to **1b**. This reaction course was confirmed by a UV/VIS/near-IR spectroelectrochemistry technique[30] that made it possible to also observe the thermal back reaction of the electrochemically formed quinoneimine **1b** to its spirocyclic isomeric form 1a.

This observation proved the complete reversibility of the overall cycle. The absence of side reactions during the transformations is characterized by isosbestic points. The overall process **1a** → **1b**$^{2-}$ → **1b**$^{\cdot-}$ → **1b** induced by reduction/oxidation is summarised in Scheme 10.



Scheme 10

Table 8.6. Reduction potentials, $E_{1/2}$ (vs. ferrocene), and Position of the Absorption Bands, λ, of the Perimidinespirocyclohexadienone **1a** (R = Me) and its Electrochemically Generated Ions.[a]

Compound	$E_{1/2}$ (mV)	λ (nm)
1a	– 2150[b]	229, 330, 340, 400
1b	– 1230	218, 304, 595
$\mathbf{1b}^{\bullet-}$	–1705	347, 525, 800
$\mathbf{1b}^{2-}$		209, 260 sh, 336,415

[a] Medium is acetonitrile/$Bu_4N^+PF_6^-$ (0.1 M). [b] Peak potential, irreversible.

Electrochemical and spectral data of the individual species and intermediates are summarized in Table 8.6.

The much less negative reduction potential of the conjugated quinoneimine isomer **1b** compared with that of its spirocyclic counterpart **1a** allows for potential application of this photochromic system as a light-to-electron conversion molecular device. By generating **1b** through irradiation of solution of **1a** in a spectroelectrochemical thin-layer cell under potentiostatic conditions and applying a potential at which **1b** is reduced to $\mathbf{1b}^{\bullet-}$, a cathodic current is observed as a signal, which decays after the light is extinguished [Figure 8.9(a)]. The slow decrease in amplitude for the subsequent light pulses is explained by the decrease in concentration of **1a** in the thin-layer cell.

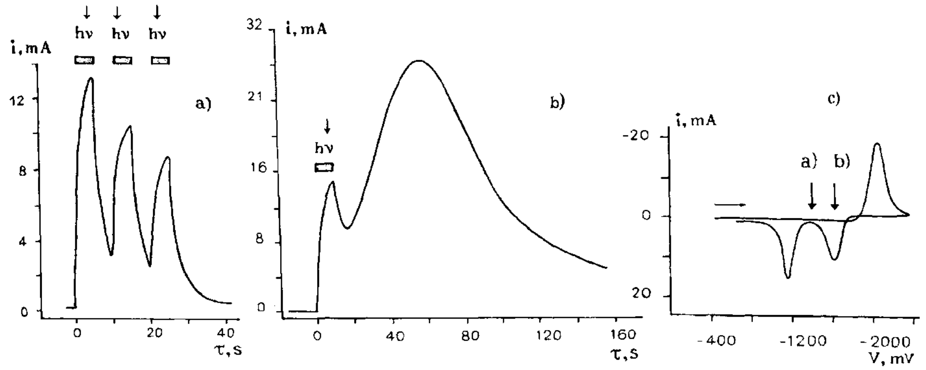
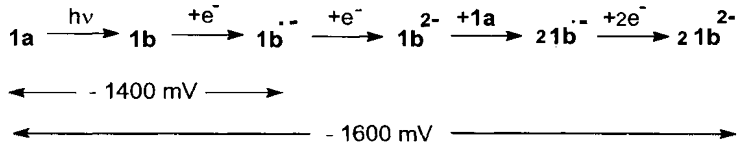


Figure 8.9. Photomodulated amperometry[29]: variation in the current signals on illumination of the acetonitrile/$Bu_4N^+PF_6^-$ 0. 1 M solution ($c = 2.5 \times 10^{-3}$ M) of **1a** (R = Me) with visible light (filter, Schott BG 14). (a) Working potential – 1400 mV vs. ferrocene. (b) Working potential – 1600 mV vs. ferrocene. (c) Record of the working potentials (a) and (b). (Reproduced with the permission of Wiley-VCH Verlag GmbH.)



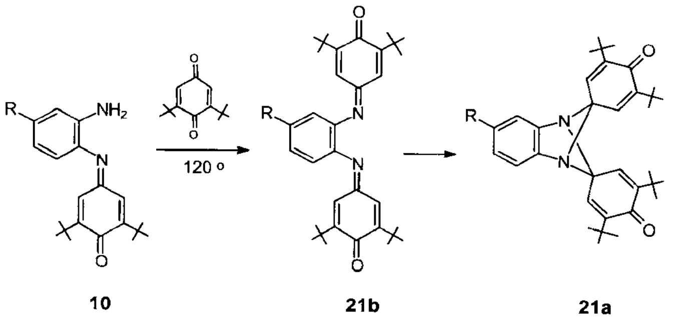
Scheme 11

If the working potential of the photomodulation amperometry is set at a value at which **1b** is reduced to the dianion, the curve shown in Figure 8.9(b) is obtained. A light pulse with duration of 10 s causes a steep increase in the current, which, however, does not drop to zero when the pulse is extinguished, but after an initial decrease rises to a new maximum before again decreasing slowly. The photomodulation thus indicates that the cathodically generated dianion **1b**$^{2-}$ accelerates the reduction of **1a**. Whereas in the experiments portrayed in Figure 8.9(a), only the first direct electrochemical reduction of the photochemically generated **1b** to **1b**$^{\bullet-}$ is responsible for the current, in the second the reduction of the photochemically generated **1b** proceeds to the dianion **1b**$^{2-}$ as well (Scheme 11). In the dark, the homogeneous cycle continues further: the **1b**$^{2-}$ formed reduces neutral **1a** with the formation of two molecules of **1b**$^{\bullet-}$. The **1b**$^{\bullet-}$ formed in this step is reduced further to **1b**$^{2-}$ at the electrode until the entire content of **1a** in the thin-layer cell is transformed. This is also in accord with the conclusion that the electrochemically induced valence isomerization of **1a** takes place at the radical anion stage, as shown in Scheme 10.

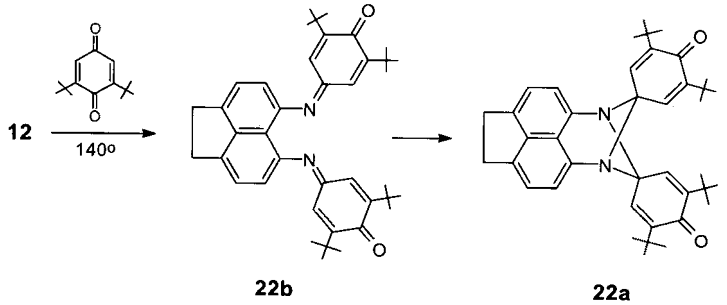
The experiments described reveal the potential of perimidinespirocyclohexadienones for the design of multiswitchable devices. Such molecular switching processes are considered to be crucial to the reversible modulation of a given physical property by means of a certain external trigger, in particular of light.[31-33]

8.7. PHOTOINITIATED INTERCONVERSION OF RING-CHAIN ISOMERS OF BIS-QUINONEIMINES DERIVED FROM AROMATIC DIAMINES

As stated in Section 8.2, the reaction between equimolar amounts of 2,6-di-*tert*-butyl-1,4-benzoquinone and such diamines as o-phenylenediamine and acenaphthylene-5,6-diamine stops at the stage of quinoneimines, respectively **10** (X = NH) and **12**. By heating these compounds with an excessive amount of 2,6-di-*tert*-butyl-1,4-benzoquinone or simply by melting together the diamines with the quinone taken in molar ratio 1:2 at 110-160°C for 4–7 h, condensation on the second amino group becomes possible, giving rise to the formation of both ring-opened and bis-spirocyclic isomers of bis-quinoneimines. The isomers can be chromatographically separated and isolated in the pure state. When allowed to stand in solution at room temperature, bis-quinoneimines derived from *o*-phenylenediamine slowly and those



Scheme 12

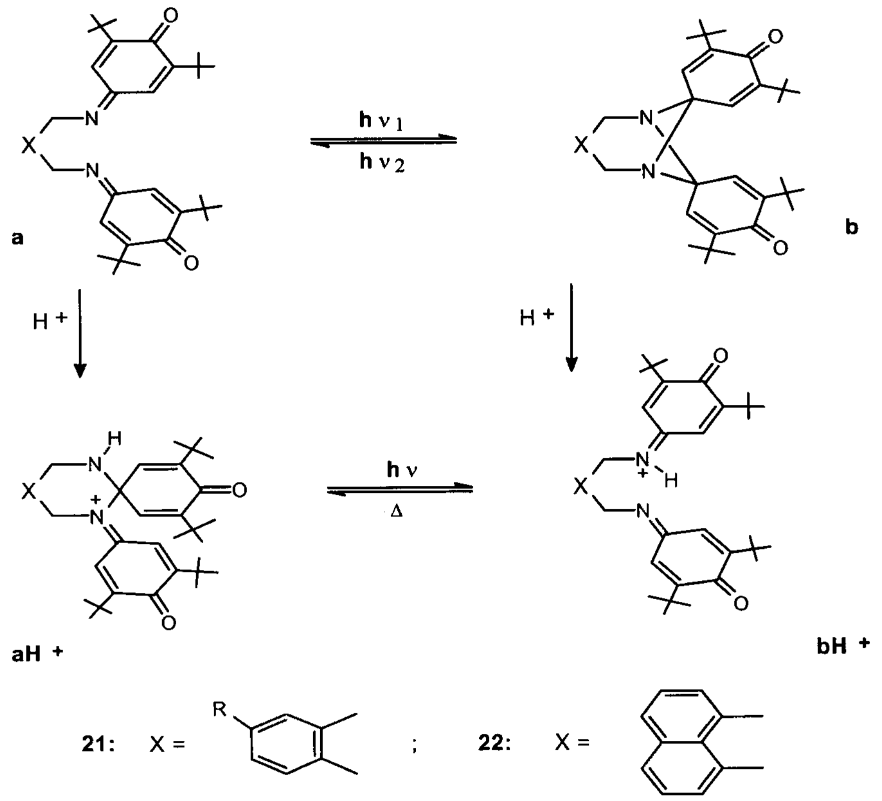


Scheme 13

derived from acenaphthylene-5,6-diamine rapidly convert to their bis-spirocyclic isomeric forms. These transformations are illustrated by Schemes 12 and 13.[34]

Upon irradiation of solutions of **21a** and **22a** with the light in their λ_{max} (high-pressure Hg lamp, glass filters), reversible isomerizations occur to form the photoisomers **21b** and **22b**. The back reactions cannot be thermally driven and proceed only on irradiation of the solutions of photogenerated colored isomers with the light corresponding to their absorption maxima. Spectral characteristics of the isomers of compounds **21** and **22** are given in Table 8.7.

Quantum yields for the interconversion of the photoisomers of compounds **21** and **22** were measured and found to be of very low value (less than 10^{-3}).Much greater are quantum efficiencies of the photochromic reactions of their cations formed by protonation of **21** and **22** upon addition of trifluoroacetic acid to solutions of these compounds in toluene. On activation by UV light, the cations **21aH**$^+$ and **22aH**$^+$ undergo rearrangements similar to that shown in Scheme 1, with the formation of the deeply colored protonated bis-quinoneimines **21bH**$^+$ and **22bH**$^+$, respectively. The structure of the latter was confirmed by identity of their UV/VIS spectra with those observed on protonation of solutions of bis-quinone-imines **21b** and **22b**. In contrast to the rearrangements of their conjugated bases



Scheme 14

Table 8.7. Spectral, Photochemical, and Kinetic Parameters of the Photochromic Reactions of bis-Spirocyclic Compounds **21** and **22** (toluene, 24°C) and their Protonated Forms (Formed by an Addition of 3–5 mol of Trifluoroacetic Acid)[34]

Structural type	**21** (R = H)	**21** (R = Me)	**21** (R = OMe)	22
a λ_{max} (nm)	474	484	502	535
($\varepsilon \times 10^{-3}$)	(8.8)	(8.5)	(12.0)	(9.2)
b: λ_{max} (nm)	593	602	597	665
($\varepsilon \times 10^{-3}$)	(8.0)	(7.8)	(12.0)	(19.6)
aH$^+$: λ_{max} (nm)	375	384	377	504
($\varepsilon \times 10^{-3}$)	(20.0)	(21.1)	(23.4)	(12.0)
bH$^+$: λ_{max} (nm)	803	810	766	833
($\varepsilon \times 10^{-3}$)	(7.0)	(7.3)	(9.9)	(11.3)
Φ (**aH**$^+ \rightarrow$ bH$^+$)	0.17	0.14	0.16	—
τ_{24} (**bH**$^+$), s	900	2400	1800	< 1

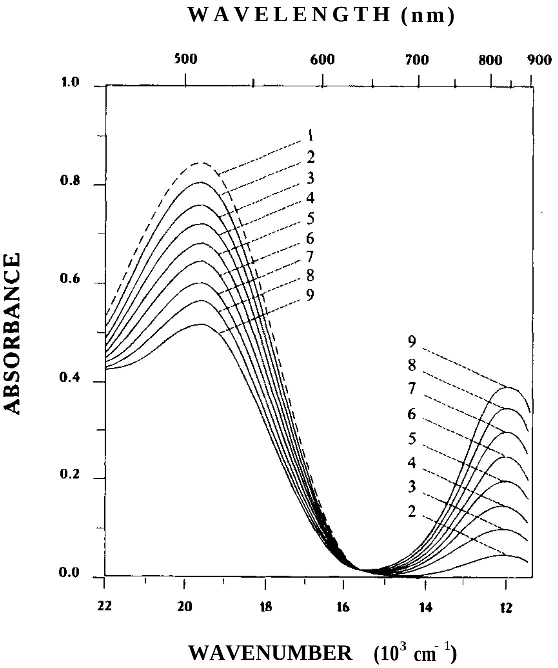


Figure 8.10. Changes in the absorption spectrum of **21aH**$^+$ (R = H) under irradiation of its toluene solution (c = 9 × 10^{-5} M; 16 μl of CF_3COOH were added to 1 ml of the solution) at 365 nm: 1, before and 2–9, after irradiation for 30, 60, 120, 240, 480, and 960 s.[34] (Reproduced with the permission of Gordon and Breach Publishing Group.)

triggered only by light, the back reactions of **21bH**$^+$ and **22bH**$^+$ readily occur as a thermal relaxation process. A generalized description of the photochromic rearrangements of compounds **21**,**22** and their protonated forms is given in Scheme 14.

It is worth noting that the longwave absorption bands of **21bH**$^+$ and **22bH**$^+$ are shifted bathochromically with respect to those of **21b** and **22b**. Table 8.7 contains some data on spectral and photochemical parameters of the novel photochromic systems described in this section. Photochromic behavior of one of the compounds is portrayed in Figure 8.10.

8.8. PREPARATIVE PROCEDURES

This section contains a brief description of the procedures for the synthesis of parent perimidinespirocyclohexadienone **1a** (R = H) and some of its derivatives.

8.8.1. 2,3-Dihydro-2-spiro-4′-(2′,6′-di-*tert*-butylcyclohexadien-2′,5′-one)-perimidine, 1a (R = H).[7]

A solution of 1,8-naphthylenediamine (4.74 g, 30 mmol) and 2,6,-di-*tert*-butyl-1,4-benzoquinone (6.6 g, 30 mmol) in propanol (10 ml) was refluxed for 5 h, then cooled to room temperature and diluted by water (20 ml). The crystalline precipitate formed was filtered off, washed with water, and dissolved in chloroform (15–20 ml). The chloroform solution was dried (Na_2SO_4) passed through a column (10 × 3 cm) filled with Al_2O_3, and the solvent removed under vacuum to give 4.46 g (yield 40.4%) of greenish-yellow crystals of **1a** (R = H), mp 163–165°C (from heptane).

^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.10 (s, *t*-Bu), 4.25 (s, NH), 6.40 (m), 7.12 (m).

8.8.2. 1-Methyl-2,3-dihydro-2-spiro-4´-(2´6´-di- *tert*t-utylcyclohexadien-2´5´one)perimidine, 1a (R = CH_3).[7]

To a solution of **1a** (R = H) 1.8 g, 5 mmol) and methyl iodide (2.84 g, 20 mmol) in dimethyl sulfoxide (10 ml), K_2CO_3 (6.9 g, 50 mmol) was added. The mixture was stirred for 10 h at room temperature and then poured into water (100 ml). The precipitate was filtered off, washed with water, dissolved in chloroform (10 ml), and passed through a column filled with Al_2O_3. The solvent was removed and a dark oily residue solidified on treatment with hexane. After two crystallizations from heptane, 1.12 g (yield 60%) of 1-methyl-2,3-dihydro-2-spiro-4´-(2´,6´-di-*ter*t-butylcyclohexadien-2´,5´-one)perimidine were obtained as yellow needles mp 179–l80°C.

^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.17 (s, *t*-Bu), 4.41 (s, NH), 4.68 (s, Me), 6.58 (m) 7.34 (m).

8.8.3. 2,3-Dihydro-2-spiro-4´-[(4*H*)-2´-*ter*t-butylnaphthalen-1´-one]perimidine, 4 (R, R´, R´´ = H).[9]

A mixture of 1,8-naphthalenediamine (3.48 g, 22 mmol), 2-*ter*t-butyl-1,4-naphthoquinone (3.21 g, 15 mmol) and p-toluenesulfonic acid (50 mg) was melted together at 165-170°C for 4 h, cooled to room temperature and dissolved in chloroform (20 ml). The solution was passed through a column (40 × 3.5 cm) filled with Al_2O_3. The column was washed with chloroform–hexane (1 : 3) and the fraction of orange color collected. After evaporation of the solvent, dark-yellow crystals of 2,3-dihydro-2-spiro-4´-[(4H)-2´-*ter* t-butlnaphthalen-1´-one]perimidine (2.06 g, yield 47.8%) were obtained, mp 211-213°C (after recrystallization from methanol and heptane).

^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.00 (s, *t*-Bu), 4.45 (s, NH), 6.40 (s), 6.90 (s), 7.10 (m).

8.8.4. 5,7,9-Trimethyl-2,3-dihydro-2-spiro-4´-(2´,6´-di-*ter*t-butylcyclohexadien-2´,5´-one)-pyrido-[4,3,2-*d,e*]quinazoline, 9 (R’ = H, R = Me, Ar = H).[15]

A solution of 5-amino-4-chloro-2,6,8-trimethylquinoline (0.22 g, 1 mmol) and 2,6-di-*ter*t-butyl-4-aminophenol (0.35 g, 1.6 mmol) in *o*-xylene (5 ml) was refluxed for 3 h, then cooled to room temperature, diluted with chloroform (5–7 ml) containing 1 ml of saturated water solution of ammonia and allowed to stand overnight at room temperature. The solution was dried (Na_2SO_4) and passed through a column (30 × 1.5 cm) filled with Al_2O_3. The fraction of yellow color was collected and the solvent removed to give 5,7,9-trimethyl-2,3-dihydro-2-spiro-4'-(2',6'-di-*tert*-butylcyclohexadien-2',5'-one)-pyrido-(4,3,2- *d,e*]quinazoline (0.31 g, yield 75%) as bright yellow crystals, mp 240–242°C (from acetonitrile).

^1H NMR spectrum, δ, ppm (nitrobenzene-d_5): 1.37 (s, *t*-Bu), 2.40 (s, Me), 2.79 (s, Me), 2.85 (s, Me), 6.30 (s, NH), 6.53 (s), 7.02 (s), 7.04 (s).

Acknowledgment

We are grateful to our co-workers, whose names are given in the appropriate references.

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9

Photochromism by Electron Transfer: ‘Photochromic Viologens’

MASATO NANASAWA

9.1. INTRODUCTION TO PHOTOCHROMISM BY ELECTRON TRANSFER

Photochromic compounds functioning by an oxidation–reduction mechanism (electron transfer), especially a photoreduction mechanism, are known in inorganic materials such as silver halides, which are utilized in eyewear lenses. Although the number of organic photochromic compounds operating via electron transfer is fewer than those by isomerization, heterolytic (or homolytic) cleavage, and pericyclic reactions, several classes of compounds have been reported, such as thiazines,[1] viologens,[2] and polycyclic quinones.[3]

The reversible reaction based on electron transfer is illustrated in Figure 9.1. Generally, the electron acceptor (A) is represented as the dye component, and there is no mutual interaction between the two components (A and D) in the ground state. Upon irradiation, the electron affinity of A or the ionic potential of D goes up or down, respectively. The resulting two components combine moderately to lead to an exciplex ([A–D]*). The electron transfer from D to A in the exciplex induces a charge separation without any external energy to produce a charge transfer complex or a radical ion pair with a different absorption than that of the starting materials.

In the sequence of electron transfer induced by light, organic compounds exhibit the following characteristic features: (1) Spectral changes occurring during a reaction as illustrated in Figure 9.1 usually take place in the ultraviolet region, so that the color change is not visually apparent. (2) The thermal back electron transfer often proceeds at a rapid rate (the observation of spectral changes is often limited except through special techniques such as flash photolysis). (3) Highly sensitive

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Masato Nanasawa • Yamanashi University, Takeda 4, Kofu, Yamanashi, 400 Japan

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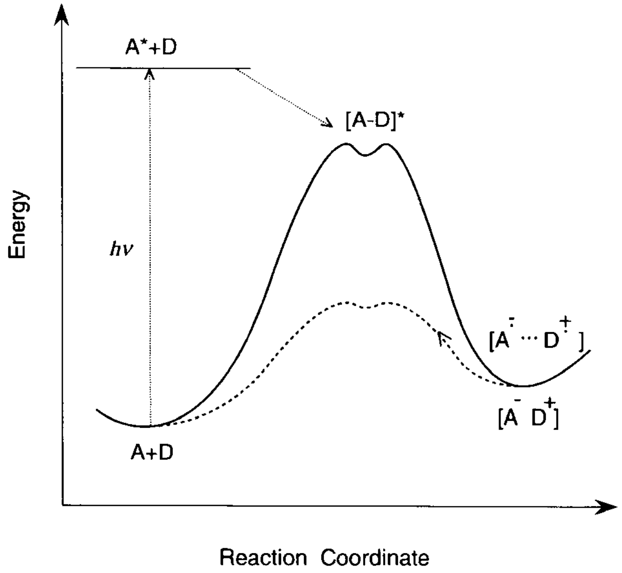


Figure 9.1. Photochromism via electron transfer.

radical ions are readily oxidized by molecular oxygen to regenerate the starting material or other oxidation products.

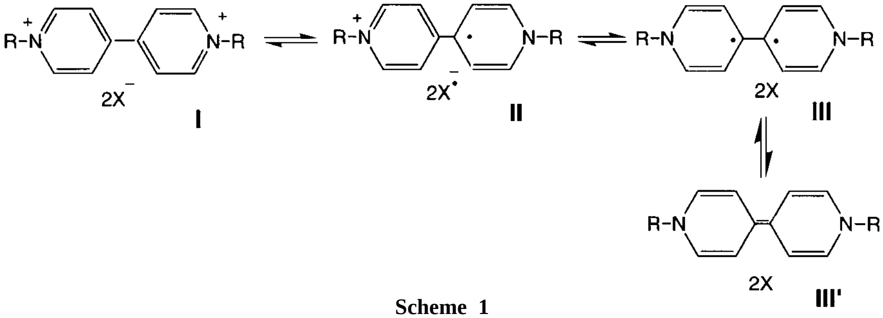
In order for the color state to persist for an extended time, a charge separation of the photogenerated ions must be produced such as that in a photosynthetic process in biological systems. Also, the rate of reverse electron transfer can be retarded by the presence of an external field.

This chapter relates to the photochromism of viologens and thionine dyes proceeding by electron transfer. The colored species spontaneously disappear in a liquid phase, because the rate of back electron transfer (dotted line in Figure 9.1) is rapid and is accelerated by the existence of oxygen in the system. If the compound is dispersed in a solid-state or layered system, the reversible reaction can be controlled. Since the color development via electron transfer is generally very rapid and the reverse electron transfer can also be carried out electrochemically,[4] the combination of both photoreduction and electrooxidation will receive much attention for application in recording devices.

9.2. PHOTOCHROMISM OF VIOLOGENS

9.2.1. Introduction

Colorless viologens composed of diquaternary salts of 4,4'bipyridine(I), 2,2'-bipyridine, and 1,10-phenanthroline turn into a violet-blue radical cation(II) by one-electron reduction,[5] and are further reduced to the yellowish quinonoid(III') via the biradical (III) (Scheme 1).



Scheme 1

Figure 9.2 illustrates a cyclic voltammogram of an *N*,*N*′-dialkyl-4,4′-bipyridinium salt and the corresponding transmittance at 560nm attributed to a dimeric radical cation.[6] The first reduction potential of viologens is at approximately –500mV. The potentials are relatively low compared with other organic compounds. Viologens have been used as herbicides and recently have received much interest as electron mediators for application in photoconversion.

The one-electron reduction in Figure 9.1 also takes place by photoreaction in the presence of appropriate reductants, such as alcohols.[2] The photoreduction does

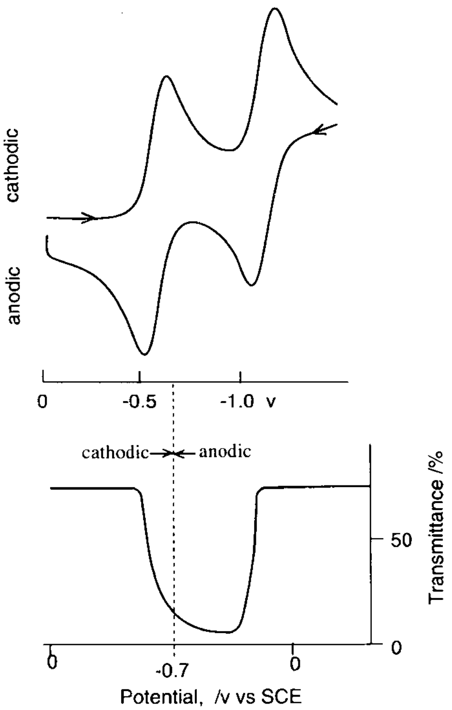
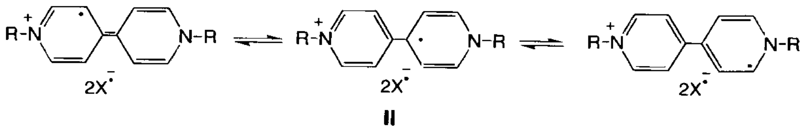


Figure 9.2. Cyclic voltammogram and the corresponding absorption change of 4,4′-viologen in acetonitrile containing tetrabutylammonium perchlorate.



Scheme 2

not proceed to the biradical state, because the difference in reduction potential between II and III is relatively large. The radical cation, II, produced by one-electron reduction, is stabilized by delocalization within the π-conjugated system of two pyridinium rings as in Scheme 2. However, the radical is highly oxidation-sensitive, so that the color development in solutions needs to be carried out free of air oxygen.[7]

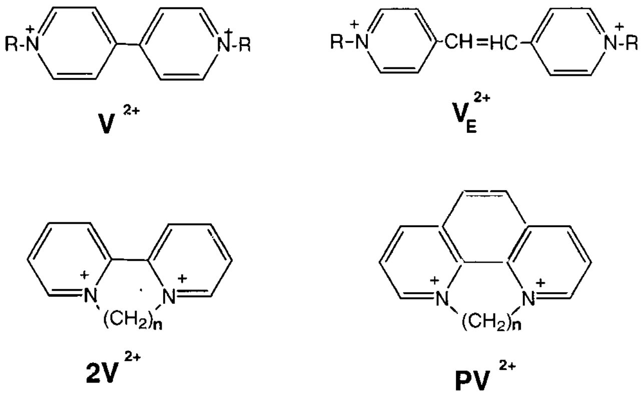
When viologens are embedded in appropriate polymer matrices, the viologen cation radicals are stabilized by the surrounding solid matrices through restriction of both air-oxidation and the thermal reverse-electron transfer. The resulting color changes in thin polymer matrix films can often be observed visibly upon exposure to ordinary sunlight or a steady-state irradiation.[8]

This section relates to the reversible color change of viologens via a photoreduction mechanism principally in the solid state. The effect of the kind of viologens (bipyridinium rings and counteranions) and polymers on photochromism is discussed. The viologens and their abbreviation under discussion in this section are given in Scheme 3.

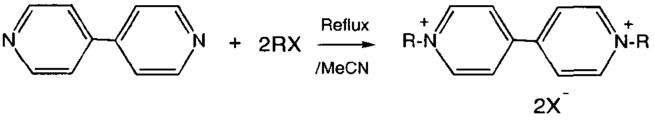
9.2.2. General Synthetic Methods

Viologens, V^{2+}, V_E^{2+}, $2V^{2+}$, and PV^{2+} are prepared by the Menschutkin reaction of the corresponding bipyridines with alkylhalide (or dihalide) as in Scheme 4.[9] *N*-Arylviologens are prepared by sequential reactions ending with the replacement of an activated 2,4-dinitrophenyl substituent with arylamine (Scheme 5).[10]

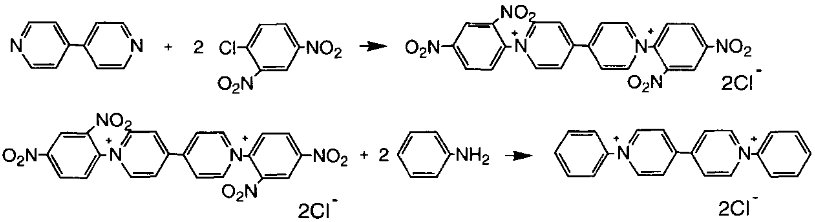
The anion-exchange reaction of the counterion in viologens is performed from the corresponding halides using an anion-exchange resin loaded with a given anion.



Scheme 3



Scheme 4



Scheme 5

Polymer films containing viologens are prepared as follows: a matrix polymer (0.5 g) is dissolved in water (5 ml). A viologen is then dissolved in the polymer solution to afford a 0.1 mol/liter concentration. The resulting solution (0.5 ml) is spread over a glass plate so as to afford a 1.2 × 2.0cm area, followed by drying overnight at room temperature. The plate is then stored in a dark desiccator held at constant relative humidity at least overnight before use. In the case of the preparation of glass-sandwiched films, a thin-layered film dried to a tacky appearance is covered tightly with another glass plate to exclude the effect of atmospheric oxygen, followed by drying for 1 week to afford an almost airtight film ranging in thickness from 0.005 to 0.1 mm.

9.2.3. Photochromic Behavior

9.2.3.1. Effect of Matrices on Photochromism

Figure 9.3 indicates the spectral changes of films with *N,N′*-dibenzyl-4,4′-bipyridinium dibromide (Bzl-$V^{2+}Br_2^{2-}$) embedded in poly (*N*-vinyl-2-pyrrolidone) (PVP) when irradiated with a 75-W high-pressure mercury lamp.[8] The absorption maximum appearing at 610nm was attributed to the monomeric viologen radical cation.[11,12] The result was quite different from the λ_{max} at 560nm, which appeared after electroreduction in solution. Presumably this was due to the lack of aggregation of the viologen radical cation in the polymer solid compared with the behavior in solution. When irradiation was stopped, the color faded to the almost colorless state by oxidation either with the radical anion or atmospheric oxygen.

Table 9.1 summarizes the effects of N-substitution and counterions on the photochromic behavior of viologens. The rate of electron transfer decreased with N-substitution as follows: dibenzyl > benzyl, propyl > dipropyl; and with the counter-anion, $C1^-$ > Br^- > I^- > BF_4^-. The order is consistent with the first dark redox potentials determined with sodium dithionite in aqueous solution.[13]

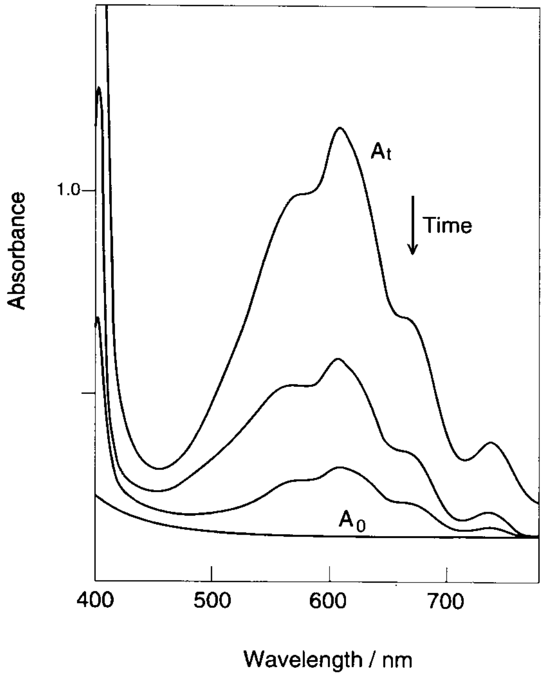


Figure 9.3. Spectral change of PVP film with Bzl-V^{2+} $Br_2{}^{2-}$ exposed to UV light. A_0, before irradiation and after complete recovery; A_t, 60-s irradiation at 15 cm from the lamp.

Table 9.1. Effect of N-Substitution and Counteranion on Photoreduction Rate

4,4′-Viologen[a]			Potential[b]	Absorbance [c]		
R	R′	X^-	(mV)	20	60	A_{20}/A_{60}[d]
Bzl	Bzl	Br	54	0.88	1.58	0.56
Bzl	Pro	Br	9	0.71	1.50	0.47
Pro	Pro	Br	−6	0.40	1.58	0.25
Pro	Pro	Cl	29	0.58	1.46	0.46
Pro	Pro	I	−86	0.16	0.58	0.28
Bzl	Bzl	BF_4	−266	0.35	0.88	0.40

[a] R,R′: *N*,*N*′-substitution group; Pro = propyl; Bzl = benzyl.

[b] First dark redox potential, determined with sodium dithionite.

[c] Absorbance (610nm) on 20-s and 60-s irradiation in poly (*N*-vinyl-2-pyrrolidone) (PVP). Irradiated from 5-cm distance with a 75-W mercury lamp.

[d] Ratio of absorbance at 20-s to 60-s irradiation.

It is well known that an anion of large molecular size serves as a good nucleophile in polar aprotic solvents and its nucleophilicity decreases with an increase in the protic property of the solvent. Accordingly, polar groups in polymer matrices could affect the photoelectron transfer in viologen molecules. Table 9.2

Table 9.2. Effect of Polymer Matrix on Photoreduction[a]

	Absorbance at irradiation time (s)[b]			
Matrix	30	60	90	*t*½[c]
PVA	0.12	0.24	0.34	60
PAM	0.00	0.04	0.04	40
PDMA	0.13	0.38	0.56	10
PVP	0.49	1.18	1.47	10

[a] Viologen: *N*,*N*′-dipropyl-4,4′-bipyridinium dibromide (Pro-$V^{2+}Br_2^{2-}$); PVA = poly(vinyl alcohol), PAM = poly(acrylamide), PDMA = poly(*N*,*N*-dimethylacrylamide).
[b] Value at absorbance maximum (610nm).
[c] Half-recovery time (min, 50% recovery).

Table 9.3. Effect of Relative Humidity on Photoreduction.[a]

Matrix	RH[b]	Irradiation time (s)	Absorbance
PVP	30	20	0.91
	58		0.74
	84		0.72
PDMA	30	40	0.43
	58		0.33
	84		0.29
PVA	30	20	0.09
	58		0.06
	84		0.06

[a] Bzl-$V^{2+}Br_2^{2-}$, from 5cm with UV lamp.
[b] 30% RH: oversaturated $CaCl_2$ solution; 58%: oversat. NaBr solution; 84% RH: oversat. KBr solution.

shows the effect of polymer matrices on photoreduction of Bzl-V^{2+}. The degree of formation of radical cations was in the order PVP > poly(*N*,*N*-dimethylacrylamide) (PDMA) > poly(vinyl alcohol) (PVA), and the amount of radical cations decreased with increasing relative humidity (RH) in the polymer matrices (Table 9.3). The extent of radical formation in both protic polymer matrices such as PVA and polymers containing a large amount of water was small compared with those in aprotic PVP and PDMA. This suggests that the photoelectron transfer of viologen was promoted by activation of the dication solvated with aprotic media and/or by the participation of the unsolvated naked anions.

Table 9.4 indicates the effect of the kind of aprotic solvents containing water on the color development of Bzl-V^{2+}. The shape and absorption maxima of the radical cation were quite similar to those in a polymer matrix (Figure 9.3).[14] Anhydrous N-methylpyrrolidone (NMP), with a poor solubility for viologens, afforded spontaneous color development and led to a small absorption change upon irradiation. This

Table 9.4. Effect of Kind of Solvent on Photoreduction

Solvent[a]	Solubility of viologen[b]	Absorbance[c]	
		A_0	A_1
MP	Very poor	0.29	0.07
MP/H_2O (9/1)	Significant	0.12	0.84
MP/H_2O (3/1)	Good	0.03	0.67
MP/H_2O (1/2)	Excellent	0.00	0.02
H_2O	Excellent	0.00	0.00
DMF	Significant	0.02	0.12
DMF/H_2O (9/1)	Good	0.02	0.18
DMSO	Good	0.00	0.02
DMSO/H_2O (9/1)	Excellent	0.00	0.00

[a] MP = N-Methyl-2-pyrrolidone, DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide.
[b] Bzl-$V^{2+}Br_2^{2-}$.
[c] A_0 = before, A_1 = after 1-min irradiation from 5 cm with UV lamp.

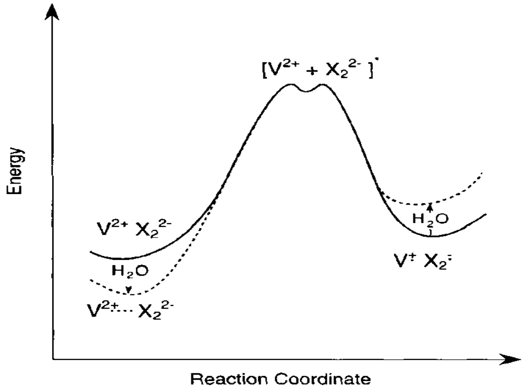


Figure 9.4. Relationship between energy and reaction coordinate indicating photochromism of viologen in PVP matrix film.

indicates that viologens in NMP are so highly activated that the electron transfer to the next reduction stage might have occurred, producing weakly colored dications, which are insensitive to light. The largest absorption change upon irradiation was obtained in NMP containing 10% water. Further addition of water induced a decrease in the absorbance owing to an increase in the hydrophilic character of the solvent. However, as can be seen from Table 9.4, the sensitivity decreased in polar aprotic solvent having a good solubility for viologens such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). In these solvents, the bipyridinium dication and the counteranion in the viologen might be dissociated. Therefore, the separated ions give less electron transfer. It is reasonable that photoelectron transfer is strongly affected by the proximity of two ions and occurs efficiently when viologens exist as ion pairs. Thus the photoreduction mechanism of viologens in polymer matrices is considered to proceed as illustrated in Figure 9.4.

Assuming from the low solubility (affinity) of viologens in NMP, $V^{2} + X_{2}^{2-}$ might be present as an ion pair so that the bipyridinium cation and counteranion are close together in the higher energy state, where anions might exist in an activated bare form. However, the films cast from aqueous solution contain water to a level of several percent, and PVP absorbs more water content at higher relative humidities. The presence of water in matrices reduces the potential energy of $V^{2+}X_{2}^{2-}$, presumably due to solvation of both dication and counteranion, leading to the separation of both ions as $V^{2+}\ldots X_{2}^{2-}$ in Figure 9.4. The depression of potential energy caused by the presence of water would prevent spontaneous color development, whereas its magnitude is not so large as to inhibit the generation of a radical cation upon irradiation. This is also shown by the fact that the addition of a small amount of water to an anhydrous NMP solution in which a viologen radical cation is spontaneously produced, still allowed color development upon irradiation. The further addition of water led to a decrease in photogeneration of radical cations. Thus, the ion pair, $V^{2+}X_{2}^{2-}$, with a high energy in PVP, could readily surmount the activation energy barrier upon irradiation via the exciplex ($[V^{2+}X_{2}^{2-}]^{*}$) to lead to the radical ion pair, $V^{+\cdot}X_{2}^{-\cdot}$. The radical cation thus formed possesses relatively good affinity for the PVP matrix to induce the stabilization of the color species.

The presence of water in PVP decreases the stability of the radical cation to favor the thermal back electron transfer, because the radical cation has relatively low solubility (affinity) in water. Figure 9.4 shows the extreme energy curves, both in the absence of water and in the presence of a substantial amount of water in PVP matrices. Actual photoreduction of viologen slightly hydrated with water might proceed between both lines in a PVP matrix.

The dark reaction takes place either by thermal back electron transfer from the radical cation to a counter radical anion, or oxidation of a radical cation with molecular oxygen when the film is exposed to air. The degree of thermal back reaction or air-oxidation is strongly dependent on the structure of the viologen and the kind of matrix polymer.

9.2.3.2. A Variety of Color Species of Viologens

The developed colors and absorption peaks of V_{E}^{2+}, $2V^{2+}$, and PV^{2+} are very different from those of the conventional 4,4'-viologen, such as Bzl-V^{2+}, and the photosensitivity of each depends strongly on its chemical structure.[15,16]

Since the photoreduction of viologen is induced by electron abstraction (oxidation) by the excited bipyridinium cation from the counteranion, it is difficult to relate the photoelectron transfer to the dark redox potential. However, the photosensitivity for the same skeleton is almost proportional to the first dark reduction potential, as mentioned in the previous section. The degree of solvation

Table 9.5. Absorption Maxima of Viologen[a]

Viologen[b]	Redox potential[c] (mV)	Irradiation[d] time	λ_{max} /nm	Absorbance[d] λ_{max}/nm	
				A_0	A_t
V^{2+}	–360	20s	610	0	0.88
$V_E{}^{2+}$		30s	525	0.03	0.82
$2V_E{}^{2+}$	–365	2 min	750	0.05	0.52
$2VP^{2+}$	–555	5 min	—	—	—
PV^{2+}	–240	2min	441	0.10	0.11

[a] PVP matrix, from 5cm with UV lamp.
[b] Abbreviation denoted in Scheme 3.
[c] Value vs. SCE cited in Ref. 17.
[d] A_0 = before irradiation, A_t = after irradiation for time *t*.

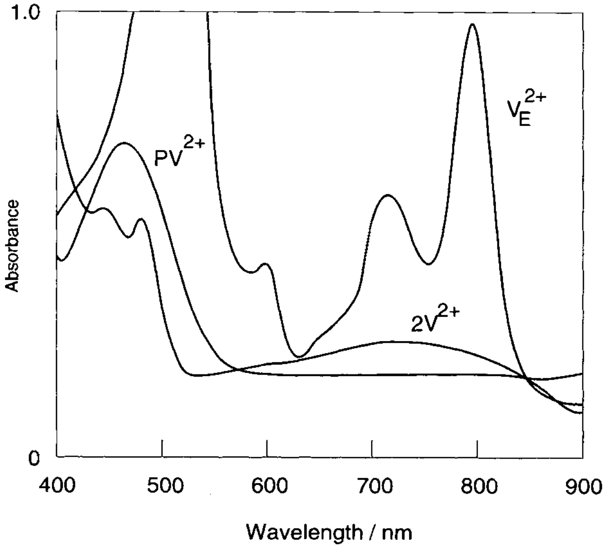


Figure 9.5. Visible absorption spectra of PVP film with various viologens exposed to UV light. Absorption spectra given qualitatively as for absorbance in order to make comparisons easier.

in polymer matrices is dependent on the skeleton of the bipyridinium cations. In this way the sensitivity to UV light might also be affected by the extent of solvation as well as the difference in redox potential. Table 9.5 summarizes the photosensitivity in PVP matrix against the dark redox potential of viologens with different bipyridinium structures, and Figure 9.5 shows typical visible absorption spectra when subjected to near-UV irradiation. PV^{2+}, possessing a higher first redox potential, spontaneously generates the radical cation and color fading does not occur, while viologen, $2VP^{2+}$ possessing a low redox potential, does not exhibit any color development. This result suggests that the first redox potential of viologens affording photochromism in PVP matrix should be in the range of about –0.3 to –0.5V [vs. saturated calomel electrode (SCE)].[17]

The color developed by photoreduction is also affected by the viologen structure, as shown in Figure 9.5. The compound V_E^{2+} is similar to the principal structure of V^{2+} except that the two pyridine rings are linked by an ethylene bridge. The shape of the absorption bands of the radical cation is the same as that of 4,4'-viologen, whereas both peaks of V^{2+} at 400 and 610 nm shift to longer wavelengths, which may be a consequence of the extension of the delocalization of the π-conjugated system in the radical cation. Thus the color of a PVP film of V_E^{2+} upon irradiation turns green through absorption at 525 and 720nm. The visible absorption spectra for the 2,2'-bipyridinium radical cation in PVP matrix is entirely different from that of the 4,4'-one: the absorption of $2V^{2+}$ of the former shows a broad peak at higher wavelength. The delocalization of the radical electron might be affected by the planarity of the two pyridinium rings and by the corresponding electrostatic interaction between positive nitrogen atoms.

The absorption of the phenanthrolinium radical cation (PV^{2+}), which is inert to air and hardly affected by light, has the Gaussian shape characteristic of 2,2'-viologen. Its absorption band is strongly affected by the substitution on the phenanthroline ring. For example, a 2-methyl substituent near the quaternary nitrogen atom induced a blue shift of approximately 30nm compared with an unsubstituted one, presumably because of steric hindrance inhibiting the delocalization of the π-electrons of the radical cation. The absorption maximum of PV^{2+} was also affected strikingly by the kind of matrix: the films were yellowish orange, brown, and blue for poly(acrylamide) (PAM), PVA, PDAM, and PVA, respectively.

Thus it is possible to vary the absorption of viologens from the visible to the near-infrared region. The latter band has been of interest for devices using semiconductor lasers.

9.2.3.3. Photochromism of Molecular Assembly

Photochromic behavior of viologens also proceeds in a molecular assembly system, including 4,4'-viologens with N-substitution of long alkyl chains or with long alkyl anions as counterions. The viologens with long alkyl chains substituted on the nitrogens could be transferred to a layered form by means of the Langmuir–Blodgett method,[18] by crystallization,[12] or by a melting method.[19,20] The former methods usually do not afford films (sheets) with enough area; therefore the photochromic behavior of layered films prepared by melting methods has been well studied. However, the melting method is also limited by the structure of viologens for film preparation, because viologens have relatively high melting points and can decompose before melting. The N-substitution of long alkyl chain lowers its melting point, but a film of the material is not transparent. This causes a low quantum yield because of scattering and low absorption of the incident light.

4,4'-Viologens exchanged with benzene sulfonate anions having long alkyl side chains ($V^{2+}2ArSO_3^-$) possess relatively low melting points and afford transparent films without decomposition. Thus, films of a viologen assembly are prepared as follows: A fine powder of V^{2+} $2ArSO_3^-$ is heated just to its melting point under a nitrogen atmosphere and then sandwiched between two glass plates to afford a transparent thin film free of oxygen. Figure 9.6 indicates the possible molecular arrangement of the arylviologen by means of X-ray diffraction study.[20] From the observation using a micromelting apparatus equipped with a polarizer, these viologens exhibit a liquid crystal phase and display smectic A-type behavior by the comparison of texture phases, as shown in Table 9.6.

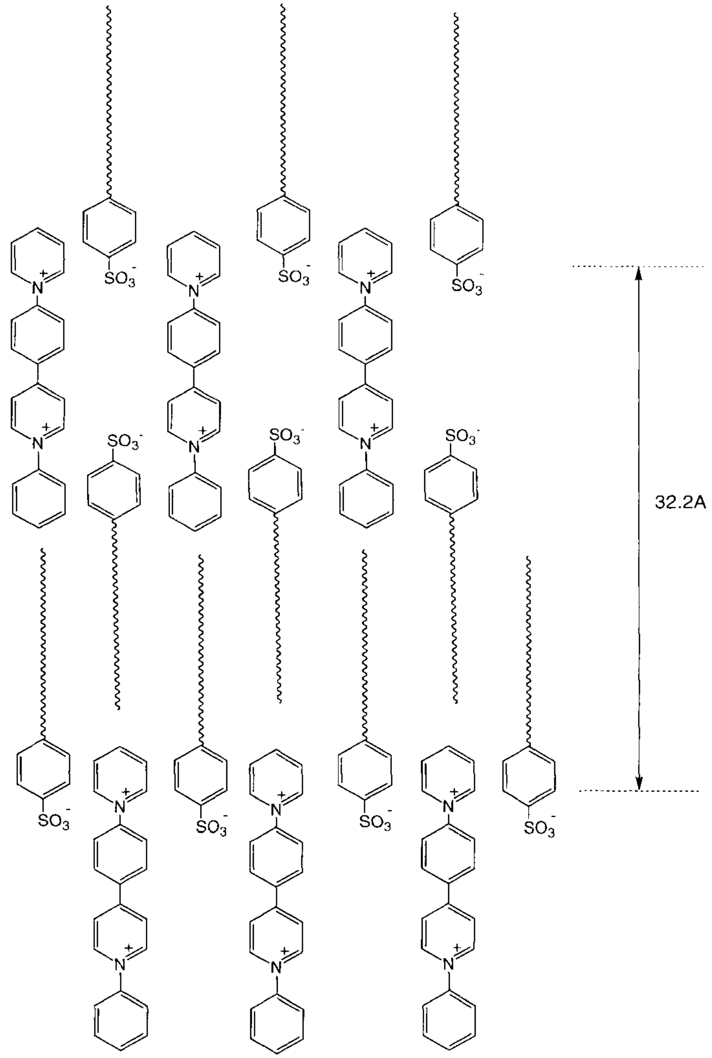


Figure 9.6. Possible molecular arrangement of layered arylviologen in Table 9.6.

Table 9.6. Phase Transition Temperature for Arylviologen[a]

Alkyl Chain in Counteranion	Phase Transition[b] Cry → Sm-A → Dec	
n-$C_{10}H_{21}$	205°C	285°C
n-$C_{13}H_{27}$	190	280
n-$C_{15}H_{31}$	168	290

[a] *N,N'*-diphenyl-4,4'-bipyridinium bis(alkylbenzenesulfonate).
[b] Cry = crystal, Sm-A = smectic-A, Dec = decomposed.

Upon irradiation with near-UV (366nm), initially colorless or pale yellow films gradually developed visible colors with almost linear increases in absorbances.[19] The photosensitivities of the viologen assembly were apparently lower than those of viologens incorporated in a polymer in which the viologen was activated by the surrounding aprotic media. The shape and position of the absorption maxima of the viologen with a highly branched alkyl anion are the same as those of the radical cations derived from the conventional 4,4'-viologens incorporated in polymer matrices (curve 1 in Figure 9.7). However, as can be seen from Figure 9.7, an increase in the anisotropic property of films decreased the characteristic absorption of monomeric radical cations at 610 nm, and the absorption spectra of viologens with a $C_{10}-C_{12}$ alkyl chain were almost consistent with those of the substantially associated radical cations.[7] Table 9.7 summarizes the effect of chain length of alkylbenzenesulfonate on the photoreduction of the layered viologen films.

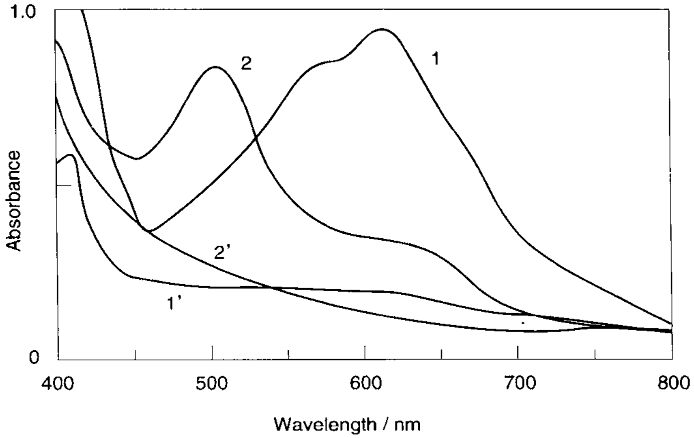


Figure 9.7. Typical visible absorption spectra for the glass-sandwiched viologen $V^{2+}\,2ArSO_3^{2-}$ upon UV irradiation: Curves **1** and **1'** indicate the spectra of films composed of highly branched alkylbenzene sulfonate after irradiation, and before irradiation or after complete recovery; curves **2** and **2'** are those of n-$C_{14}H_{29}$. Absorption spectra given qualitatively as for absorbance in order to make comparisons easier.

Table 9.7. Effect of Chain Length of R on Photoreduction of Viologen Layered Films

	Absorbance[b]			
R[a]	A_1/500	A_h/610	A_h/A_1	Property of film[c]
n-C_6H_{13}	0.362	0.190	0.52	A little anisotropic
n-C_8H_{17}	0.625	0.318	0.51	A little anisotropic
n-C_9H_{19}	0.788	0.421	0.53	Isotropic
n-$C_{10}H_{21}$	0.787	0.451	0.57	Isotropic
n-$C_{11}H_{23}$	0.783	0.441	0.56	Isotropic
n-$C_{12}H_{25}$	0.690	0.379	0.55	Isotropic
n-$C_{13}H_{27}$	0.571	0.279	0.49	Isotropic
n-$C_{14}H_{29}$	0.469	0.200	0.49	A little anisotropic
n-$C_{15}H_{31}$	0.360	0.179	0.49	A little anisotropic
n-$C_{12}H_{25}$[d]	0.242	0.798	3.30	Isotropic
Mixture[e]	0.612	0.522[f]	0.85	Isotropic

[a] Alkyl side chain of alkylbenzenesulfonate as counteranion of 4,4′-dibenzylviologen.
[b] Absorbance increase at ca. 500nm (A_1) and 610nm (A_h) induced with near-UV light, value reduced to 0.01-mm film thickness.
[c] Determined with crossed polarizers.
[d] 70% n- + 30% highly branched.
[e] Mixture of n-C_8H_{17}, $C_{10}H_{21}$, n-$C_{12}H_{25}$, and $C_{14}H_{29}$ in an equimolar quantity.
[f] Shoulder.

The absorbances at both 500 and 610nm, which appeared first, became larger with increasing number of carbons, reached a maximum of $C_{9–11}$, and then became smaller with further increases in the carbon number. Presumably this is due to crystallization (orientation) of the long alkyl chains. As shown in Figure 9.6, the dication and counteranion moieties in an anisotropic phase are situated next to each other at the site, and the distance between both ions is large compared with that in an isotropic (disordered) phase. Thus the electron transfer from counteranion to dication hardly takes place via the exciplex mechanism.

This hypothesis is supported by a comparison of the ratio of the absorbance at higher wavelength (A_h) with that at a lower one (A_1) in Table 9.7. The film possessing good photosensitivity had a large absorption at a longer wavelength assignable to a monomeric radical cation produced from the disordered state, whereas, with increasing anisotropic character of the film, the photosensitivity decreased., and the absorption of associated radical cations became large.

The color species developed by near-UV light are hardly affected by irradiation with visible light, suggesting that the back electron transfer is thermal in nature. This is promising for photo-memory, that is, color development by photon-mode and heat-mode bleaching.

9.2.3.4. Viologen Bearing a Metal Complex as Counteranion

Since photoelectron transfer of viologens proceeds from counteranions to dications in spite of the large difference of dark redox potentials between both ions (> 1.4V), the energy gap of both ions must become small in the excited state. The value of the quantum yield on photoreduction of V^{2+} is greatest upon irradiation with UV light at 320–330nm,[12] in which region there is no detectable absorption for halide ions. Therefore, color development is considered to be initiated by the excitation of the bipyridinium dication, and its electron affinity might rise to a considerable extent. This causes the electron transfer (or charge transfer, CT) from the counteranion (see Figure 9.1). When the counteranion of viologens is exchanged with a metal ion possessing a relatively low redox potential, the electron transfer can be controlled at both ground state and excited state as well as the back electron transfer. On the basis of this assumption, several kinds of viologen–metal complexes have been synthesized.[21,22]

The blue-colored V^{2+}-FeCl$_4$ complex decomposed in water or in methanol, and the solution became colorless, whereas a CT band appeared at 450nm in a mixture of ethanol and methanol (1 : 4), the absorption of which was not affected by near-UV irradiation. In contrast, a pale purple-colored aqueous solution of V^{2+} with K$_4$[Fe(CN)$_6$]$_4$ having a low redox potential turned an intense violet upon near-UV irradiation, and there was no absorption peak around 398nm, which is characteristic of a radical cation, as shown in Figure 9.8.

The compounds with [Fe(CN)$_6$]$^{4-}$ anions in Figure 9.8 were colored., varying from orange to pale green, and these colors gradually became deeper when exposed to air oxygen. A pale indigo blue Bu-V^{2+-} [Fe(CN)$_6$]$^{4-}$ solid turned to violet immediately upon dissolution in an aqueous solution. The absorption peak at 530nm, which was confirmed as due to a charge transfer complex,[23] shifted by approximately 5 nm to a longer wavelength compared with the equimolar mixture of V^{2+} X^{2-} with the externally added tetrakis-(hydroxyethyl) ammonium hexacyano-

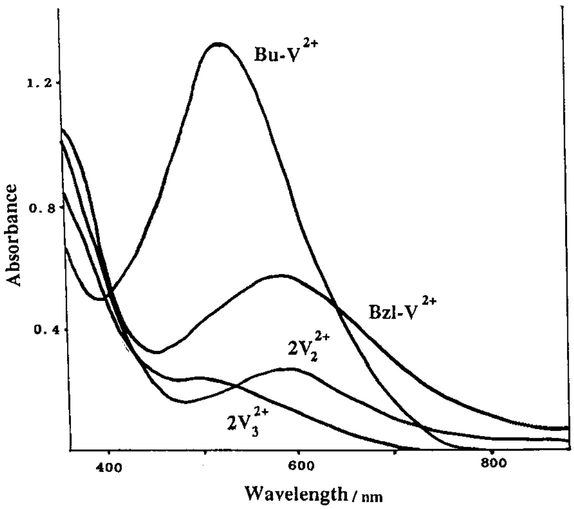


Figure 9.8. Absorption spectra of [Fe(CN)$_6$] complexes after UV irradiation: 1-min irradiation of 1% solution of complexes in water (1-mm pathlength cell).

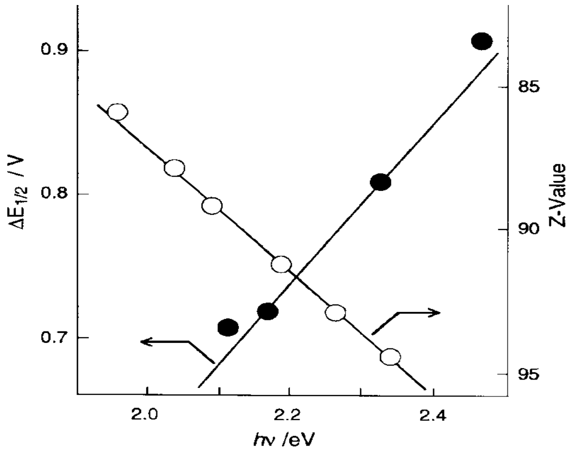


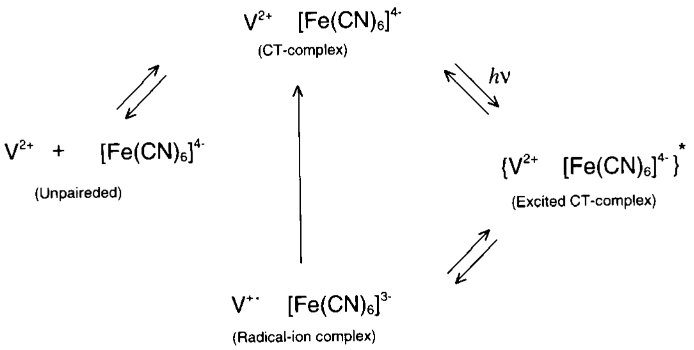
Figure 9.9. Relationship of the transition energy against the half-redox potential of viologens and the Z value of aqueous ethanol: 0.5% solution at 25°C.

ferrate (II). The red shift became larger with a higher ethanol content in solution. As can be seen in Figure 9.9, the linear relation between the Kosower Z value of aqueous ethanol and the band transition energy ($h\nu$) indicates that the complex exists in the π–δ structure.[24]

Benesi–Hildebrandt plots were linear in a low concentration range; however, the linear relationship did not exist between the transition energies and the difference in the half-redox potential of $2V^{2+}$. The solvation of 2,2′-bipyridinium dication is relatively small compared with that of the 4,4′-isomer possessing a symmetrical molecular structure. This decreases the electrostatic interaction to lead to a low transition energy. The CT bands for Bu-V^{2+} and Bzl-V^{2+} with $[Fe(CN)_6]^{4-}$ ions almost linearly increase in an absorbance upon near-UV irradiation, and the absorbance decreases progressively in the dark and even more rapidly upon heating.

Scheme 6 is proposed to account for the reversible color change in solution. The excited CT complex is generated from the ground-state CT complex by application of UV light, leading to the formation of the radical ion complex by intramolecular electron transfer. As can be seen from Figure 9.8, there is no absorption peak at around 398nm, which is characteristic of the viologen radical cation in the absence of oxygen, and the absorption is not affected by introducing air oxygen. The radical complex in solution might react even with $Fe^{III}(CN)_6$ ion. This would cause a spontaneous reverse electron transfer to generate the ground-state CT complex, which, upon standing in the dark, reaches equilibrium with the unpaired mixtures (Scheme 6).

The films cast from an aqueous polymer solution of these $[Fe(CN)_6]$ complexes became opaque with evaporating water in the polymer solution due to the low



Scheme 6

compatibility of the metal complexes with PVA and PVP.[25] The absorbances at the CT bands decreased with a decreasing water content in the polymer solution, and radical cation peaks appeared at longer wavelengths after evaporating the water. Figure 9.10 indicates the typical visible reflection spectra of $[Fe(CN)_6]^{4-}$complexes sandwiched tightly between two glass plates. Their spectral changes when the near-UV irradiation is stopped after 1 min are summarized in Table 9.8.

In the solid state, the intramolecular electron transfer to a naked dication may partly take place from the proximal hexacyanoferrate(II) anions. The extent of electron transfer at the ground state becomes large with an increase in the half-redox potential. The low photosensitivity for Bzl-V^{2+} in the solid state appears to be caused by the fact that the electron transfer already takes place in the ground state and/or the bulky hexaferrate (II) ion is barely brought close to the positive pyridinium nitrogens attached to the benzyl group possessing a relatively bulky molecular size.

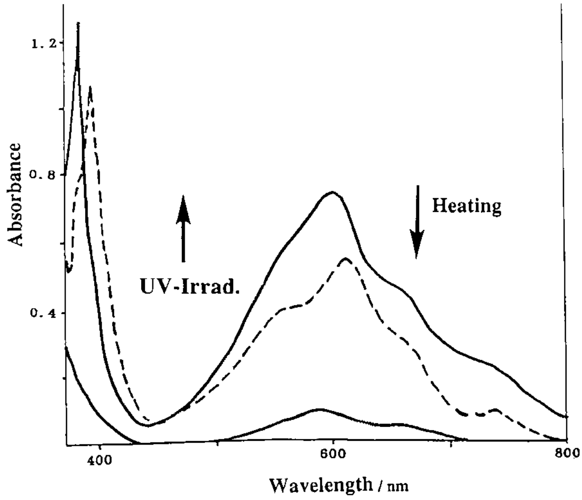


Figure 9. 10. Visible reflection spectra of Bu-V^{2+} -$[Fe(CN)_6]^{4-}$ complex in a PVA matrix. The dashed spectrum, Bu-$V^{2+}Br_2^{2-}$ under the same irradiation conditions.

Table 9.8. Visible Reflection Spectra of Viologen-$[Fe(CN)_6]$ Films Incorporated in Polymer Matrices

Viologen[a]	Appearance	λ_{max} (nm)	Absorbance[b]		$t_{1/2}$[c]	
			A_0	A_1	25°C (h)	60°C (min)
$2V_E^{2}$ /PVA	Pale green	680	0.12	0.12		
$2V_P^{2+}$/PVA	Pale orange	500	0.15	0.16		
BuV^{2+}/PVP	Pale orange	500	0.15	0.16	6	<1
BuV^{2+}/PVA	Pale blue	600	0.08	0.73	50	2
BzV^{2+}/PVP	Pale green	610	0.21	0.26	2	
BzV^{2+}/PVA	Pale green	610	0.17	0.20	3	

[a] Abbreviation of viologens denoted in Scheme 3.
[b] Absorbance before (A_0) and after (A_h), UV irradiation for 1 min.
[c] Half-recovery time.

The absorption of viologen halides induced by near-UV irradiation was made stable for more than 1 year in the absence of oxygen by sandwiching them between two glass plates,[26] whereas the developed color of Bzl-V^{2+} returned to the original state at room temperature after 4 days or heating at 60°C for 5min. This indicates that a reverse electron transfer to the hexacyanoferrate (II) ion possessing a low redox potential takes place. The reversible redox reaction by the photo and heat mode can be repeated; bleaching is also possible by an electrochemical oxidation–reduction of both ions.

9.2.4. Applications

Since the developed color of viologens induced by photoreduction is vivid, and a variety of color species can be obtained by changing their chemical structure, it can be expected that there are several kinds of potential applications using photochromic viologens, especially an erasable-direct-read-after-write (EDRAW) media for recording devices with high storage density and reliability.

As for recording devices, viologens have been well studied from the standpoint of their electrochromic properties. However, this system is not yet in practical use because species inactive for electroreduction are accumulated after many repetitions. When viologens are employed as photorecording devices, it is preferable to bleach using irradiation with light of another wavelength or/and of different intensity. However, the back electron transfer does not proceed photochemically, as mentioned in Section 9.2.3.3. Therefore the bleaching has been examined by thermal process or by oxidation with molecular oxygen. In the latter case, it is not obvious whether the oxidation product of the radical cation would reduce its counter radical anions or become an irreversible product.[27] Since the colored radical cation can be readily oxidized by an electronic process as shown in Figure 9.2, an effective solid electrode would certainly promise an erasable photoelectrochromic device.

This section discusses the erasable photomemory of polymer films composed of viologen copolymers or layered viologen assemblies. A copolymer with a 4,4′-bipyridinium salt as a pendant unit[28] or as part of the main chain[29] has been synthesized to prevent the migration or the precipitation of viologen molecules in films. Several kinds of viologen monomers bearing vinyl groups have been synthesized (Scheme 7).[13] Radical polymerization of the viologen monomers with *N*-vinyl-2-pyrrolidone in aqueous solution gave low values of both conversion and intrinsic viscosity. They were also accompanied by colored products insensitive to near-UV light. Therefore the vinyl copolymers bearing viologen units were prepared by the chemical modification of conventional polymers according to Scheme 8.[30] In Table 9.9, the N-substitution groups and the counteranions in these copolymers are listed.

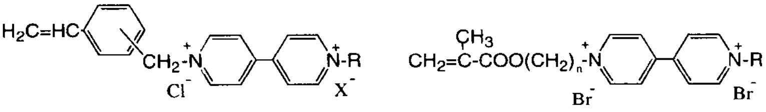
When sandwiched between two glass plates, films of viologen copolymer exhibited an infinite color development because of the absence of oxygen affecting the bleaching rate. For the purpose of repeating the cycle of color development and bleaching, the films of copolymers (approximately 10μ thickness) were made by spreading an aqueous solution over the inner walls of a quartz spectrophotometric cell, followed by evaporating the water, and then the sealed cell atmosphere was displaced by nitrogen.[31] The absorption changes of the films after 30s of UV irradiation are shown in Table 9.9. From these results, it can be seen that when the films were placed under a nitrogen atmosphere, the absorbance of the radical cation immediately after irradiation was maintained above approximately the 80% level in

Table 9.9. Relative Time Decay of Colored Viologen under Nitrogen

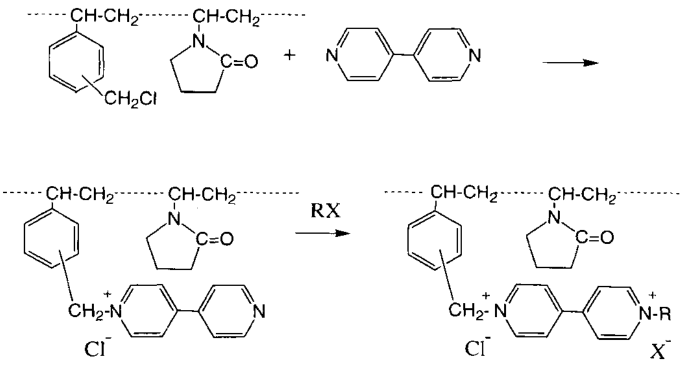
4,4′-Viologen[a]		
R	X	A_t/A_0[b]
Benzyl	Cl	0.60(4)
Benzyl	Br	0.81(12)
Propyl	Br	0.85(3)
p-$CH_3OC_6H_4CH_2$	Cl	0.82(3)
p-$CH_3C_6H_4CH_2$	Cl	0.87(3)
p-$CH_3C_6H_4CH_2$	Br	0.90(3)
p-Cl-$C_6H_4CH_2$	Cl	0.88(3)

[a] R and X: N-substitution and counteranion of copolymer in Scheme 8.

[b] Ratio of absorbance (A_t) after time *t* under nitrogen to that immediately after irradiation (A_0). Numbers in parentheses denote time *t* (h).



Scheme 7



Scheme 8

the dark. When air was introduced into the cell, the absorbance decreased rapidly and reached the original state within about 30min. The time dependence of the absorbance is illustrated in Figure 9.11. The cycles could usually be repeated many times. This result suggests that the erasable photomemory of viologens either incorporated in a PVP matrix or in the form of a copolymer can be produced with UV light under a nitrogen atmosphere and its stable color can be erased by introducing oxygen.

Erasing the developed color for molecularly layered viologens was also possible by the application of heat, as mentioned in Section 9.2.3.3. Table 9.10 summarizes the effect of temperature on bleaching of the viologens with a long alkyl sulfonate as counteranion ($V^{2+}2ArSO_3$), and Table 9.11 indicates the repetition of the color development with different alkylbenzene sulfonate anions.[19] The films were prepared by melting viologens under a nitrogen atmosphere, sandwiched

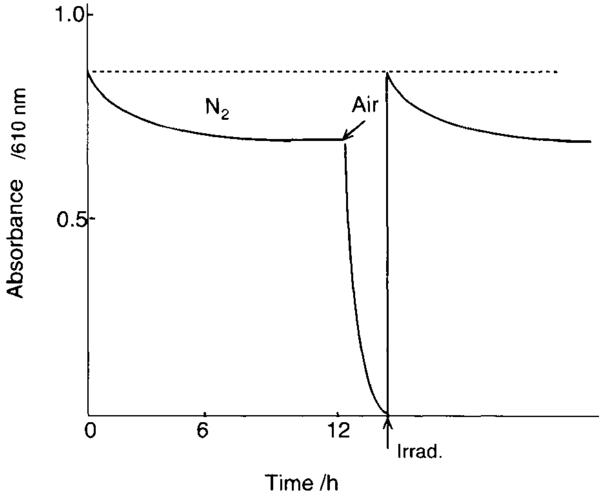


Figure 9.11. Reversible absorption change of viologen–copolymer film by writing optically and introducing air oxygen. Copolymer, R, benzyl; X, Br in Table 9.9.

Table 9.10. Effect of Temperature on Bleaching of Colored Viologen Assembly[a]

Temp. (°C)	Bleaching rate[b] A/A_0 (613 nm), (min)
30	0.03
40	0.24
50	0.66
60	0.72
70	0.99
80	1.00
90	1.48
70	2.10[c]
Xe lamp[d]	0.01

[a] Bzl-V^{2+} with *p*-alkylbenzene sulfonate anion possessing 70% n- + 30% highly branched $C_{12}H_{25}$.
[b] A_0 = absorbance increase at 613 nm induced by light. A = initial decrease of absorbance reduced to 1 min.
[c] In the presence of a half-molar excess of *p*-dodecylbenzenesulfonic acid.
[d] 150W, >590nm, from 5cm for 1h.

between two glass plates to exclude air, and the color developed upon near-UV irradiation for 10min. From the result in Table 9.10, it can be seen that the initial bleaching rate (A/A_0) at the absorption maxima increased with increasing temperature, and the bleaching was completed at 70°C within 1min. The absorption upon irradiation was almost consistent with the original one after 50 cycles. Thus, an image written optically (near-UV) in the polymer state or in layered assembly can be stored, read with a diode laser, and erased by introducing oxygen or by heating, when the proper conditions are selected.

Table 9.11. Repetition of Color Development of Viologen Assembly

	Abs. increase induced by light[b]	
R[a]	A_1	A_{50}
n-$C_{12}H_{25}$	0.690(506)[b]	0.686(506)
$C_{12}H_{25}$[c]	0.793(613)	0.791(613)

[a] Alkyl side chain of *p*-alkylbenzene sulfonate as counteranion of Bzl-V^{2+}.
[b] A_1 = values at λ_{max} indicated in parentheses, A_{50} = after 50 cycles of irradiation and subsequent thermal bleaching (70°C for 10min).
[c] 70% n- + 30% highly branched.

9.3. PHOTOCHROMISM OF THIAZINES

9.3.1. Introduction

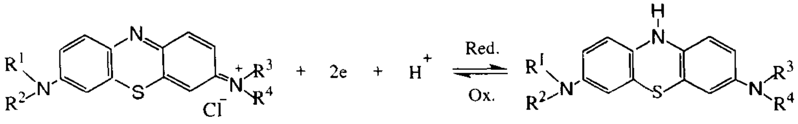
Thiazine dyes such as thionine; methylene blue; and the azules A, B, and C are well known to be reduced with appropriate sensitizers or reductants to become colorless leuco dyes, as shown in Scheme 9. The reduction product (II) is highly sensitive to oxidation if air is present in the system. It is simultaneously oxidized with molecular oxygen, generating the colored original state ($\lambda_{max} = 600–700$nm). When an oxygen-free solution of methylene blue or thionine in dilute sulfuric acid was subjected to flash photolysis with a wavelength shorter than 250nm, reversible bleaching proceeded; this is assumed to be caused by the formation of the semiquinones produced.[32]

The bleaching process also proceeded on steady-state irradiation with visible light in the presence of moderately reductive compounds.[33] Since this oxidation–reduction reaction is not possible in the dark, the reactions have been well studied with a variety of combinations of reductants such as the Fe(II)–Fe(III) system in aqueous solutions.[1] This section discusses reversible spectral changes using a combination of two functions, i.e., oxidative (thionine) and reductive ones in a polymer matrix.[34,35]

9.3.2. Photochromic Properties

The photochromic process under visible light irradiation does not take place with a single function; therefore the reaction may proceed as in Scheme 10.

The thionine function, possessing a relatively high redox potential, acts as an electron acceptor upon irradiation with visible light, which is considered to first form the electron-donor-acceptor (EDA) complex (exciplex) with the electron donor (D:reductant). The electron in the exciplex further added to the thionine function to produce the colorless leucothionine and the electron acceptor (A). The A may be an oxidized form of D. The dark reaction may take place either by back electron transfer to the thionine function via the EDA complex or by air oxidation of the leucothionine when atmospheric oxygen is present.



Blue(I) Colorless(II)

	R^1	R^2	R^3	R^4
Thionine	H	H	H	H
Azule C	H	H	H	CH_3
Azule B	CH_3	CH_3	CH_3	H
Methylene Blue	CH_3	CH_3	CH_3	CH_3

Scheme 9

$$\text{(Thionine Function)} + \text{D} \overset{h\nu}{\rightleftarrows} \text{(EDA complex)} \overset{h\nu}{\rightleftarrows} \text{(Leucothionine Function)} + \text{A}$$

Scheme 10

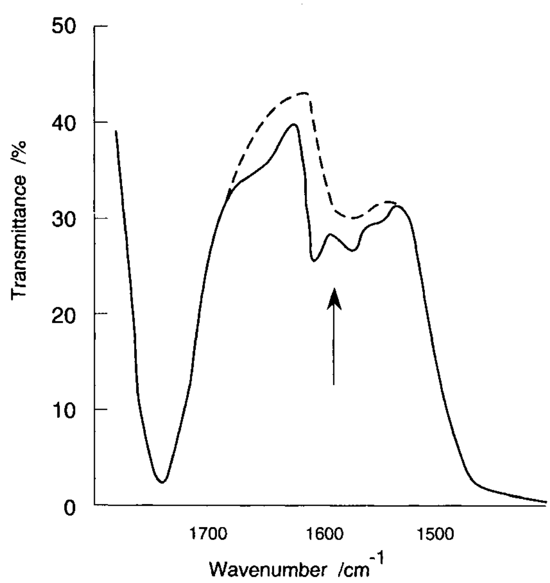


Figure 9.12. IR spectral change of a PVA film containing 2% of thionine and 20% of TEA by 5-min irradiation 30cm from the lamp; solid spectrum before irradiation and after complete recovery; dotted spectrum immediately after irradiation. (Reprinted from Ref. 36 with permission of copyright owner: John Wiley & Sons, Inc.)

The reversible reaction between thionine (blue) and leucothionine (colorless) was rationalized by determination of a π-conjugated imminium form by means of an IR spectrometer.[36] Figure 9.12 shows the IR spectral change of films with thionine and triethanolamine (TEA, D-function) incorporated in poly(vinyl alcohol). As can be seen in Figure 9.12, the absorption around 1600cm^{-1}, assignable to the quinoid structure, disappears upon irradiation with visible light, in which case the absorption increases with an increasing blue color. This corresponds exactly to the visible spectral change (see Scheme 9) in which the complete recovery of color (visible spectrum) also coincides with the complete recovery of the IR spectrum.

9.3.3. Applications

9.3.3.1. Thiazine Dyes

Figure 9.13 indicates the typical change in reflection spectra for the thionine reductant system in a PVA matrix coated on paper with a water-repellent property.[36] The blue color, with an absorbance of approximately 1.0 at 610nm, faded rapidly upon irradiation with visible light; this absorption gradually recovered when the material was stored in a desiccator at constant relative humidity in the absence of light. The recovery was complete except when the exposure was to an extremely intense light.

Table 9.12 summarizes the effect of thiazine dyes on the photoreaction. The replacement of the amino hydrogen by methyl groups possessing an electron-donating character induced a decrease in photosensitivity that was accompanied by a red shift of the absorption maxima. The rate of photoreduction (color fading) was highest in the case of thionine possessing the highest dark oxidation potential. This indicates that the rate-determining step in the photoreduction might correspond to the reaction of the excited thionine function with the reductant. The result is analogous to the color development of viologens, as cited in the previous section.

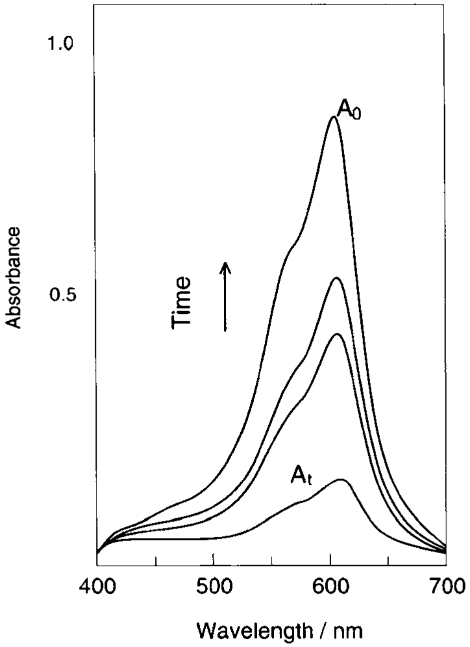


Figure 9.13. Photochromic spectral change of paper T coated with a PVA containing 1% of thionine and 50% of TEA (58% RH). A_t, immediately after 10-s irradiation 30cm from the lamp; A_0, before irradiation and after complete recovery. (Reprinted from Ref. 36 with permission of copyright owner: John Wiley & Sons, Inc.)

Table 9.12. Effect of Kind of Thiazines[a]

Thiazines	Potential[b] (V)	Abs. peak (nm)	A/A_0 at R (%)[c] 84	58	30
Thionine	–0.30	610	0.46(45)	0.46(45)	0.48(45)
Azule C	–0.30	610	0.64(43)	0.68(80)	0.71(130)
Azule B	–0.28	650	0.67(40)	0.68(100)	0.82(100)
Methylene blue	–0.24	665	0.75(58)	0.79(70)	0.80(80)

Source: Reprinted from Ref. 36 with permission of copyright owner, John Wiley & Sons, Inc.

[a] Paper T coated with a solution consisting of 0.01g of dye, 1.0g of PVA, and 10ml of water.

[b] Polarographic half-wave potential.

[c] A=absorbance at λ_{max} immediately after 10-s irradiation at a distance of 30cm with a 500-W tungsten lamp. A_0=absorbance before irradiation. Numbers in parentheses indicate 50% recovery times (min) at 20°C.

As can be seen from Table 9.12, photochromism is also strongly affected by humidity. It is well known that thiazine and its derivatives undergo photoreduction smoothly in the presence of such activated surfaces as silica gel and alumina with water molecules,[37] and that methylene blue is also photochemically reduced in acid solution, even with only available water as the reducing agent.[38] Therefore the water present in polymer films must produce a thionine–water hydration system, which accelerates the rate of the photoreduction of thionine, as well as promoting the contact of reductants by a plasticizer effect. PVA, used as the matrix, can also play the role of reductant, but its extent may be minor as compared with the added reductant. The effect of water is supported by the fact that a less hydrophilic polymer matrix such as poly(methyl methacrylate) does not exhibit photochromism even though the system contains an appreciable amount of reductants.

9.3.3.2. Effect of the Kind of Reductants

Table 9.13 summarizes the effect of the kind of reductant on the photochromic behavior of thionine dye. All reductants afforded transparent films upon irradiation and complete color recovery in the dark. The greatest photosensitivity was obtained with TEA as the reductant. The reversibility decreased in the order, tri->di->mono-ethanolamine. The difference cannot be explained by an electron-donating character such as the basicity of the reductant (PK_a value of their ammonium salt: tri-<di-<mono-ethanolamine). A potential explanation is that TEA(bp, 335.4°C/760mmHg) is so hygroscopic that the moisture absorbed in TEA and TEA itself acts as a plasticizer, providing tough films that afford higher color reversibility, as mentioned earlier.

9.3.3.3. Effect of Coating Substrate

In a typical preparation of a coating composition, 0.01g of thionine is dissolved in 5ml of hot water. To the resulting solution is added a solution of 1g of PVA in

Table 9.13. Effect of Kind of Reductant[a]

Reductant (g)	A/A_0 at RH (%)[a]		
	84	58	30
None	1.00	1.00	1.00
EDTA (0.01)	0.80(160)	0.83(200)	0.85(210)
EDTA-diNH_4 + salt (0.1)	0.84(70)	0.86(100)	0.87(150)
EDTA-diNa + salt (0.1)	0.82(75)	0.85(100)	0.89(120)
$H_2NCH_2CH_2OH$ (0.1)	0.96(60)	0.96(110)	0.98(120)
$HN(CH_2CH_2OH)_2$ (0.1)	0.80(60)	0.81(90)	0.86(120)
$N(CH_2CH_2OH)_3$(0.01)	0.70(60)	0.72(90)	0.77(150)
(0.05)	0.63(60)	—	0.66(80)
(0.10)	0.46(45)	0.46(45)	0.48(45)
(0.50)	0.20(20)	0.19(20)	0.19(20)

[a] The same as in Table 9.12 except for the amount of reductants.

5ml of water, and the mixture is stirred at 50–60°C for 30min. Upon cooling below 50°C, 0.1g of TEA is added and stirring is continued for 30min to afford a dark-blue coating composition. The solution is cast on several kinds of substrate (Table 9.14) so as to afford a dry absorbance of approximate unity at the absorption peak around 600–700nm. The coated substrate is then dried at room temperature or below 90°C and stored in a dark-brown desiccator at constant relative humidity except for irradiation or measurement of absorption spectra.

As shown in Table 9.15, irradiation from a short distance with a 500-W reflector lamp (tungsten) (i.e., an intense irradiation) afforded a smoother color fading, while too high intensity caused loss of reversibility, as shown in Table 9.15. Presumably this is due to the deformation (decomposition or aggregation) caused by overheating. As can be seen from Table 9.14, the kind of substrate papers used for coating also affects both light (color fading) and dark (recovery) reactions. The

Table 9.14. Effect of Coating Substrate[a]

No.	Substrate paper	A/A_0[b]	50%-Recovery[c]	Remarks
1	Paper T	0.26	45 min	
2	Polyester sheet	0.22	1–3h	
3	Tracing paper	0.76	1–3h	
4	Paper without coating	0.74	1–3h	
5	Baryta paper	0.85	1–3h	Inactive peak at 480nm
6	Silicone-coated paper	0.69	1–3h	

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[a] Papers coated with a solution consisting of 0.3g thionine, 3g of triethanolamine, 30g PVA, and 300ml of water.

[b] Irradiation for 20s at a distance of 30cm with a lamp, A, A_0 for 610-nm peak.

[c] At 20–30% RH and 10–15°C.

Table 9.15. Effect of Irradiation Intensity[a]

Distance from lamp (cm)	A/A_0 at RH (%)[b]		
	84	58	30
30	0.69(60)	0.70(90)	0.75(120)
10	0.24(80)	0.24(110)	0.25(150)
3	0.13(75)[c]	0.12(120)[c]	0.16(150)[c]

[a] Triethanolamine (0.1g) used as reductant; others same as in Table 9.12.
[b] A=absorbance immediately after 5-s irradiation.
[c] Recovery is not complete.

water-repellant papers (nos. 1 and 2) afforded the highest light sensitivities, whereas papers nos. 3 and 4, which were hydrophilic, yielded a low sensitivity. That is to say, hydrophobic sheets such as polyester coated on paper are preferable from the viewpoint of light sensitivity. Too high a hydrophobicity, however, induced the aggregation of the coating composition, yielding a nonhomogeneous film (no. 6). Interactions between coating components and substrate papers caused an appearance of new inactive absorption peaks (no. 5). An absorbance recovery exceeding 90% leaves practically no residual images, and several repetitions should be assured under practical conditions.

Since conservation of wood and protection of the environment are becoming more important, a reusable (erasable) recording paper would certainly meet a contemporary requirement.

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