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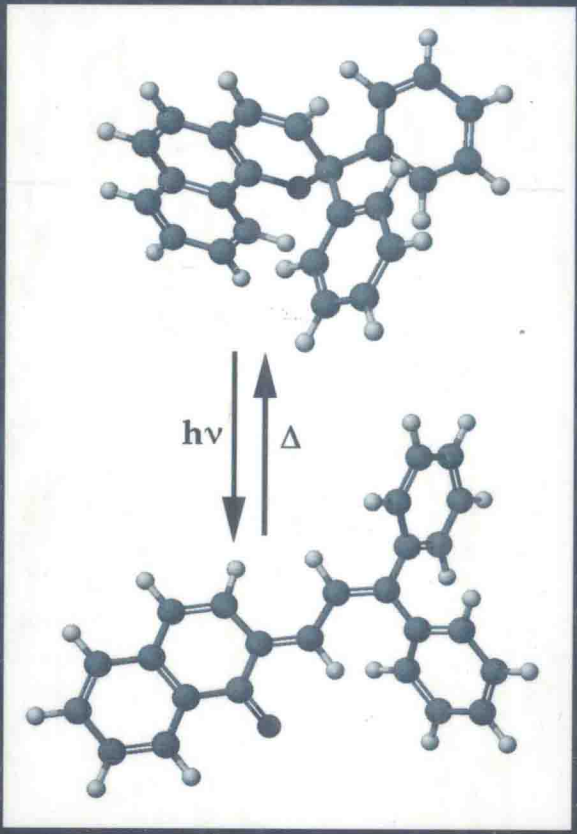
Organic Photochromic and Thermochromic Compounds

Volume 1

Main Photochromic Families



Edited by

John C. Crano and Robert J. Guglielmetti

Organic Photochromic and Thermochromic Compounds

Volume 1: Main Photochromic Families

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Monroeville, Pennsylvania

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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.

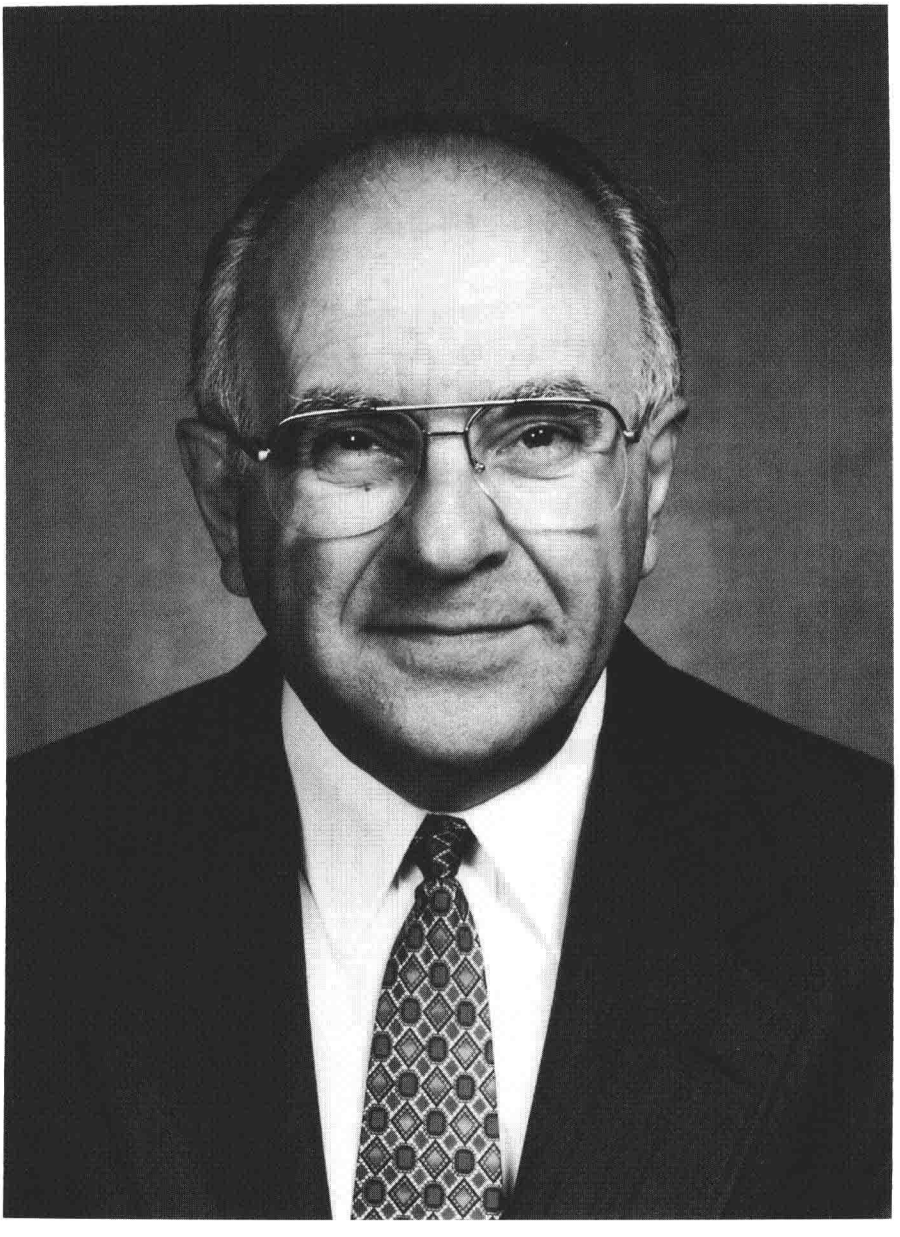
A second generation lens, the Transitions® Plus lens, was introduced in November 1992. In the years since, Transitions Optical has marketed a succession of new lenses. In September 1994 the EuroBrown™ lens appeared, formulated to give when activated a brown color, especially favored in the European market. 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).

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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
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April 1998

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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.

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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.

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