Heinrich Zollinger

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Syntheses, Properties and Applications of Organic Dyes and Pigments

Second, revised edition

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Preface to the Second Edition

The first edition of this book met an unexpectedly good response. The book was sold out after slightly more than four years. This fact and a series of favorable reviews were a welcome stimulus to update and revise the content for a second edition. The result is an enlargement from 367 to 496 pages; 718 new references have been added to 844 of the 860 references used for the first edition.

It is interesting that the enlargement is not at all uniform throughout the book. Aside from the addition of two new Sections (15.8 Color-Specific Application of Colorants for Therapeutic Purposes, and 11.1 Analysis and Purification of Colorants) the content is arranged in the same way as before. A comparison of the two editions will show clearly that the chapters and sections related to the classical application of dyes and pigments, namely coloration of materials like textiles, plastics, paper, *etc.*, has changed only marginally, except for the sections on disperse dyes, reactive dyes and carbonyl pigments. Substantial changes and additions, however, have been made in most sections in which so-called functional dyes are discussed, in particular in those parts where new information storage technology is described. I can fully subscribe to the first sentence in the preface of the book "Infrared Absorbing Dyes"*, edited by my former coworker M. Matsuoka (1990): "New laser technology has developed a new dye chemistry!" How interesting functional dye chemistry is became evident from the large number of scientifically and technologically excellent papers presented at the First International Symposium on Functional Dyes, which took place 1989 in Osaka on the initiative of Z. Yoshida and T. Kitao. I hope there will be many subsequent conferences after this successful start. I also hope that the organizers of the "Farbensymposien", which have taken place triannually and alternately in Germany and Switzerland since 1960, will accept the offer of the Japanese chemists to combine both series of conferences in one really international regular event, covering above all the frontiers of a new chemistry of colorants.

New material has also been added to the chapter on azaannulenes. Clearly, in recent years a synergism can be observed between phthalocyanine chemistry and

* Thanks to the help of Professor Matsuoka, I got a copy of this very remarkable book at the end of February 1991, although it was ordered from the publisher in New York earlier. Fortunately, I had already received page proofs of two chapters from Professor Matsuoka. Nevertheless I was unable to include valuable information in other chapters of this book because my manuscript was sent to the publisher in early January 1991.

porphyrin chemistry. Battersby *et al.* (1980) call the porphyrins the "pigments of life" because of their central role in living systems. Their behavior in biochemical reactions has become much better understood in recent years; it has stimulated the investigation of the corresponding processes with phthalocyanines, *e.g.* in catalysis. Furthermore, it has supplied fascinating examples of effects, for which Lehn (1988) has coined the term "supramolecular chemistry". This field is also called "the chemistry of non-covalent bonds". It will be proposed in this book that such effects can also be found in other areas of color chemistry. Examples are the bathochromic shifts of colorants based on aggregation. I am pleased with the terms mentioned above. They replace almost completely what I called "through-space interactions of molecules" and "surface chemistry" in the Preface of the first edition.

As even a highly esteemed scientific journal, *Accounts of Chemical Research,* recently published a review on Tyrian Purple in antiquity, I have not hesitated to include a few paragraphs on this most famous natural dye in the context of indigoid dyes (Sec. 8.3). I have also added some short historical remarks in various other contexts.

These additions demonstrate the wide spectrum of color chemistry from ancient times to very modern problems that have been the subject of recent Nobel Prizes*. Another "dimension" of the presence of color chemistry in the recent literature is the paper by Yuan and Song (1989) published in China on the subject "Color reaction of thorium with chlorophosphon-azo-DBC and its application". This paper is mentioned here because with it Chemical Abstracts Service reached the milestone of having published the 13 000 000th abstract!

I am very grateful to a number of colleagues who helped me by reading the manuscripts of certain sections and for providing information on various subjects, namely Dr. H. H. Bosshard (Ciba-Geigy AG, Basle), Professor H. Böttcher (Technical University of Dresden), Professor M. Grätzel (Ecole Polytechnique Fédérale de Lausanne), Dr. A. Iqbal and Dr. R. Kirchmayr (both Ciba-Geigy AG, Marly-Fribourg), Professor W. Lüttke (University of Göttingen), Dr. J. Marx (Filmfabrik Wolfen AG, Wolfen), Professor M. Matsuoka (University of Osaka Prefecture, Sakai), Dr. B. S. Nagar (Indian Dyestuffs Industries Ltd., Kalyana), Dr. M. S. Simon (formerly Polaroid Corp., Cambridge, MA), Dr. H. van den Bergh (Ecole Polytechnique Fédérale de Lausanne) and Professor Kaspar Winterhalter (ETH Zürich). Also very useful were the contacts with authors who wrote chapters related to color chemistry for the 5th edition of Ullmann's Encyclopedia of Industrial Chemistry, provided by Dr. Gail Schulz, member of the editorial staff of that encyclopedia. These authors were Dr. D. M. Allen (Cranfield Institute of Technology, Bedford), Dr. C. Eckardt (Ciba-Geigy AG, Basle), Dr. D. J. Gravesteijn (Philips Research Laboratory, Eindhoven), Dr. K. Grychtol (BASF Aktiengesellschaft, Ludwigshafen) and Dr. K. Hunger (Hoechst AG, Frankfurt-Hoechst). I also thank Dr. Schulz for information on Ullmann chapters that will only be available in 1991 and 1992.

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* See, in addition, to supramolecular chemistry, Corey's retrosynthesis, for which a recent example is discussed in Section 8.13 (Diketopyrrylo-pyrrole pigments).

Three of my former coworkers helped me in improving the manuscript: Dr. M. D. Ravenscroft (now Dow Rheinmünster) read most of the chapters, brushed up the English and made comments and suggestions to the content. Dr. P. Skrabal (ETH Zürich) helped me by reading the page proofs. Mrs. S. Braun-Heizmann (now Zollikerberg) typed the manuscript. I am very thankful to all three former coworkers.

The cooperation with Dr. Christina Dyllick-Brenzinger, who was in charge of the editing work at VCH Verlagsgesellschaft was, as for the first edition, very agreeable.

I thank all these colleagues and former coworkers for their work. Without their help it would hardly have been possible for me to finish this work in retirement within a relatively short space of time.

Küsnacht-Zürich, April 1991 Heinrich Zollinger

Preface to the First Edition

The origin of this book can be traced back in part to impressions formed during my early years as a research chemist in the area of industrial color chemistry. I realized then the extent of the knowledge and experience accumulated by generations of chemists who had been involved in the synthesis of thousands of dyes and pigments since 1856, when William H. Perkin by chance obtained Mauve, the first commercially successful synthetic dye. However, I was also struck by the fact that color chemists were in possession of a wealth of observations which would also be of interest to other branches of chemistry. Therefore, I have devoted practically all my own research activities since that time to the strengthening of the crosslinks between color chemistry and other areas of the chemical sciences; first, mainly to physical organic chemistry and reaction engineering, later also to physical chemistry. Finally, links have been traced to some – admittedly small – sections of the engineering and biosciences (electrophotography, biodegradation and color vision).

This field of experience is reflected in the present book. I intend to demonstrate *how* the domain of organic colorants is connected with principles of modern inorganic, organic and physical chemistry and also various branches of engineering and of biology. Examples are to be found in the through-space interactions of molecules and in the field of surface chemistry: In the former, chemists and biologists have recently become interested, while in the latter case there has been a renaissance of the once unfashionable area 'surface science'. Color chemistry, on the other hand, has been involved in both areas for decades.

The book was written for three potential groups of readers:

Firstly, for organic chemists who regard color chemistry as closed, conservative and not readily amenable to new discoveries and methods. I hope that they will see in Chapters 3 to 10 that color chemistry must not be an enumeration of thousands of structures, but that dyes and pigments show a series of characteristic and fundamentally interesting structural features, and that they allow an understanding of a number of reactions of general relevance for organic chemistry. Natural dyes are included in the appropriate chapters.

Secondly, for color chemists who are either starting their career in that field or have worked in it for years. I hope that they will discover modern aspects of color chemistry related to their field of experience. Coverage is given to dye synthesis, emphasizing mechanisms, catalytic processes, *etc.,* as well as to the scientific basis of traditional coloration. New applications of dyes, *e. g.* for information storage devices, for liquid crystal displays, optical data disks or for solar energy conversion, are also of interest to the color chemist. Last but not least, a discussion of color *per se,* from principles of molecular orbital theory to color vision, will be found not only stimulating but useful.

Thirdly, for physical chemists, as well as engineering and biological scientists, who use dyes or pigments as a tool. I hope that they will gain insights from the purely chemical and physicochemical chapters, *e. g.* in rationalizing their observations when staining biological tissues by understanding the structure and reactivity of the dyes they use, or by investigating other colored compounds for the many new imaging, information and light energy storage systems which are in development at present. The sections originating from their own area of specialization offer little new information *per se.* For example, electronic spectra are not described for physical chemists, nor are lasers or liquid crystals and fluorescent staining described for physicists, engineers and biologists, respectively, but rather for the previously mentioned two groups of chemists.

It needs to be emphasized that this book is not intended to be a mere compilation of more topics than former books on color chemistry. In particular, it should not be regarded as a collection of unrelated chapters, each written by and for specialists in the respective subject area. It is not a reference book, but a book for reading.

This general aim of the book coincides with recent ideas about the future development of chemical science and technology, as discussed in a short article by Kline (1984) and in the voluminous report "Opportunities in Chemistry" written on behalf of the National Academy of Sciences (USA) by a committee under the chairmanship of Pimentel (1985). These publications emphasize the fact that the last twenty years have seen the near-extinction of the old subdisciplines in chemistry and the need for cooperation with neighboring disciplines. I fully support this as well as Kline's conclusion: "They will . . . have to overcome the formidable obstacles to innovation created by minds set in old patterns by the parochialism of university departments and by the conservatism of industrial executives."

I hope this book will contribute to that extinction of parochialism and of conservatism. I hope also that the greater range of topics covered in this book on color chemistry does not influence unfavorably the depth of treatment of fundamental phenomena. This book, it is hoped, will be a tool for chemists in the context of another recent and critical statement written by two well-known technologists, Davies and Weisz (1981): "Color science and technology have become different, but chemists haven't noticed the opportunities."

In order to keep the size of the book within reasonable limits, it was necessary to concentrate on major colorants of the past and present. Coverage also had to be given to new areas, as well as to promising, future-oriented projects – even if their scientific or technological success is still an open question. The literature mentioned was chosen on the basis of these principles, whenever possible, in the form of recent books and reviews. Key research papers are discussed, in some cases even if they are 20, 50 or more years old, but still relevant. Patents are mentioned too, but only for recent inventions if they have had an impact on industrial products. There is a total of some 800 references; 35 % of these were published in and after 1981.

A problem for every author of a book or review covering industrial colorants is the unfortunate fact that dye and pigment manufacturers do not publish the structures of their products. This is a serious obstacle for any scientist who is working with such compounds. I did not choose the solution of this problem which is usually applied by review authors working in industry who mention many patents, but do not indicate which example of which patent is really a commercial product! (Here Sandoz Ltd. should be commended for publishing the structure of Foron Brilliant Blue S-R, a disperse dye with a fundamentally new chromogenic system, in 1982 immediately after bringing it onto the commercial market; see formula **3.21** in Sec. 3.3.)

With very few exceptions, I include only commercial products with known structures in this book. I thank my senior coworker Dr. P. Skrabal, who has elucidated some structures of important dyes for publication in this book.

In the preparation of this book I am indebted to several friends, colleagues and coworkers. First of all, I would like to thank Prof. W. Lüttke (University of Göttingen) and Prof. T. Iijima (Tokyo Institute of Technology), who were patient critics of the text of some chapters, as they evolved and who made many suggestions and prevented many errors. For advice and discussions of specific problems, I am indebted to Dr. G. Back, Dr. H. H. Bosshard and Dr. D. Reinecke (Ciba-Geigy A.G.), Prof. L. Dulog and Prof. H. E. A. Kramer (University of Stuttgart), Dr. D. H. Dybvig and his coworkers (3M Research Ltd., Harlow, England), Prof. E. Fischer, Prof. A. Grinvald and Prof. V. A. Krongauz (Weizmann Institute of Science), Prof. M. Grätzel (EPF Lausanne), Prof. G. W. Gray (University of Hull), Dr. W. Koch (Sandoz A.G.), Dr. H. H. Kuhn (Milliken Research Corp.), Dr. B. S. Nagar (Indian Dyestuff Ind., Kalyan), Prof. E. S. Olson (Clemson University). Parts of the manuscript were written during my stays as a Visiting Guest at the Weizmann Institute of Science in Rehovot, Israel, at Kyushu University in Fukuoka and at the Tokyo Institute of Technology. I thank my hosts Profs. Y. Mazur, D. Samuel, H. Taniguchi and T. Iijima for their hospitality.

I thank also Drs. P. Ball, M. D. Ravenscroft and G. Tovstiga, research assistants at ETH Zurich, for improving the English style of my manuscript and Dr. M. Gisler and S. Müller for their help in literature work for this book.

My association with VCH Verlagsgesellschaft has not been the usual type of business relationship. Dr. H. F. Ebel suggested I write this book, and Dr. Christina Dyllick-Brenzinger read and improved the typescript with respect to language and content. I am very thankful to both of them for their friendly collaboration.

I hope that this monograph will arouse the interest of chemists in academia and in industry for an old but still fascinating field of chemistry.

Zurich, March 1987 Heinrich Zollinger

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1 Introduction

1.1 Classification of Colorants

Colorants are characterized by their ability to absorb visible light (400 to 700 nm); in fact it is for this reason that they appear to be colored. Natural organic and inorganic colorants have been used by man since prehistoric times. However, it was the discovery of Mauve by W. H. Perkin in 1856 which marked the start of the synthetic dye industry (see Sec. 1.2). In the last 130 years several million different colored chemical compounds have been synthesized and about 10000 of these were or are produced on an industrial scale. Some form of classification of this enormous family of compounds is clearly necessary.

Two large groups of colorants have already been mentioned, these being the inorganic and organic colorants. Each of these groups can be subdivided further into natural and synthetic compounds. This second differentiation is, however, generally not meaningful, as there are colorants which originally had a natural source, but which are today produced synthetically.

A very important differentiation of colorants is the following: Colorants are either *dyes* or *pigments*. These terms are often used indiscriminately, in particular, pigments are quite often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied (for details see Sec. 12.1). Pigment particles have to be attached to substrates by additional compounds, *e. g.* by a polymer in a paint, in a plastic or in a melt. Dyes, on the other hand, are applied to various substrates (textile materials, leather, paper, hair *etc.*) from a liquid in which they are completely, or at least partly, soluble. In contrast to pigments, dyes must possess a specific affinity to the substrates for which they are used.

The often rather inaccurate distinction made between pigments and dyes has several origins. Firstly, the words "dye" and "dyeing" are much better known by the general public than the more technical term "pigment" or even the word "colorant". Furthermore, most organic pigments are closely related to dyes with respect to their chemical structure, and, finally, there are dyes which become pigments after application (vat dyes).

In this book only organic colorants are described. In Chapters 3 to 9 dyes and pigments are arranged according to their chemical structure. The content of these chapters follows basic concepts on the color of organic compounds, introduced in

Chapter 2. The discussion begins with polyenes, *i. e.* compounds whose visible light absorption is based only on a sequence of methine groups (—CH=), and with polymethines, *i. e.* polyenes with an electron donor and an electron acceptor at the respective ends of the conjugated system. Increasingly more complex structures are treated in the following chapters, namely, those containing ring systems of methine groups, and colorants in which one or more methine groups are replaced by nitrogen atoms. Here we find the largest class of colorants, those containing azo groups ($-N{=}N-$). Finally, dyes and pigments are discussed for which – in addition to conjugated systems – carbonyl groups or sulfur bridging units are characteristic.

An alternative method of classification is that by area and method of application (coloristic classification). Chapter 11 discusses the physicochemical basis of the classical application of dyes, mainly that on textile fibers. In Chapter 12 the application of pigments is treated, and Chapters 13 to 16 deal with applications involved in physical and technical processes (*e. g.* dyes for lasers, liquid crystal displays, solar energy conversion, dyes in photography and in reproduction techniques). Furthermore, applications in analysis, biochemistry, biology, medicine and food technology are discussed. The purpose of applications of dyes treated in Chapters 13 to 16 is not the coloration of bulk materials like textiles, paper, plastics *etc.*, but a wide variety of other uses. For some years, dyes for such purposes have been called functional dyes, a field in which Japanese chemists in industry and academia are very active (see remark at the end of Section 1.3).

A compound which absorbs radiation takes up energy which can be released in various ways. One possibility is fluorescence, *i. e.* the emission of light from singlet excited states at longer wavelengths than absorption (see Sec. 2.4). This effect is used in fluorescent colorants and, particularly, in optical brightening agents. The latter are compounds which absorb near-ultraviolet light and release energy by fluorescence in the visible light range. They can be applied to various substrates and cause emission of visible light from the surface of these substrates (see Chap. 10).

There are also proposals by Griffiths (1976), Dähne and others to classify colorants according to the type of electronic excitation occuring on light absorption (summary: Klessinger, 1982). Lüttke (1985) classifies colorants as absorption colorants, fluorescent colorants and energy transfer colorants, depending on whether the light energy absorbed is dissipated predominantly (*i. e.* with high quantum yields) by internal conversion, by fluorescence or by intersystem crossing (see Fig. 2-8).

The two classifications based on chemical structure and on area and method of application overlap, *i. e.* there is hardly a chemical class of dye which occurs solely in one coloristic group, and *vice versa*. Furthermore, some coloristic groups can be applied to two or more substrates, whilst others are specific to a single substrate. Reactive dyes, for example, are classified chemically as colored compounds having a group capable of forming a covalent bond with a substrate. The colored parent substance can, in principle, be derived from all classes of Chapters 3 to 9, but in practice the compounds of interest are mainly of the triphenodioxazine, azo, anthraquinone and aza annulene types (Sec. 4.4, 7.12, 8.6 and 5.2, respectively).

When classified according to the dyeing method, one speaks of anionic, direct or

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