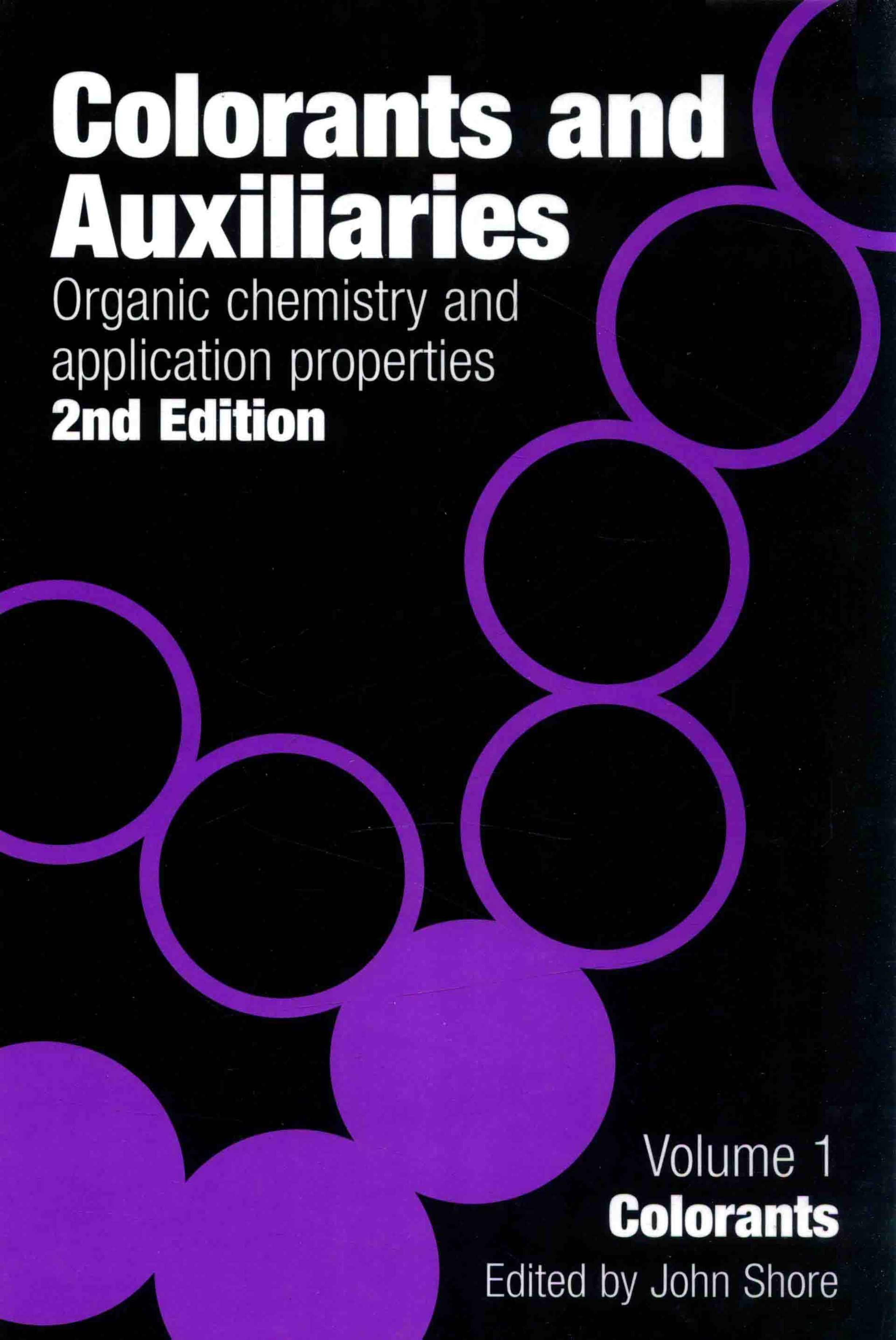

Colorants and Auxiliaries

Organic chemistry and application properties

2nd Edition

Volume 1

Colorants

Edited by John Shore

Colorants and auxiliaries
ORGANIC CHEMISTRY AND APPLICATION PROPERTIES

Second Edition

Volume 1 – Colorants

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Formerly of BTTG/Shirley and ICI Dyes (now DyStar), Manchester, UK

2002

Society of Dyers and Colourists

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COLORANTS AND AUXILIARIES

ORGANIC CHEMISTRY AND APPLICATION PROPERTIES

Second Edition

Volume 1 – Colorants

Contributors

John Shore
Formerly of BTTG/Shirley and ICI Dyes (now DyStar), Manchester, UK

David Patterson
Formerly senior lecturer, Department of Colour Chemistry and Dyeing, University of Leeds, UK

Geoff Hallas
Formerly senior lecturer, Department of Colour Chemistry and Dyeing, University of Leeds, UK

Preface to Volume 1

This Second Edition of a textbook first published in 1990 forms part of a series on colour and coloration technology initiated by the Textbooks Committee of the Society of Dyers and Colourists under the aegis of the Dyers' Company Publications Trust Management Committee, which administers the trust fund generously provided by the Worshipful Company of Dyers.

The initial objective of this series of books has been to establish a coherent body of explanatory information on the principles and application technology of relevance for students preparing to take the Associateship examinations of the Society. This particular book has been directed specifically to the subject areas covered by Section A of Paper B: the organic chemistry and application of dyes and pigments and of the auxiliaries used with them in textile coloration processes. However, many qualified chemists and colourists interested in the properties of colorants and their auxiliaries have found the First Edition useful as a work of reference. For several reasons it has been convenient to divide the material into two separate volumes: 1. Colorants, 2. Auxiliaries. Although fluorescent brighteners share some features in common with colorants, they have been treated as auxiliary products in this book.

This first volume of the book is concentrated on the chemical characteristics of dyes and pigments, with emphasis on attempts to interpret their colouring and fastness properties in terms of the essential structural features of colorant molecules. This Second Edition has been extensively updated and greater attention has also been given to factors associated with the potential impact of colorants and their metabolites on the environment. All chapters have been affected by these changes, but the concluding chapter on reactive dyes contains more new material than the others. Rationalisation of the global dyemaking industry during the 1990s means that many of the traditional commercial names of dyes and pigments have disappeared. For this reason Part 2 of the Colorants Index has been eliminated and colorants have been specified almost always by their CI Generic Names. The fundamental value of the unique *Colour Index International* to colorant makers and users is recognised worldwide.

Chapters 4 and 7 in the First Edition were written by Vivian Stead and Chapter 5 by Frank Jones. Sadly, Frank died in 1989 and Vivian in 1996, but my co-authors and myself would like to record our tribute for the major contributions to this volume by our former friends and colleagues. We have tried to preserve their original style intact during the necessary updating process. Our grateful thanks are due to John Holmes and Catherine Whitehouse for their patient copy editing and to the publications staff of the Society, especially Carol Davies, who have prepared all the material in this new edition for publication.

JOHN SHORE

Chapters in Volume 2

Chapter 8 Functions and properties of dyeing and printing auxiliaries

Chapter 9 The chemistry and properties of surfactants

Chapter 10 Classification of dyeing and printing auxiliaries by function

Chapter 11 Fluorescent brightening agents

Chapter 12 Auxiliaries associated with main dye classes

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CHAPTER 1

Classification and general properties of colorants

John Shore

1.1 INTRODUCTION

It is important to distinguish clearly between dyes, pigments and colorants. Such terms are sometimes incorrectly used in various major scientific languages, as though they were synonymous [1]. All dyes and pigments are colorants: when present on a substrate they selectively modify the reflection or transmission of incident light. During application to a substrate, a dye either dissolves or passes through a state in which its crystal structure is destroyed. It is retained in the substrate by adsorption, solvation, or by ionic, coordinate or covalent bonding. A pigment, on the other hand, is insoluble in and unaffected by the substrate in which it is incorporated. These inherent characteristics mean that dyes and pigments have quite different toxicological and environmental profiles [1].

Synthetic dyes and pigments have been available to the colorant user since the mid-nineteenth century. The important naturally occurring substrates of pre-industrial societies (cotton, linen, silk, wool, leather, paper, wood) share certain similarities, since they are all essentially saccharidic or peptide polymers. They could thus be coloured using a relatively short range of dyes and pigments, also of natural origin. An early objective of planned research on synthetic dyes, therefore, was to replace the leading natural extracts (alizarin and indigo) by their synthetic equivalents. Simultaneously with this diligent and ultimately successful effort, other chemists were discovering totally new chromogens unknown in nature: azine, triarylmethane and others from arylamine oxidation, azo colorants from the diazo reaction, and eventually azo–metal complexes and phthalocyanines. Building on success with indigo and anthraquinone derivatives, the systematic approach led on to related but new chromogens with outstanding properties: vat dyes and novel pigments.

Linked to this research by a common interest in certain versatile intermediates and a similar urge to extend the limited range of natural substrates, a new breed of organic chemist, the polymer specialist, was vigorously developing novel regenerated and synthetic fibres, plastomers, elastomers and resins. Most of these differed markedly in structure and properties from natural polysaccharides or polypeptides. Particularly in the mid-twentieth century, urgent demands arose for special new colorants and application techniques designed to colour these substrates. Disperse dyes for ester fibres, modified basic dyes for acrylic fibres and pigments for the mass coloration of fibres and plastics are typical examples of the response of the colour chemist. Natural fibres also gained from this broad wave of research: reactive dyes for cellulosic and protein fibres, and fluorescent brighteners for undyed textiles, paper and detergent formulations were discoveries stemming essentially from this exceptionally active period.

In the closing decades of the twentieth century, the emergence of an unknown substrate became a rare event. The rate of introduction of radically new colorants, auxiliary products and processes fell markedly. An increasingly adverse balance arose between the escalating costs of the research effort and of much more stringent hazard testing, as against the diminishing value of marginal technical or economic improvements to existing ranges of colorants on standard substrates. Many of the pathways of colorant research have turned away from conventional outlets for dyes and pigments towards more esoteric applications [2–7]. Although colorants of these types are unlikely to match the traditional textile dyes in terms of total sales value, their unit prices and profit margins can often be exceptionally high.

Many specialised applications of colorants are related to the way in which they absorb and emit light. The ability of a dye molecule to absorb depends critically on its orientation with respect to the electrical vector of the incident light, i.e. the polarisation of absorption. In recent years this has become of practical significance in the field of liquid crystal displays [8]. Colorants exhibiting high absorption of infrared light have found many diverse applications, ranging from solar energy traps to laser absorbers in electro-optical devices [9,10]. Dye lasers are based on dyes that fluoresce with high quantum efficiency. They must show good photostability and be marketed in a state of high purity, thus commanding a high unit price. Fluorescent dyes are also used in biochemical and medical analysis where extremely low detection limits are required. Polymeric colorants have been developed as potential food colourings [11], since chemicals of relative molecular mass greater than about 20 000 cannot be absorbed into the gastro-intestinal tract. Such colorants should pose no toxicological problems as food additives.

The chemical or photochemical activity of dyes forms the basis of many of their innovative uses. Indicator systems and lactone colour formers exploit reversible colour changes. Thermochromism is applied in novelty inks, temperature sensors and imaging technology. Photosensitising cyanine dyes are used to transfer absorbed light energy to silver halides in photography. Certain dyes are effective sensitisers of free-radical reactions, thereby initiating the crosslinking or photodegradation of polymers on exposure to light. Photochromic colorants have been employed in light monitors, reversible sun screens, optical data recording and novelty surface coatings.

1.2 DEVELOPMENT OF COLORANT CLASSIFICATION SYSTEMS

A major objective of this chapter is to outline the principal system by which colorants are classified, namely the widely accepted *Colour Index* classification. After tracing the developments from which this system has evolved [12,13], the distribution of existing dyes and pigments among the various classes listed therein will be introduced. Each of these classes will be discussed in turn, illustrated by structural formulae.

The earliest comprehensive alphabetical listing [14] of synthetic products used in the coloration industry was published in 1870. The beginnings of systematic classification based on chemical structure, with subgrouping according to hue, were first seen in the 1880s. A typical presentation of this period [15] listed about 100 'coal-tar dyes' in hue order. It is interesting that 50% of them were acid dyes and 20% basic dyes, about 40% being placed in the 'red' category. Undoubtedly the most successful of these early systems were the famous '*Farbstofftabellen*' of Gustav Schultz, which ran through seven editions between 1888 and

1932. The number of chemical entries rose from about 280 to nearly 1500 over these years. The later editions of this work pioneered many of the features eventually adopted in the *Colour Index*.

The Society of Dyers and Colourists embarked on the First Edition of the *Colour Index* in 1921 as a series of monthly issues that were first offered as a bound volume in 1924. There were over 1200 entries for synthetic colorants, as well as sections on natural dyes and inorganic pigments. Updating was discontinued in 1928, so that by 1945 the need for a Second Edition had become urgent. Much detailed information on the products of German manufacturers became available following the Second World War. Collaboration with the American Association of Textile Chemists and Colorists resulted in the four-volume Second Edition published in 1956–58. This contained about 3600 colorants differing in constitution and an especially useful innovation was the separate listing of commercial names (31,500) under equivalent CI generic names (4600 entries).

This edition and the completely revised five-volume Third Edition (1971) established the *Colour Index* as the leading reference work for the classification of colorants, fully justifying the cognomen International belatedly added in 1987. The fourth revision (1992) of the Third Edition consisted of nine volumes. The original data on technical properties (Volumes 1–3) and chemical constitution (Volume 4) was supplemented (Volumes 6–9) at roughly five-year intervals.

The latest revision of the *Colour Index* has become an electronically searchable database available on CD-ROM as well as the traditional book form, providing improved functionality and better value for money. Chemical constitutions, indexes of commercial names and lists of manufacturers have been computerised for ease of reference and search purposes. The commercial listing function Volume 5 was detached in 1997 to form a new annual publication, the *SDC Resource File*. The aim of this novel concept was to provide colorant users with the latest comprehensive information on relevant products and services. This is provided by suppliers to the colour-using industries and coordinated by the SDC through its *Colour Index* organisation [13]. In 1998 a new edition covering pigments and solvent dyes designed explicitly for the pigment industry was published [16], the technical and scientific content of the material being upgraded [17].

This divergence is a response to certain problems that have arisen, particularly in relation to commercial product listings. As non-traditional suppliers based in low-cost countries have taken a greater share of world trade in colorants, the attitude of established European and Japanese producers towards disclosure of information has changed. When such companies have already expended substantial resources on research, development and hazard testing to launch a new product, they are understandably reluctant to surrender commercially sensitive data into the public domain and thus give their competitors a head start. Colorant users rely on the equivalence of CI generic names of commodity products as a basis of comparison between suppliers, but the long-established dyemakers are wary of this equivalence for novel products because it offers low-cost competitors an easy entry into traditional markets [13].

The *Colour Index* has become a standard reference for customs and importing authorities in many countries. Health and safety inspectorates have used CI designations in dealing with colorant manufacturers notifying hazard testing data for their products. As with some other European Union initiatives, administration of legislation governing the notification of commercial chemicals for hazard control purposes has generated problems for suppliers, users and enforcing authorities. Distinguishing between 'existing' (i.e. notified in 1981) and 'new' products is not as easy as it sounds. Organic colorants present special difficulties because of their complex structures and chemical nomenclature, variations of counter-ions with the same ionic dye, obsolete or confusing identities of 'existing' products, and, not least, the ubiquitous marketing of mixed colorants to match specific colours or technical properties [18].

1.3 COLOUR INDEX CLASSIFICATION

Most organic colorants in the *Colour Index*, including many of those not assigned a specific chemical constitution number, are placed in one of 25 structural classes according to their chemical type (where this is known). The largest class, azo colorants, is subdivided into four sections depending on the number of azo groups in the molecule. Metal-complex azo colorants are designated separately by description but are classified together with their unmetallised analogues in the same generic class. Excluding the colorant precursors, such as azoic components and oxidation bases, as well as the sulphur dyes of indeterminate constitution, almost two-thirds of all the organic colorants listed in the *Colour Index* belong to this class, one-sixth of them being metal complexes. The next largest chemical class is the anthraquinones (15% of the total), followed by triarylmethanes (3%) and phthalocyanines (2%). No other individual chemical class accounts for more than 1% of the *Colour Index* entries.

The distribution of each chemical type between the major application groups of colorants is far from uniform (Table 1.1). Stilbene and thiazole dyes are almost invariably direct dyes, also containing one or more azo groups. Acridines and methines are usually basic dyes,

Table 1.1 Percentage distribution of each chemical class between major application ranges

	Distribution between application ranges (%)								
Chemical class	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Unmetallised azo	20	5	30	12	12	6	10	5	
Metal-complex azo	65		10				12	13	
Thiazole		5	95						
Stilbene			98					2	
Anthraquinone	15	2		25	3	4	6	9	36
Indigoid	2					17			81
Quinophthalone	30	20		40				10	
Aminoketone	11			40	8		3	8	30
Phthalocyanine	14	4	8		4	9	43	15	3
Formazan	70						30		
Methine		71		23		1		5	
Nitro, nitroso	31	2		48	2	5		12	
Triarylmethane	35	22	1	1	24	5		12	
Xanthene	33	16			9	2	2	38	
Acridine		92		4				4	
Azine	39	39				3		19	
Oxazine		22	17	2	40	9	10		
Thiazine		55			10			10	25

whereas nitro, aminoketone and quinophthalone derivatives are often disperse dyes. Metal-complex azo and formazan types are mainly acid dyes but phthalocyanines are important for reactive dyes. Indigoids are predominantly vat dyes but anthraquinones retain considerable significance as acid, disperse or vat dyes. The data in this table are given in percentages because the actual numbers of dyes recorded gradually increase as new products are added. They relate to all those dyes listed where the chemical class is known, including products no longer in commercial use.

There are nineteen generic name groups (application ranges) listed in the *Colour Index*. CI Acid dyes constitute the largest range, with about 55% of them still in commercial use. Next come CI Direct dyes (40% still active) and CI Disperse dyes (60% active). CI Reactive dyes (75% active), CI Basic dyes, CI Solvent dyes and CI Pigments (all 60% active) continue to progress, but CI Vat dyes (45% active) and CI Mordant dyes (33% active) are in decline [19]. CI Sulphur dyes can be regarded as a distinct chemical class as well as an application range, although a few vat dyes are manufactured in a similar way. Essentially CI Food dyes and CI Leather dyes are selections from the larger ranges of textile dyes. Several of these application types are represented in the CI Natural dyes and pigments category. The groupings according to generic name also include colorant precursors (CI Azoic Components and CI Developers, CI Ingrain dyes, CI Oxidation Bases) and uncoloured products (CI Fluorescent Brighteners and CI Reducing Agents) associated with textile coloration.

Chemists concerned with innovative applications for specialised colorants have highlighted the need for an independent directory covering all such products and uses that do not fit easily into the above textile-oriented categories [5]. Quite often these research projects signal a need for a specific combination of relatively unorthodox properties, such as fluorescence, infrared absorption or photosensitivity combined with solubility in an unusual solvent. Often this has involved a time-consuming search through the hardcopy *Colour Index* and other more specialised catalogues. Now that a searchable CD-ROM version has become available, together with the annual *SDC Resource File* in which to locate suitable suppliers, it has become easier for less conventional demands on the database to be adequately met [13].

1.4 CHEMICAL CLASSES OF COLORANTS

A brief description of each class of colorant is given below, in order to show how they contribute to the overall distribution outlined in Table 1.1. For further details the reader is referred to the later Chapters 2 to 7. Many of the lesser-known chemical classes are more fully described in Chapter 6.

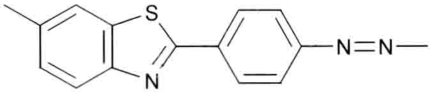
The order of discussion of the chemical classes included here differs somewhat from that in the *Colour Index*. Thiazole dyes are dealt with immediately after the stilbene class because both of these, like the polyazo types, contribute notably to the range of direct dyes. The anthraquinone, indigoid, quinacridone, quinophthalone, benzodifuranone and aminoketone classes form another series with certain structural similarities and important applications in vat or disperse dyes and pigments. Phthalocyanine and formazan are stable metal-complex chromogens. The remaining seven categories included are already less important and still declining in commercial significance. The arylmethane, xanthene, acridine, azine, oxazine and thiazine chromogens share a limited degree of resemblance in structural terms.

1.4.1 Azo colorants

The presence of one or more azo (–N=N–) groups, usually associated with auxochromic groups (–OH or –NH–), is the characteristic feature of this class. Hydroxyazo dyes exhibit benzenoid–quinonoid tautomerism with the corresponding ketohydrazones [4,20,21]. At least half of all commercial azo colorants belong to the monoazo subclass, that is, they have only one azo group per molecule. This proportion is considerably higher among the metal-complex azo dyes. Direct dyes represent the only application range where monoazo compounds are relatively unimportant; disazo and trisazo dyes are preferred in order to confer higher substantivity for cellulose. The numerous ways in which diazo and coupling components can be used to assemble azo colorants for many purposes are discussed in Chapter 4. Yellow azo chromogens are occasionally linked to blue anthraquinone or phthalocyanine structures in order to produce bright green colorants.

1.4.2 Thiazole dyes

The characteristic chromogen of this class is the thiazole ring itself, normally forming part of a 2-phenylbenzothiazole grouping. Most are yellow direct dyes of the azophenylthiazole (1.1) type, but a minority are simple basic dyes with an alkylated thiazolinium group (1.2), such as Thioflavine TCN (CI Basic Yellow 1) shown. The thiazole ring enhances substantivity for cellulose and thus has been incorporated into certain anthraquinonoid and sulphurised vat dyes. Several important blue basic dyes are 2-phenylazo derivatives of 6-alkoxybenzothiazolinium compounds (1.3). A typical red disperse dye for cellulose acetate in this class is the 6-methoxybenzothiazole CI Disperse Red 58 (1.4).



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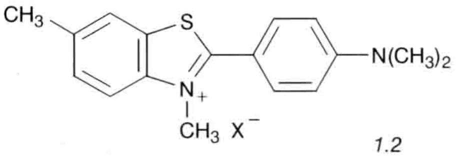

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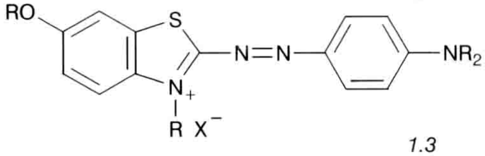
CI Basic Yellow 1



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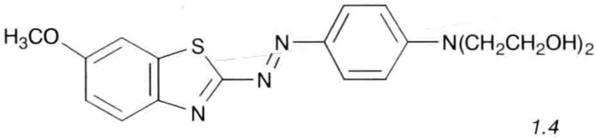
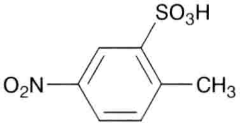


1.4

CI Disperse Red 58

1.4.3 Stilbene dyes and fluorescent brighteners

Stilbene dyes are mixtures of indeterminate constitution resembling polyazo direct dyes in their application properties. They result from the alkaline self-condensation of 4-nitrotoluene-2-sulphonic acid (1.5) or its initial condensation product (1.6; X = NO_2), either alone or with various arylamines. The characteristic chromogens are azo- or azoxystilbene groupings (1.7). As with sulphur dyes, the CI generic names of stilbene dyes refer not to specific chemical entities but to mixtures of related compounds with closely similar dyeing and fastness properties. Almost all of them are yellow to brown direct dyes for cellulosic fibres and leather.



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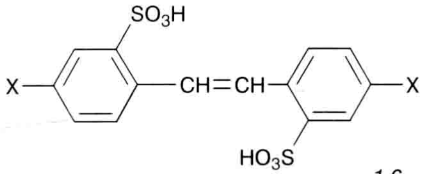

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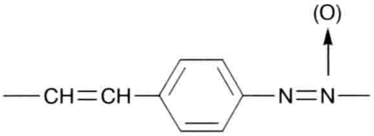
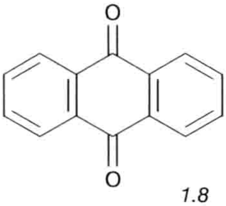


1.7

Approximately 75% of fluorescent brighteners belong to the stilbene class. These are almost invariably derived from 4,4′-diaminostilbene-2,2′-disulphonic acid (1.6; $X = NH_2$), often condensed with cyanuric chloride to take advantage of the further contribution of the s-triazine rings to substantivity for cellulose.

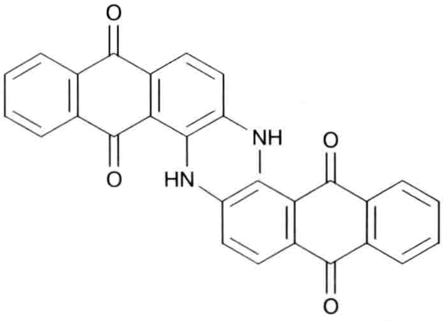
1.4.4 Anthraquinone colorants

Strictly speaking, the characteristic chromogen of these should be anthraquinone (1.8) itself, but the term, 'anthraquinonoid', is frequently extended, in the *Colour Index* as elsewhere, to include other polycyclic quinone structures. These are often synthesised from anthraquinone derivatives and most of them, including dibenzopyrenequinone (CI Vat Yellow 4), pyranthrone (CI Vat Orange 9), isoviolanthrone (CI Vat Violet 10) and violanthrone (CI Vat Blue 20), are strongly coloured even in the absence of auxochromes. Indanthrone (1.9; CI Vat Blue 4), the first polycyclic vat dye to be discovered, resulted from an unsuccessful attempt to link two anthraquinone nuclei via an indigoid chromogen. Polycyclic pigments are dealt with in Chapter 2 and the many derivatives of anthraquinone applicable as acid, basic, disperse, mordant, reactive and vat dyes are discussed in Chapter 6.



1.8

Anthraquinone



1.9

Indanthrone