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

Chemical class	Distribution between application ranges (%)								
	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).

1.1

1.2

CI Basic Yellow 1

1.3

1.4

CI Disperse Red 58
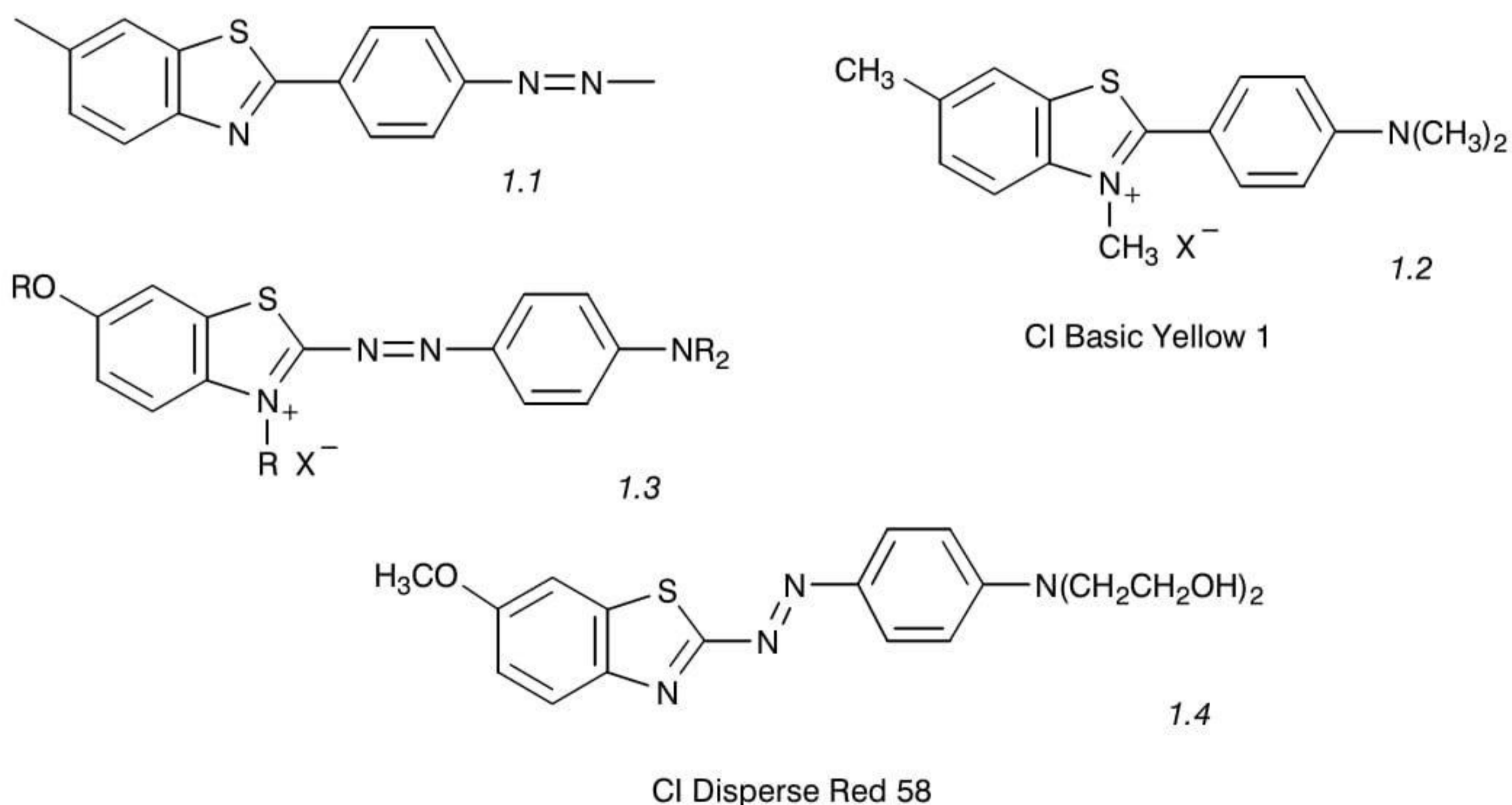
1.4.3 Stilbene dyes and fluorescent brighteners

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.

1.5

1.6

1.7
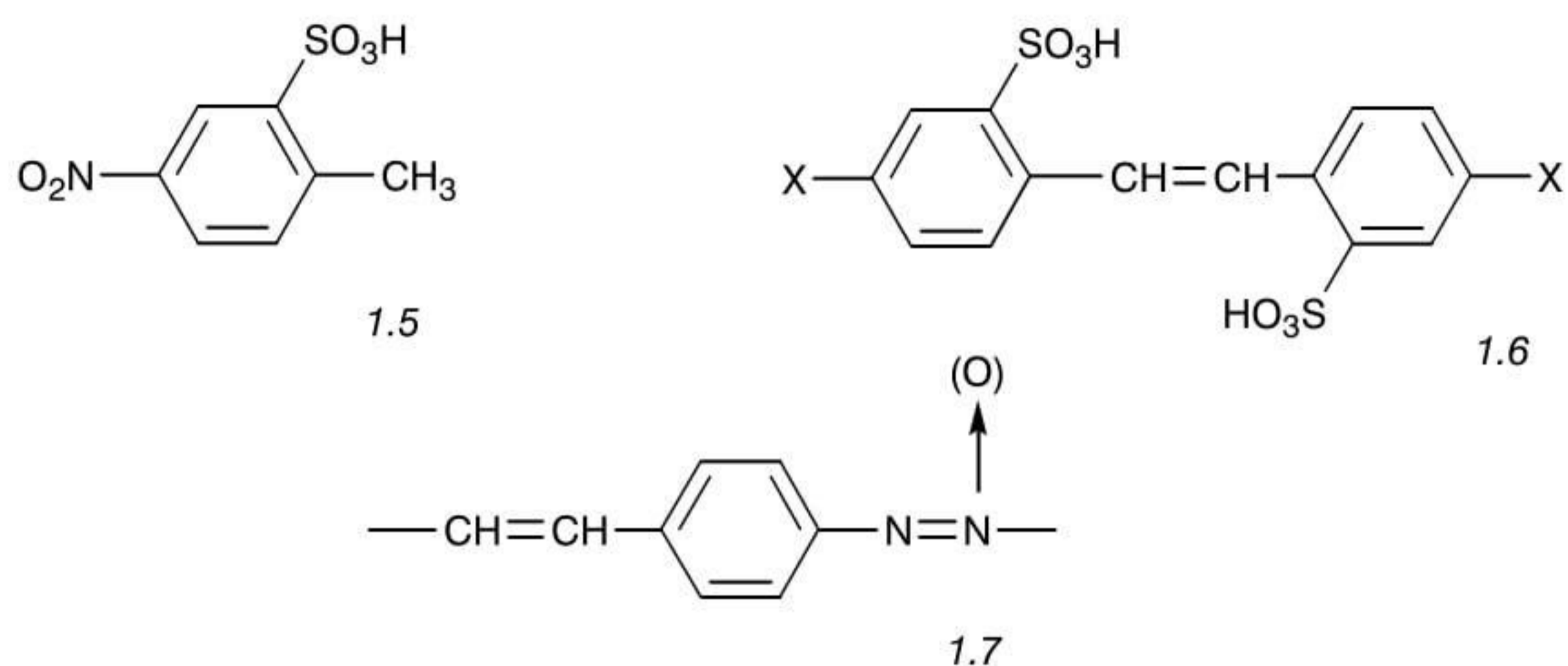
Approximately 75% of fluorescent brighteners belong to the stilbene class. These are almost invariably derived from 4,4′-diaminostilbene-2,2′-disulphonic acid (1.6; X = NH$_2$), often condensed with cyanuric chloride to take advantage of the further contribution of the s-triazine rings to substantivity 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
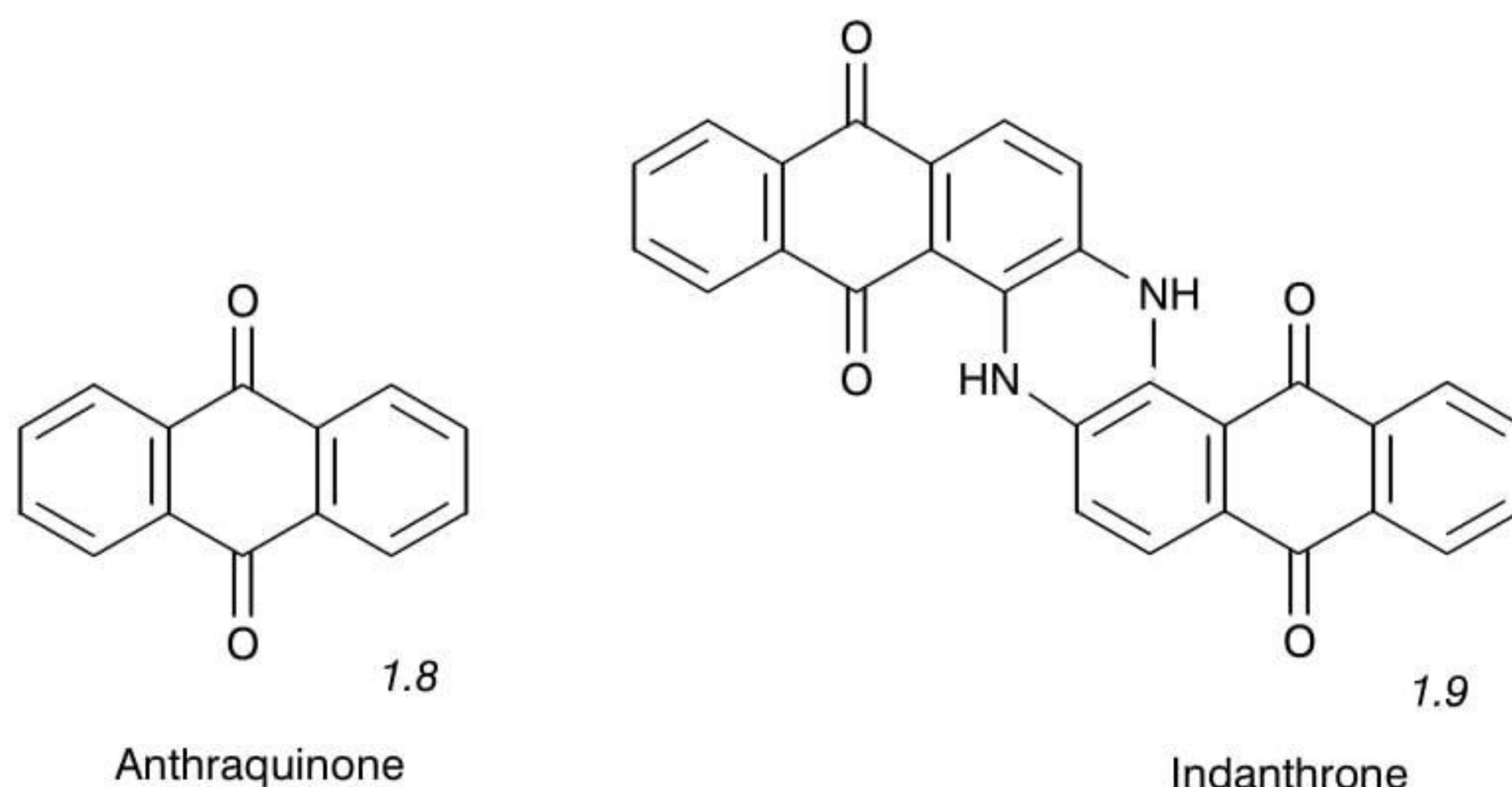
1.4.5 Indigoid colorants

This substantial class of vat dyes and pigments has declined markedly in importance relative to the anthraquinone derivatives. The still pre-eminent representative is indigo (1.10; CI Vat Blue 1), the dye most consistently in demand of all time. Originally obtained from natural sources, indigo was probably the decisive impetus for the early development of the synthetic dye industry [22]. In indigo and thioindigo (1.11; CI Vat Red 41) the chromogenic system is symmetrical. These dyes can exist in both *cis* and *trans* forms; the latter is the more stable form that predominates in the solid state. Unsymmetrical indigoid dyes are also known, in which the two halves of the molecule united by the central C=C bond differ in substitution pattern, heteroatom or orientation of the hetero ring, as in the monobrominated indolethianaphthene analogue (1.12).

Indigo   *1.10*

Thioindigo   *1.11*

1.12
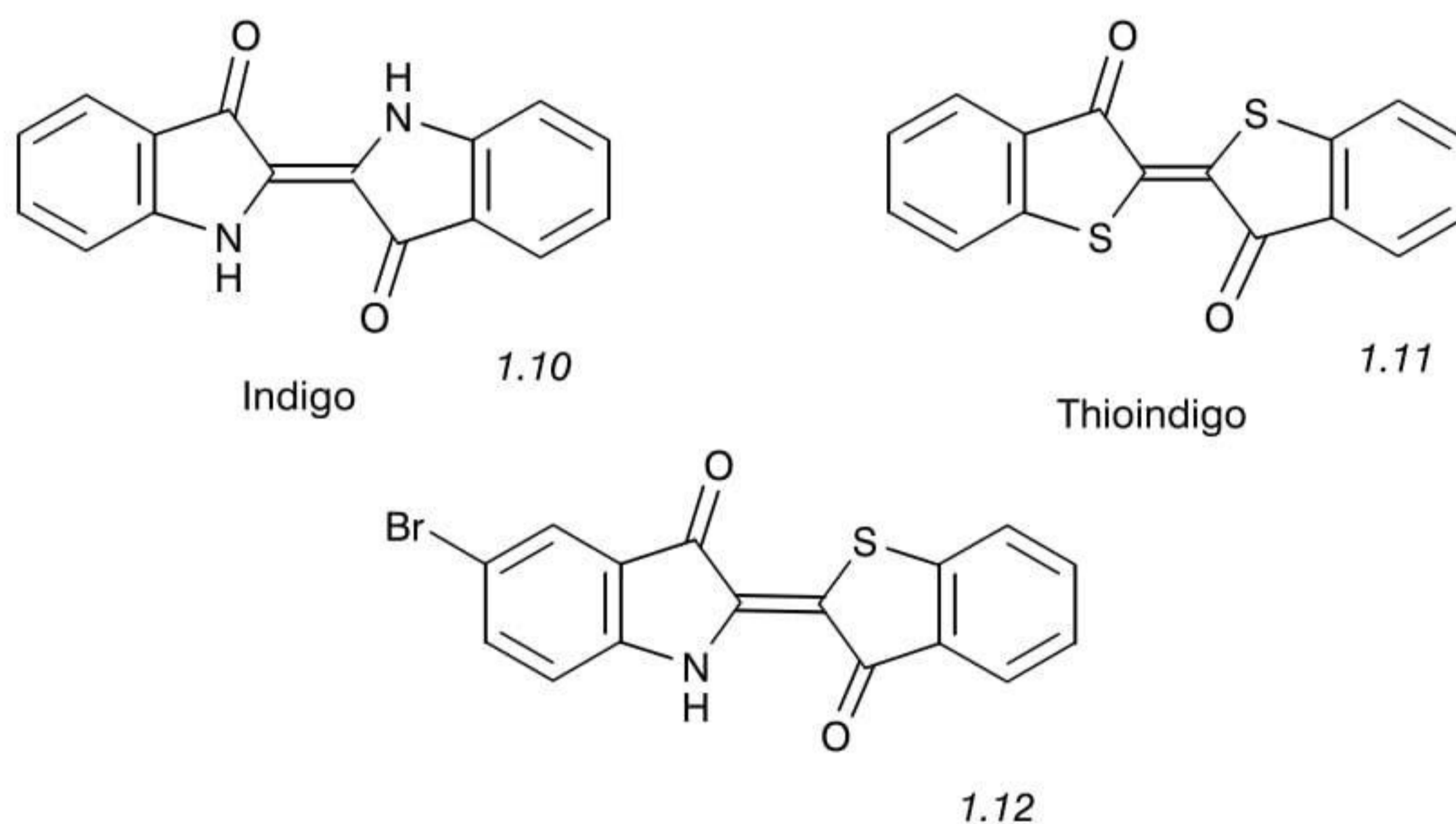
1.4.6 Quinacridone pigments

This chromogen (1.13) is somewhat reminiscent of the indigoid and anthraquinone types but it has not yielded useful vat dyes. Bluish red pigments of the quinacridone class are especially important in violet and magenta colours or for deep reds in admixture with inorganic cadmium scarlets.

1.13

Quinacridone
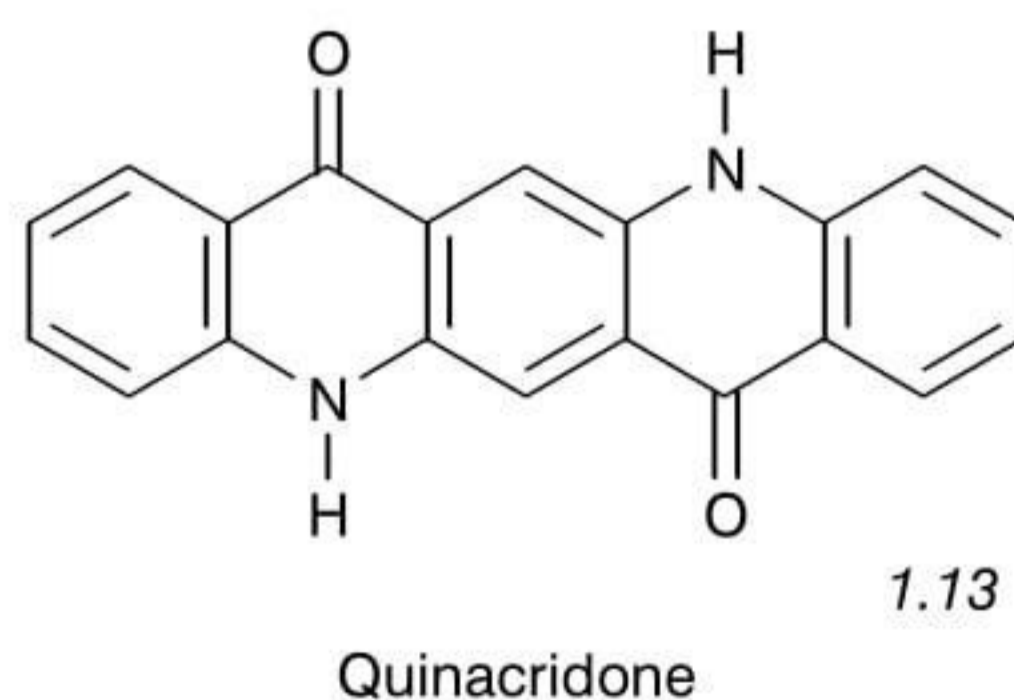
1.4.7 Benzodifuranone dyes

The discovery in 1979 of the benzodifuranone chromogen (1.14) and its exploitation in red disperse dyes for polyester fibres [23,24] emerged from ICI research towards new chromogens of high colour value, brightness and substantivity to overcome the relative weakness of anthraquinones and dullness of monoazo alternatives in the red disperse dye area. A striking improvement in build-up properties was found by introducing asymmetry

into the dye molecule, especially where the substituents R are different. Benzodifuranone derivatives are unlikely to yield useful water-soluble dyes for cotton or wool, since the lactone rings in the chromogen are readily hydrolysed. In fact this property is utilised to advantage when these disperse dyes are applied to polyester, the dyeings produced being readily cleared with alkali [25].


1.14
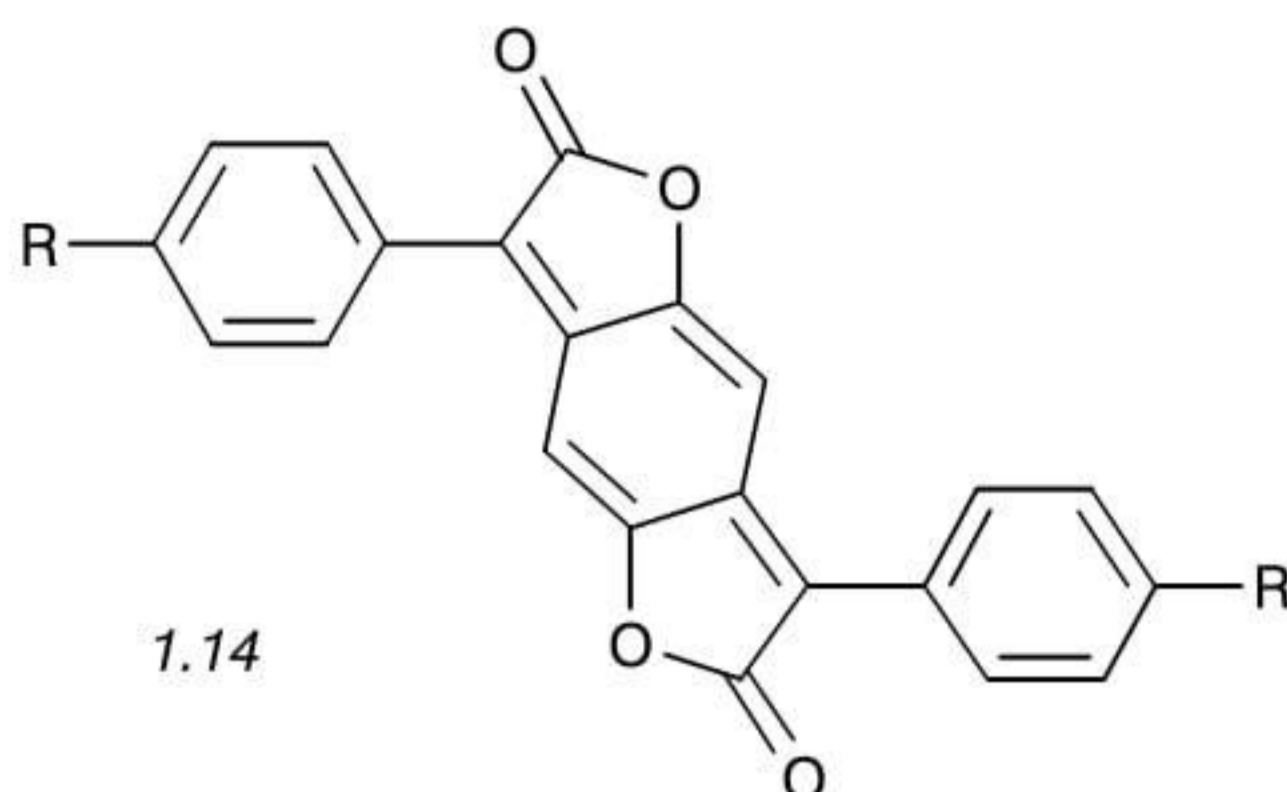
1.4.8 Quinophthalone dyes

The name of this structural class ('quinoline') in the *Colour Index* is not ideal because quinoline derivatives feature in other related classes, such as the methine basic dyes with a quinolinium cationic group. The class is more precisely associated with quinophthalone (1.15), the characteristic chromogen derived by condensation of quinoline derivatives with phthalic anhydride. This small class of yellow compounds contributes to the disperse, acid, basic and solvent ranges of dyes.


1.15
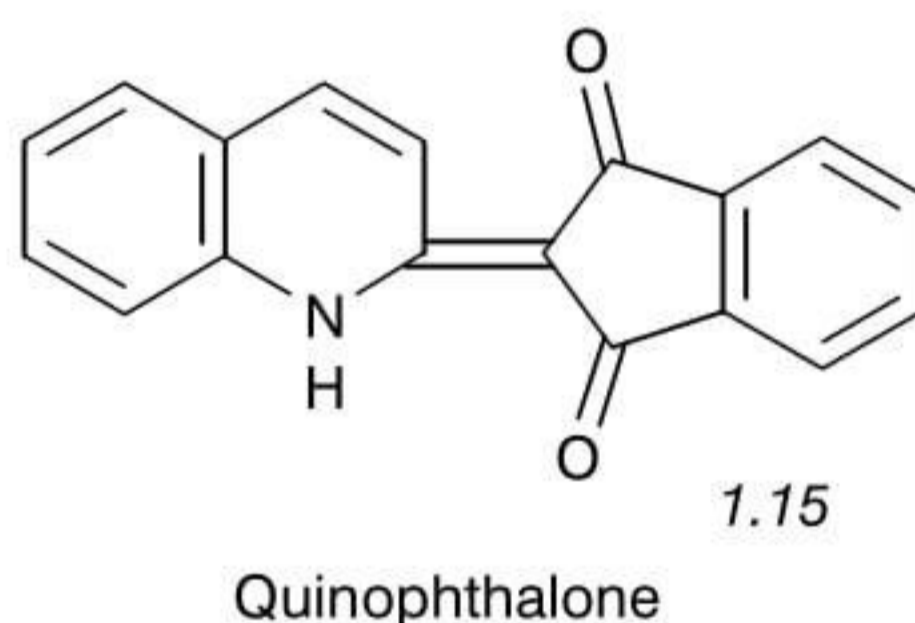
Quinophthalone

1.4.9 Aminoketone and hydroxyketone dyes

This small group of hydroxyquinone (1.16), arylaminoquinone (1.17) and aminophthalimide (1.18) derivatives has contributed a few members of some application ranges, mainly yellow disperse dyes and reddish brown vat dyes, but there are superior alternatives available from the major chemical classes.


1.16

1.17

1.18
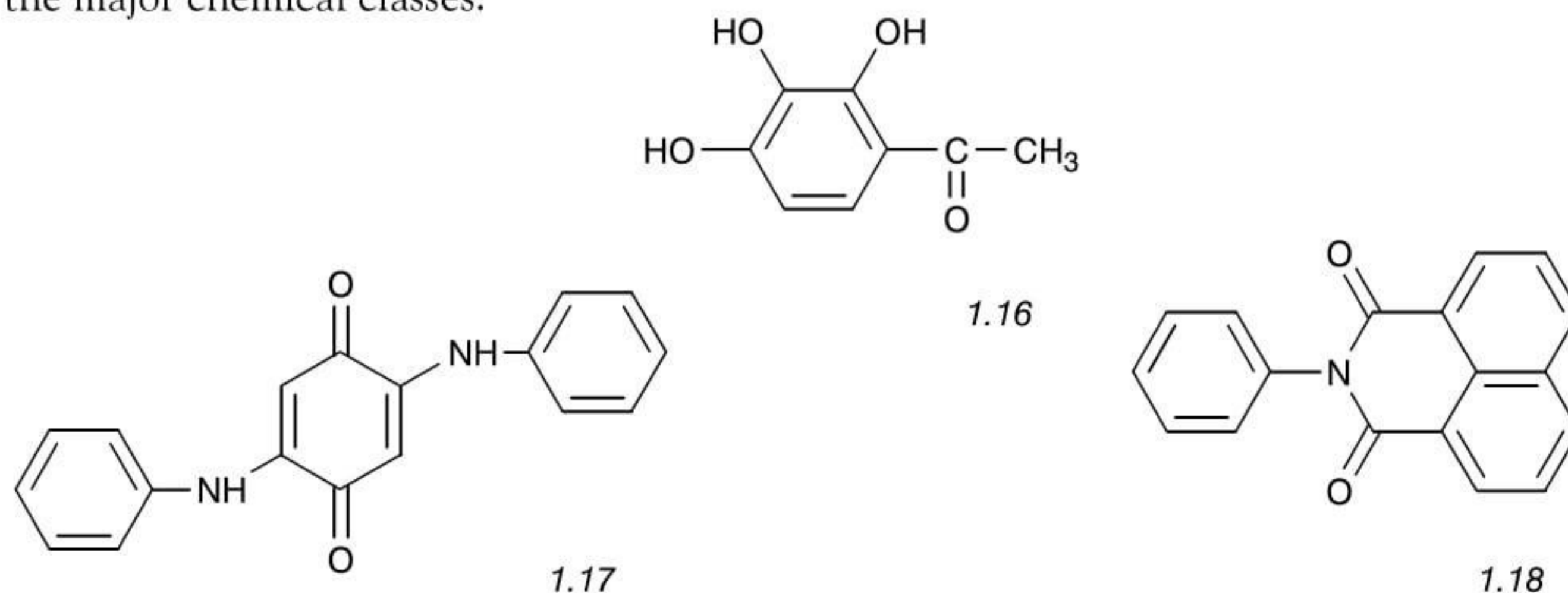
1.4.10 Phthalocyanine colorants

Substituted derivatives of metal-free phthalocyanine (CI Pigment Blue 16) and a series of metal complexes, notably copper phthalocyanine (1.19; M = Cu; CI Pigment Blue 15), contribute brilliant blue and green colours to several application ranges [26]. Pigments and reactive dyes are especially dependent on this chemical class, but examples exist in all the important ranges except disperse dyes. These colorants are discussed in more detail in sections 2.4, 5.4.3 and 7.5.10. More recently, owing to their complex molecular structure and high electron-transfer ability, phthalocyanine derivatives are being used increasingly in non-coloration applications such as catalysis, optical recording, photoconductive materials, photodynamic therapy and chemical sensors [27].

1.19
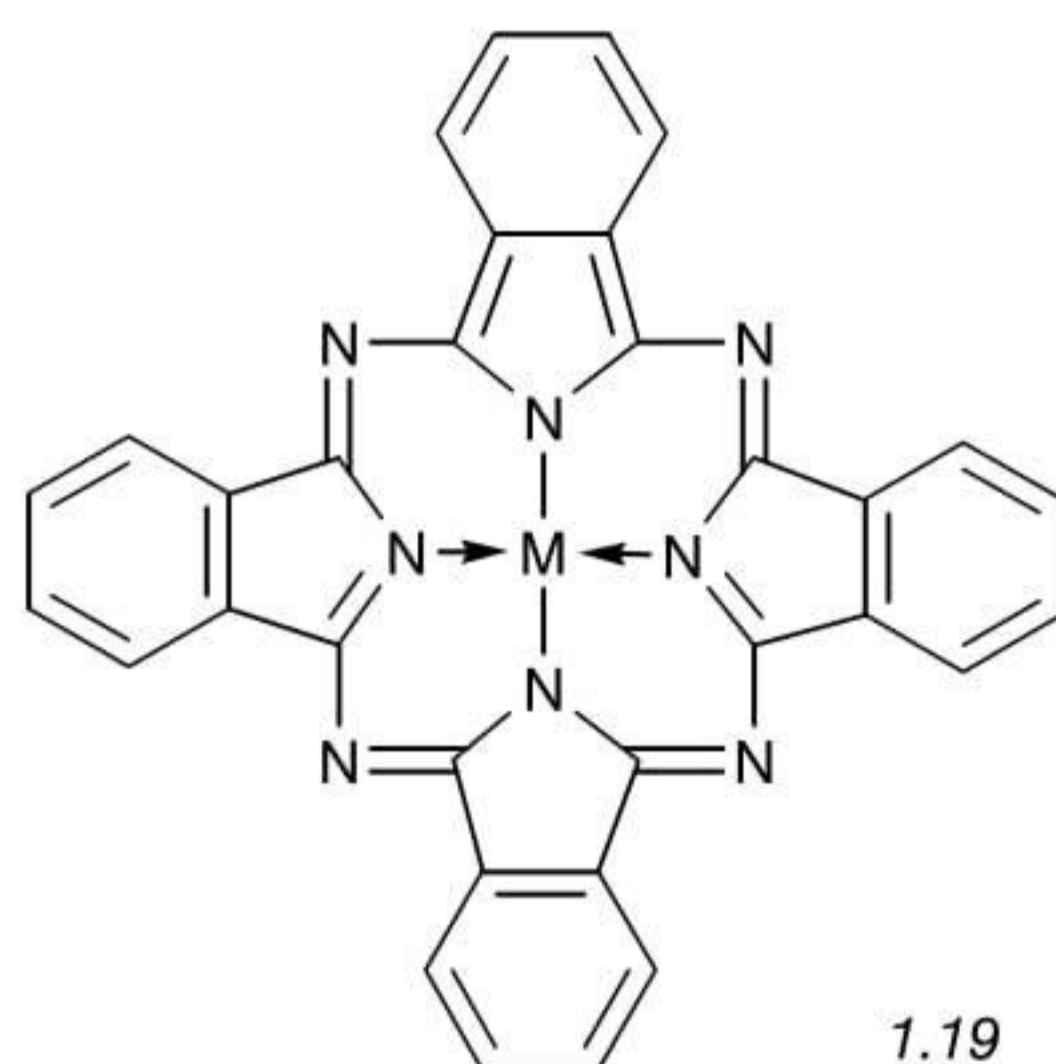
1.4.11 Formazan dyes

This small class of blue copper-complex dyes has made a significant contribution to the acid and reactive ranges in recent years (sections 5.4.2, 5.4.3 and 7.5.8). The essential chromogen is the bicyclic 1:1 chelated grouping illustrated (1.20). Trivalent metals such as chromium, nickel or cobalt will give tetracyclic 1:2 complexes with a central metal atom, analogous to conventional 1:2 metal-complex azo dyes.

1.20
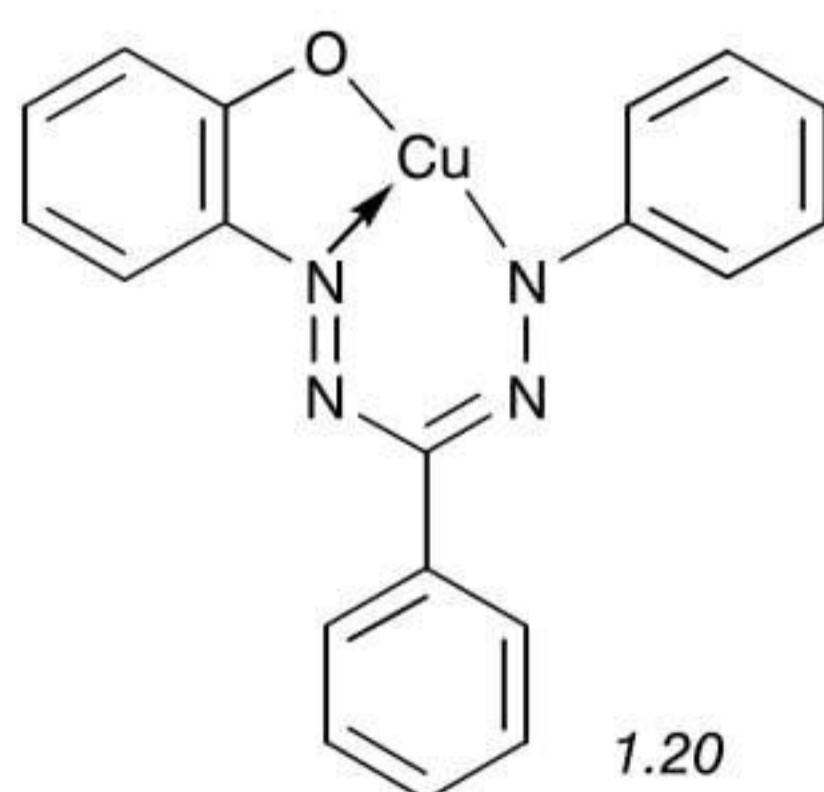
1.4.12 Cyanine colorants

Dyes in this category, classified as methines (1.21) and polymethines (1.22) in the *Colour Index*, characteristically contain a conjugated system through one or more methine (–CH=) groups terminating with heterocyclic atoms, usually nitrogen as in the quinoline (1.21) and

trimethylindoline (1.22) types [4]. The most important function of cyanine colorants is as sensitisers in photography. One or more methine groups may be replaced by nitrogen atoms, as in the azacyanines. Many methine compounds intended for textiles are yellow or red basic dyes, but uncharged yellow methine disperse dyes (1.23) and azomethine chromium-complex solvent-soluble dyes (1.24) are also significant.
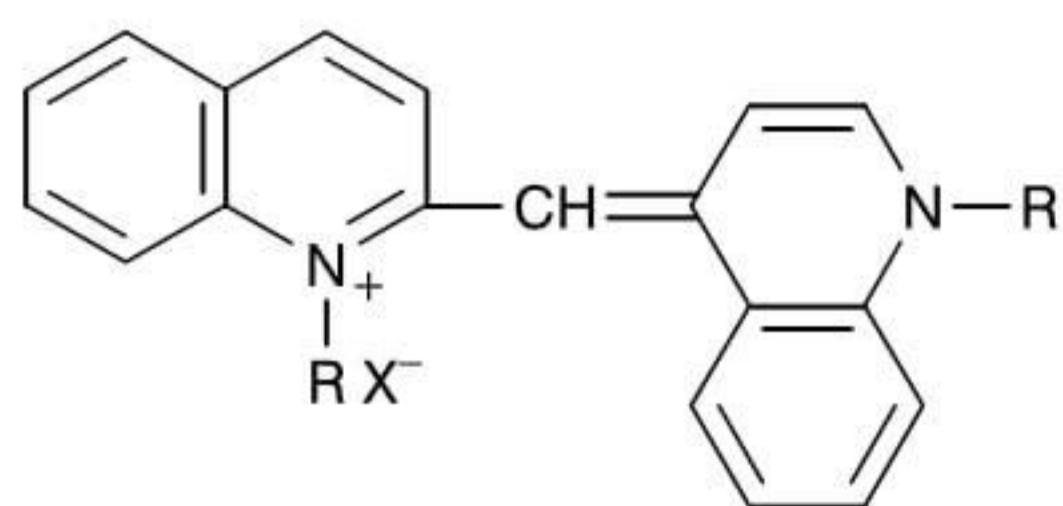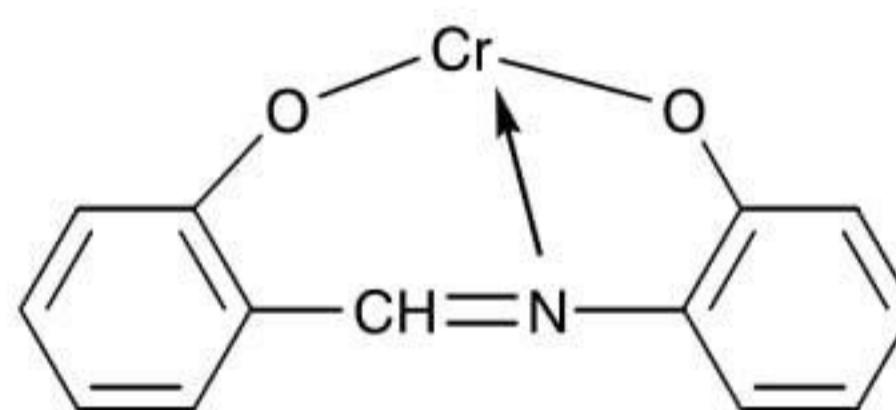
1.21
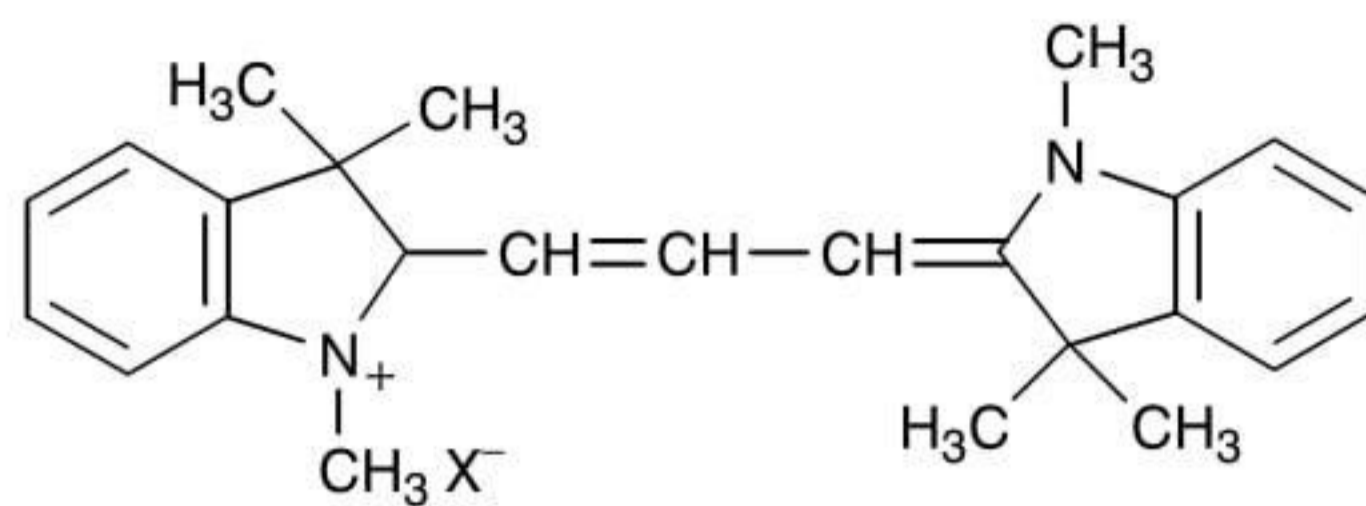
1.22
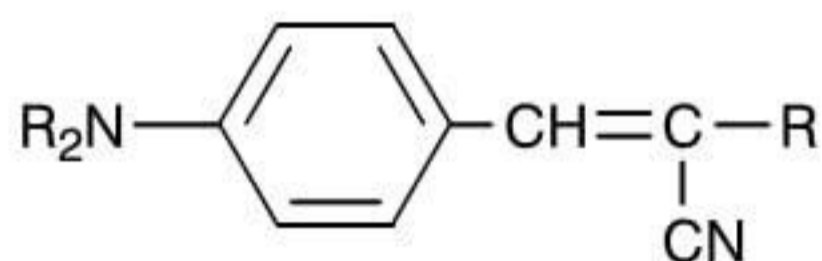
1.23

1.24

1.4.13 Nitro and nitroso colorants

Nitro dyes exhibit benzenoid-quinonoid tautomerism (1.25) and their colour is attributed mainly to the o-quinonoid form, since this can be stabilised by hydrogen bonding. The tautomeric o-nitrosonaphthols (1.26) readily form chelate complexes with metals. A few yellow nitro disperse dyes, including CI Disperse Yellow 1 (1.25), and brown acid dyes remain of significance. The remaining nitro and nitroso colorants, such as (1.26) and its 1:3 iron (II) complex (1.27), are no longer of commercial interest.
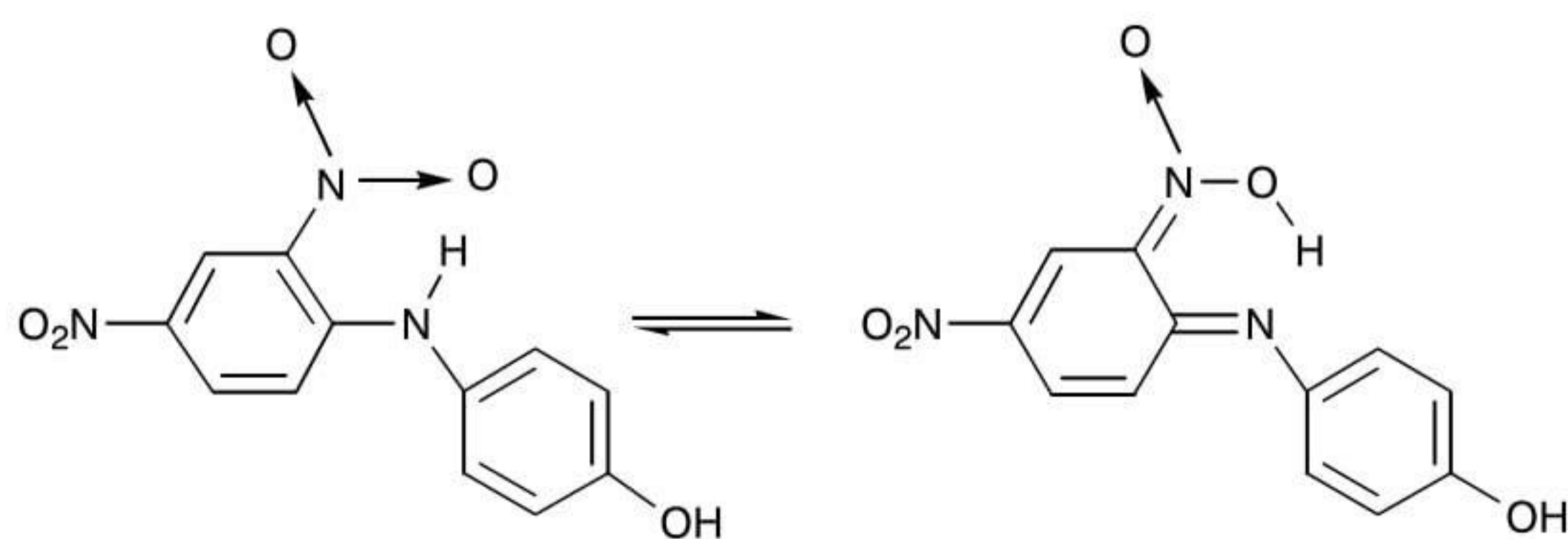
CI Disperse Yellow 1

1.25

1.26

1.27
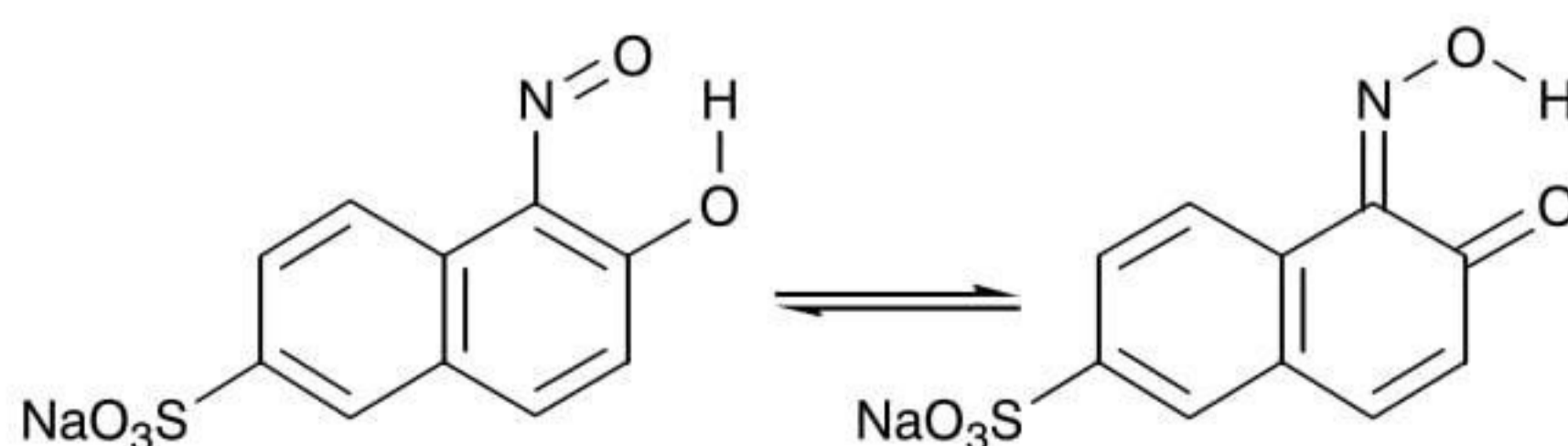
CI Acid Green 1

1.4.14 Diphenylmethane and triarylmethane colorants

Although treated as separate classes in the *Colour Index*, these structural types are closely related and the few diphenylmethane dyes such as auramine (1.28; CI Basic Yellow 2) are now o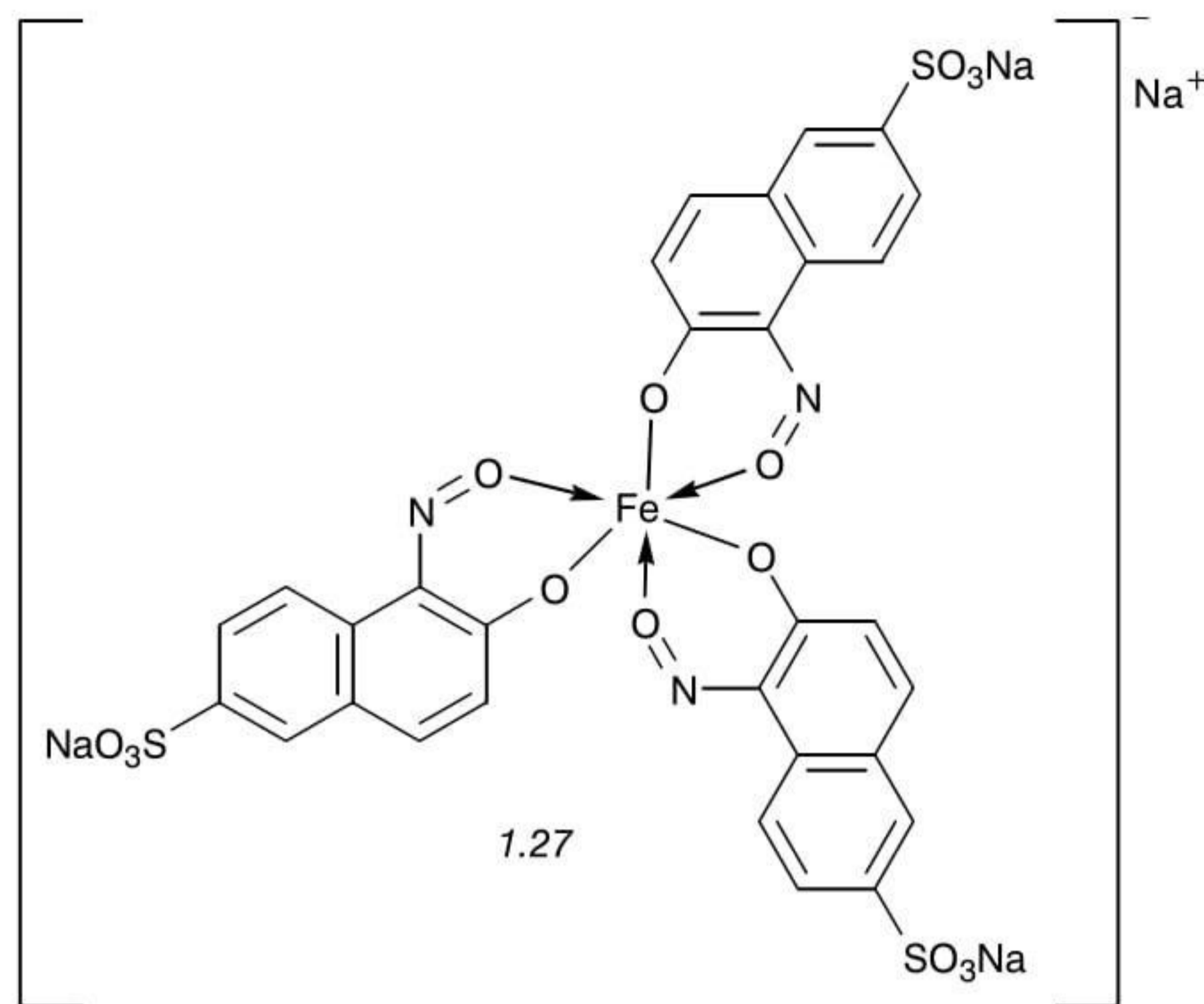f little practical interest. Commercial usage of the triarylmethane dyes and pigments has also declined considerably in favour of the major chemical classes. They were formerly noteworthy contributors to the acid, basic, mordant and solvent ranges, primarily in the violet, blue and green sectors. Numerous structural examples are recorded in the *Colour Index*. The terminal groupings can be amine/quinonimine, as in auramine and crystal violet (1.29; CI Basic Violet 3), hydroxy/quinone, or both. The aryl nuclei are not always benzenoid (section 6.5).

1.28

Auramine

1.29
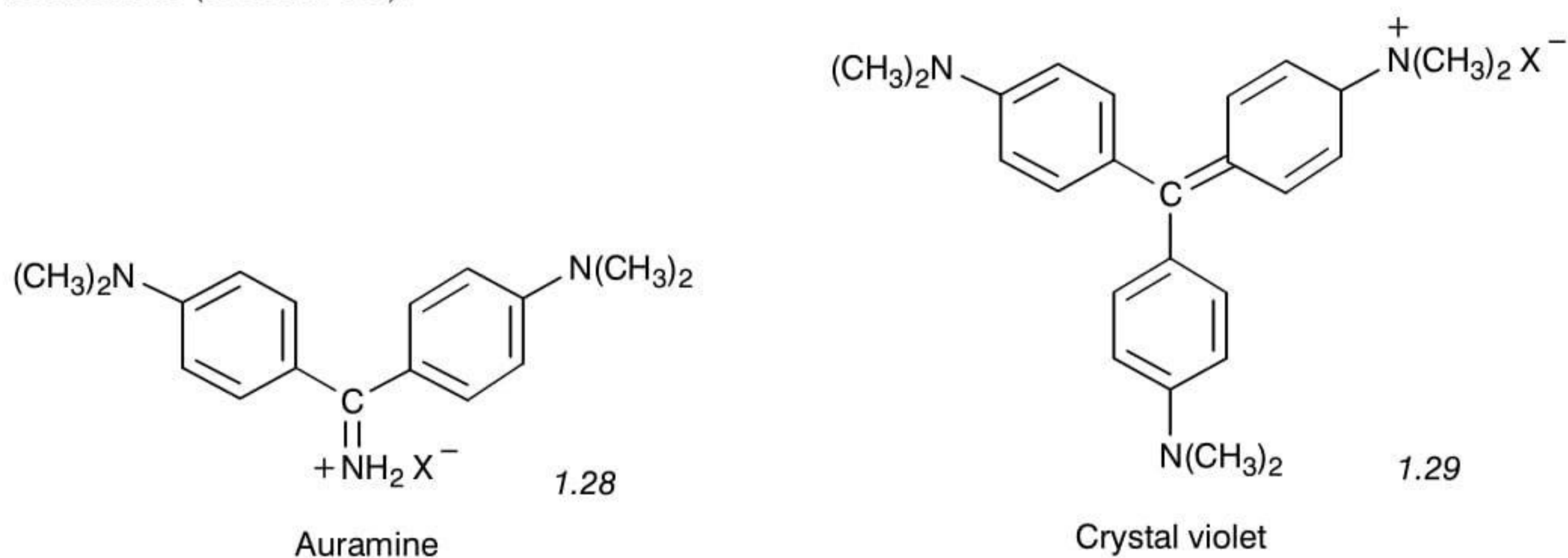
Crystal violet

1.4.15 Xanthene colorants

Structurally related to the triarylmethanes is the xanthene chromogen (1.30), in which two of the aryl nuclei are linked by an oxygen atom to form a pyrone ring. Similar terminal groupings (amino, hydroxy, or both) are usually present. Xanthene dyes have mainly

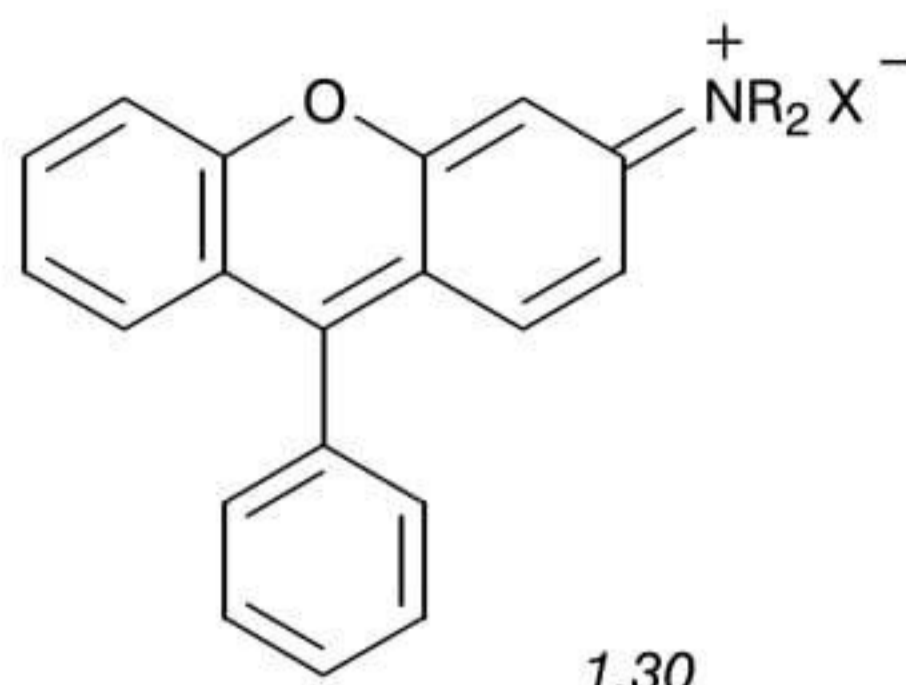contributed red members to the acid, basic, mordant and solvent ranges, but there has been slow decline in their commercial importance.

1.30

1.4.16 Acridine dyes

Acridine derivatives, such as acriflavine (1.31), can be regarded as relatives of the diphenylmethane class in which the two benzene nuclei are linked by nitrogen to form a pyridine ring. Their insignificance nowadays resembles that of their relatives, but they were formerly useful mainly as orange or yellow basic dyes [28].

1.31

Acriflavine
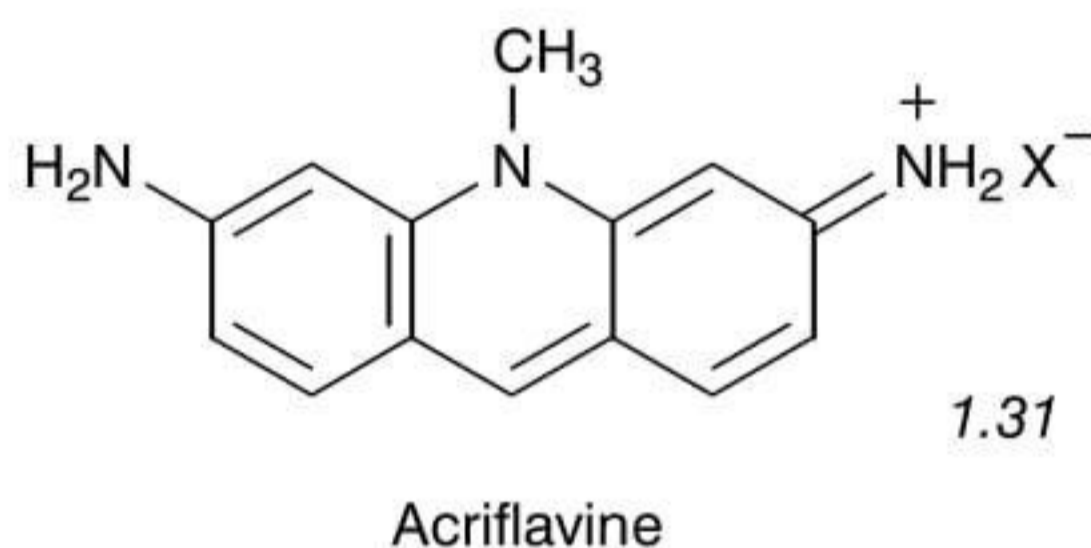
1.4.17 Azine, oxazine and thiazine colorants

These three classes are treated separately in the *Colour Index* but it is useful to compare them in view of their structural similarity. Their chromogenic groupings differ only in the bridging link of the central pyrazine (1.32), oxazine (1.33) or thiazine (1.34) ring. Azine dyes from a wide variety of structural subclasses (quinoxalines, eurhodines, safranines, aposafranines, indulines, nigrosines) are illustrated in the *Colour Index*. Their commercial importance, mainly as red to blue basic dyes, blue acid dyes and blue or black solvent-soluble dyes, has declined markedly. Thiazine dyes, such as methylene blue (1.34; CI Basic Blue 9), were never of much real significance. Only the oxazine class has retained its standing, not only for long established products such as CI Basic Blue 3 (1.33), but also as bright blue members of the direct and reactive dye ranges containing the triphenodioxazine chromogenic system (1.35) [29]. Bluish violet pigments of exceptionally high tinctorial strength have also been derived from this chromogen.

1.32

1.33
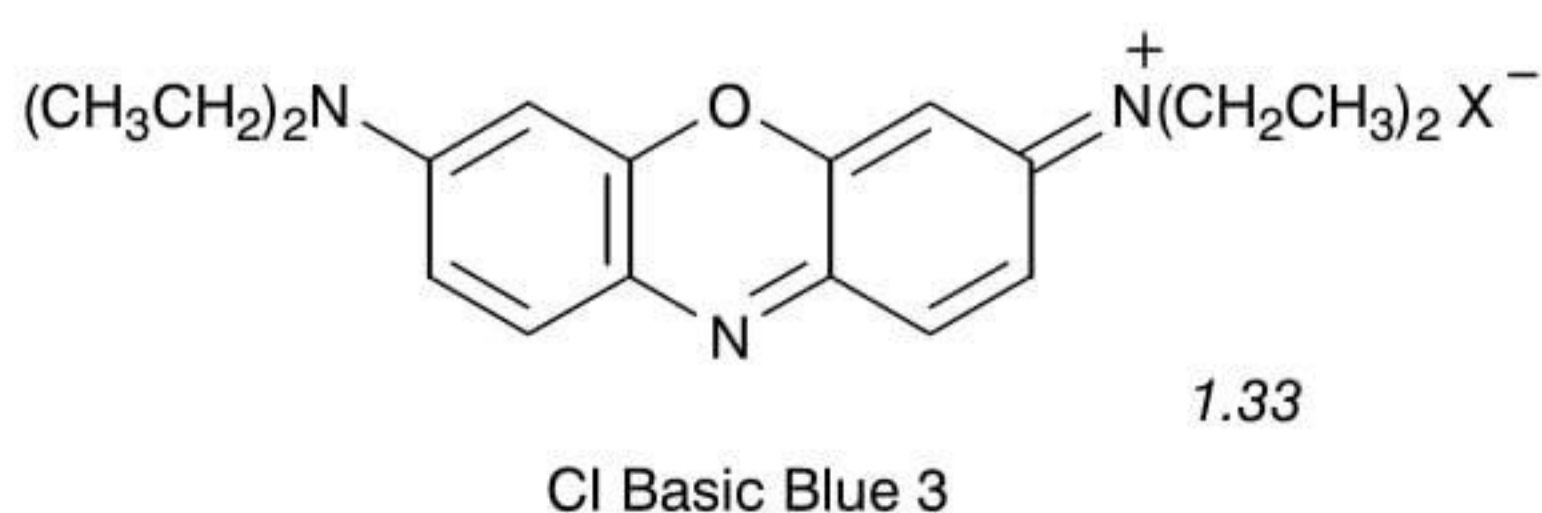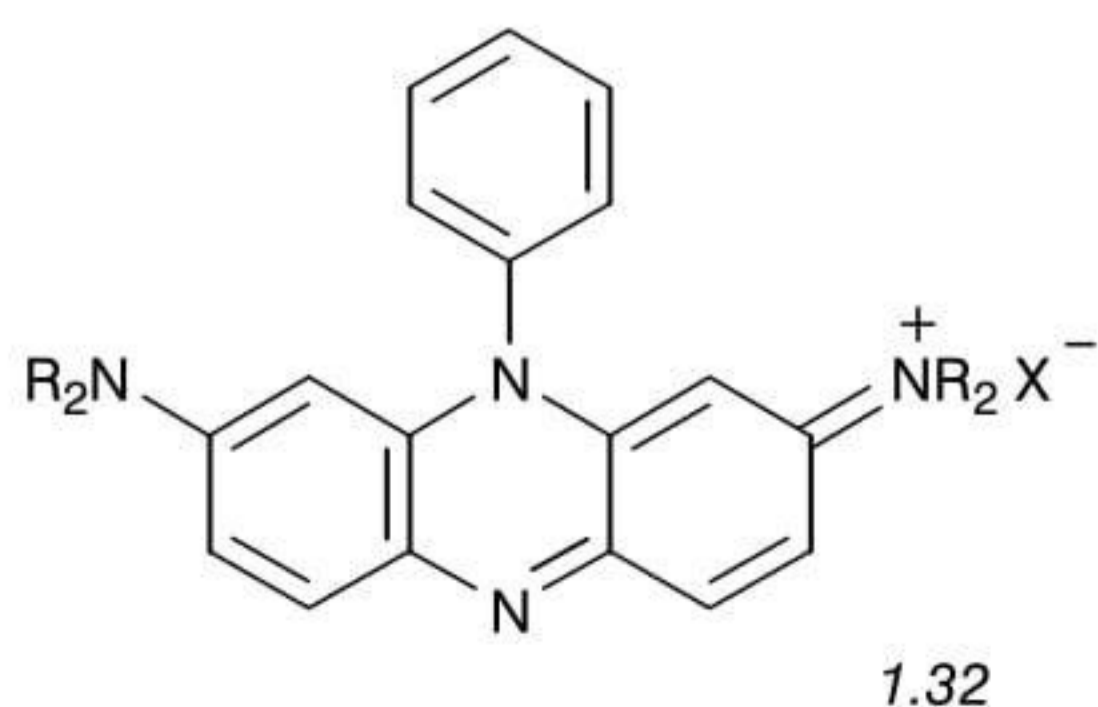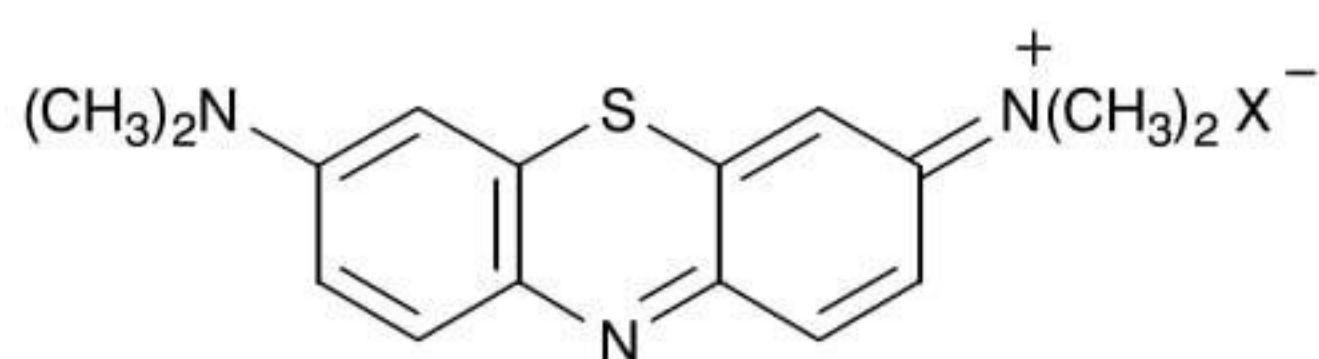
CI Basic Blue 3

1.34

CI Basic Blue 9

1.35
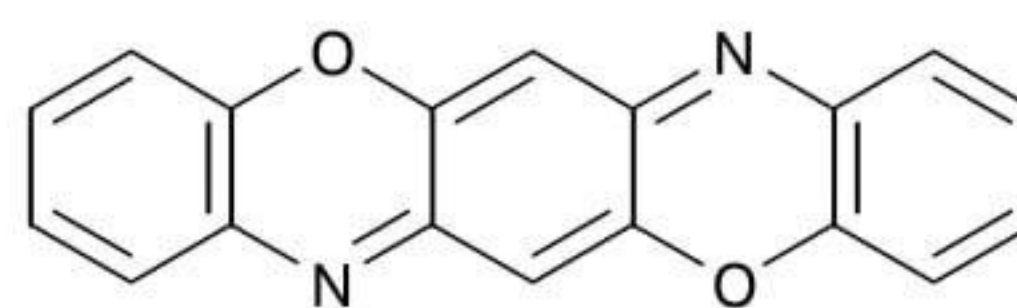
Triphenodioxazine

1.4.18 Indamine, indophenol and lactone dyes

These three chemical classes listed in the *Colour Index* are no longer of any practical significance. They are mentioned here only for their resemblance to quinonoid and ketone dyes already discussed. The chromogens are quinonimine (1.36), with amino or hydroxy auxochromes respectively in the indamines and indophenols, and a lactone ring (1.37) with a hydroxy auxochrome.

1.36

1.37

1.5 COLOUR AND CHEMICAL STRUCTURE

Before moving on to a description of the application ranges of dyes and pigments, it is appropriate to trace briefly the developments in understanding of the relationship between colour and chemical constitution. This subject has been reviewed most thoroughly elsewhere [30–33] and the intention here is only to outline the basic principles so that the reader can appreciate the need for such a variety of structural types of colora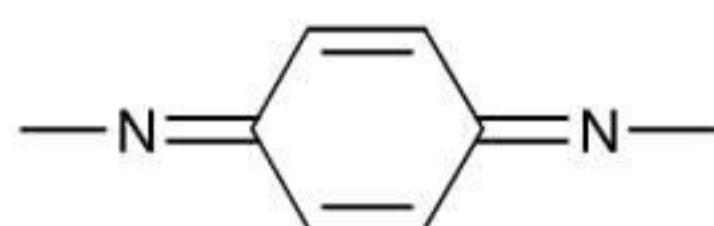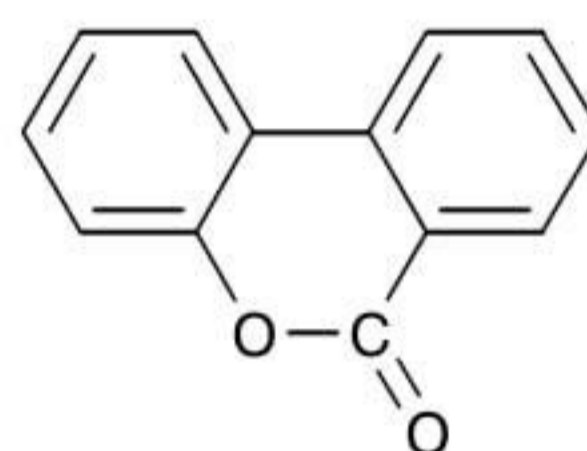nt. The requirements of colour and application are often in conflict and this forms a major part of the subject matter in succeeding chapters.

The first general theory relating depth of colour to molecular structure was made by Witt (1876), who recognised that all dyes then known contained aryl rings bearing unsaturated groups, such as =C=O, –N=O or –N=N–, which he termed 'chromophores'. Intense colour could be developed from such a 'chromogenic' grouping by attaching weakly basic substituents such as –OH or –NH– groups, called 'auxochromes', to the aryl ring. Subsequent developments recognised the particularly strong chromophoric effect of charged centres, as in the triarylmethane dyes that lack conventional uncharged chromophores. Although no longer tenable, the quinonoid theory of Armstrong (1888) helped to explain the intense colour of these and related basic dyes so prevalent at that time. The influence of multiple auxochromic substitution on colour was examined by Kauffmann (1904), who showed that the deepest (most bathochromic) colour was obtained with auxochromes in the 2,5-positions relative to the chromophore, as in the dihydroxyazobenzene anions 1.38 (orange) and 1.39 (blue).

Improved understanding of the interaction of visible and ultraviolet radiation with organic structures aroused interest in the tautomeric capabilities of dye molecules such as benzenoid-quinonoid tautomerism in azo (1.40), anthraquinone (1.41) and triarylmethane (1.42) systems. According to Watson (1913), if a dye could show a quinonoid structure in all

1.38   1.39
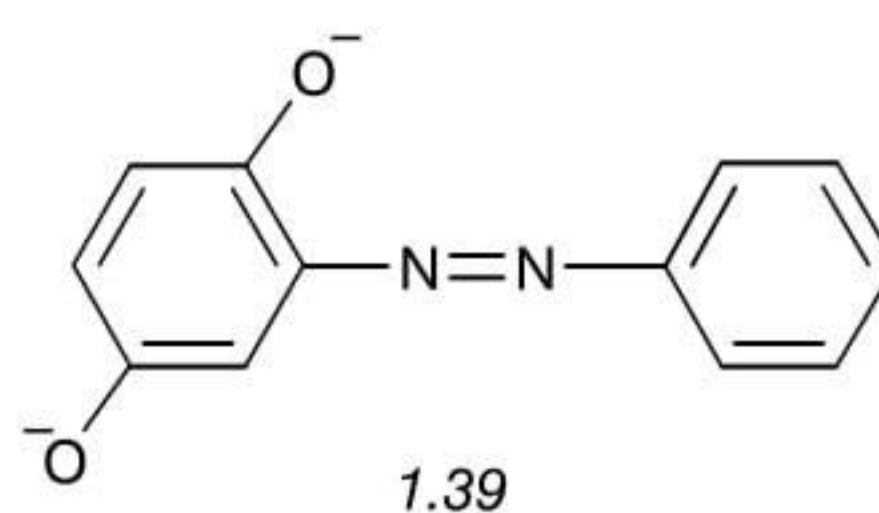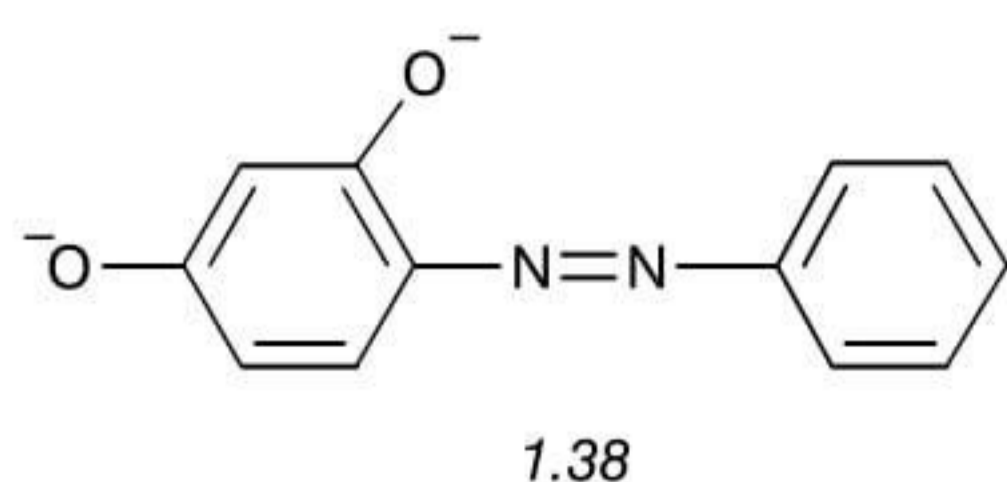
of its possible tautomeric forms, then it would be deeply coloured, however small its molecular size. For example, the blue indamine (1.43) may be contrasted with the yellow 4,4′-diaminoazobenzene (1.44), even though the latter has the greater degree of conjugation. Watson and Meek (1915) suggested that the oscillation between tautomeric forms corresponded to the reversal of double and single bonds along the conjugated chain of the molecule: the longer the chain, the slower the period of vibration. This accorded qualitatively with the relation between conjugation and absorption.

1.40   1.41

1.42

1.43   1.44
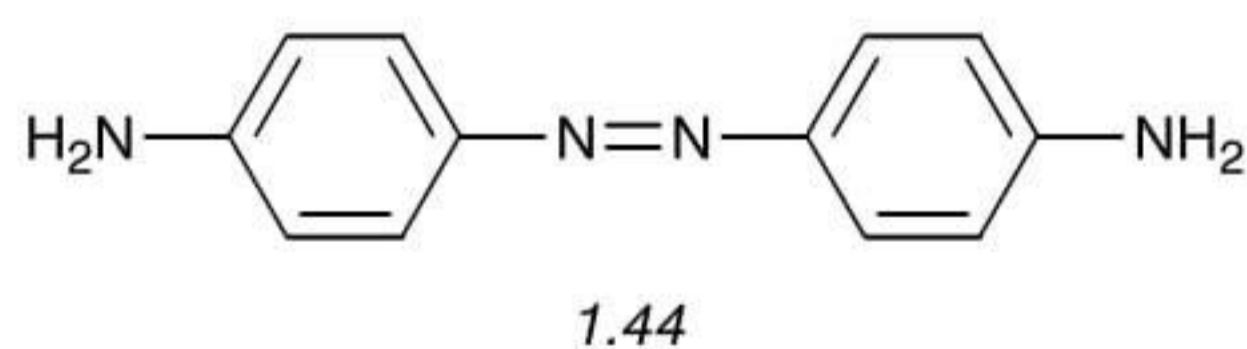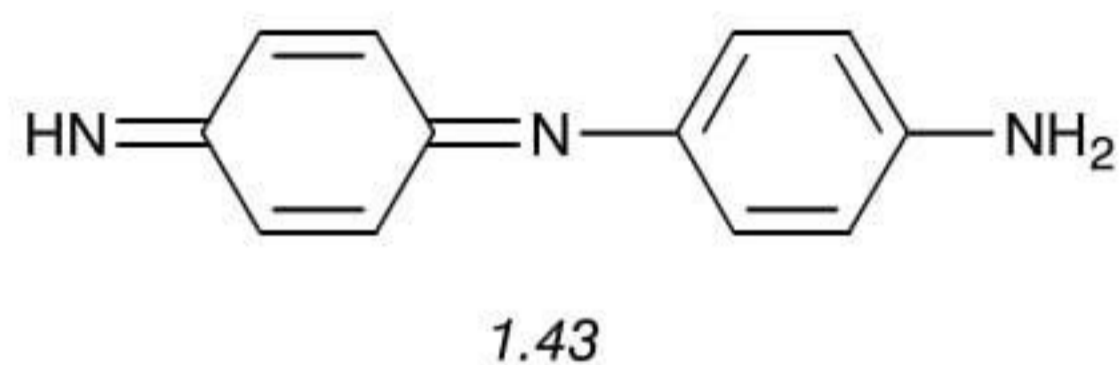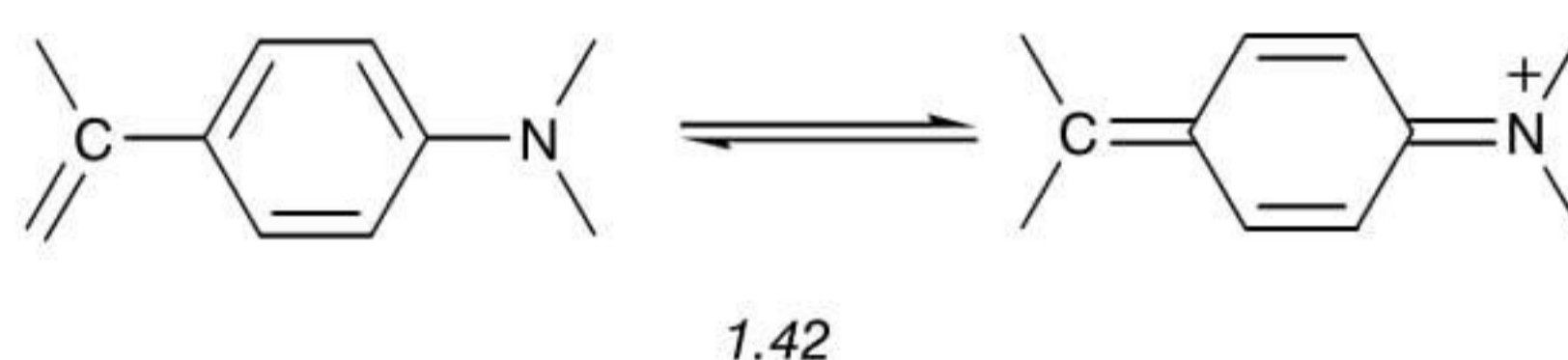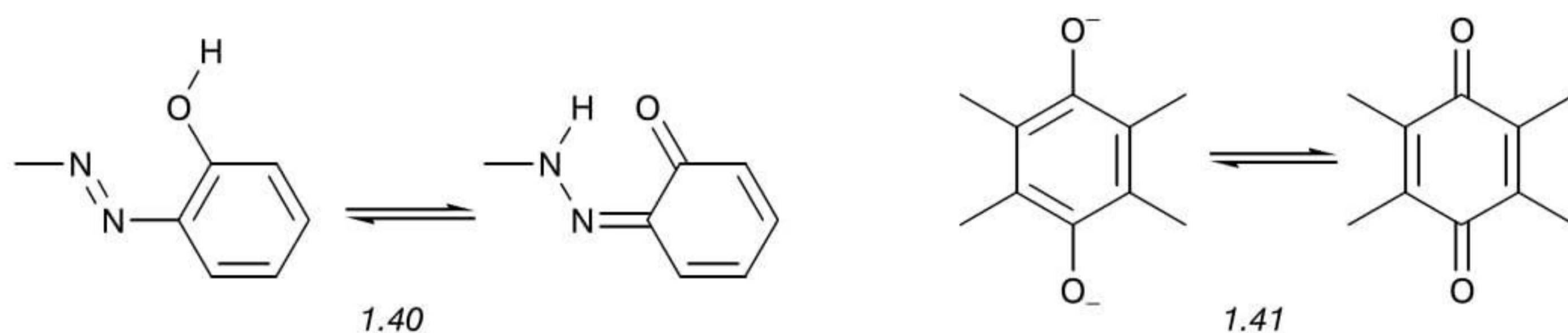
Mathematical elucidation of the principles of quantum mechanics in the 1920s, leading to the concept of molecular orbitals and a much more precise understanding of the nature of chemical bonding in the 1930s, provided the first opportunity for chemists to develop qualitative predictive methods of relating colour to chemical constitution. The equations involved are so complicated, however, that approximation methods had to be employed, particularly for calculating transition energies in organic molecules. Three distinct theoretical approaches were adopted: the valence bond, the free electron and the molecular orbital methods.

Valence bond theory was initially the most widely accepted approach, probably because it depended on familiar concepts of mesomeric effects in conjugated systems. The theory assumed that the true wave function for the mesomeric state of a molecule is a linear sum of those of the contributing canonical forms. The technique was never successful for quantitative calculation of the absorption spectra of dyes, however, because of the difficulties encountered when introducing the numerous canonical structures necessary for computational precision.

The free electron (FEMO) theory had its origins in work on the conduction electrons of metals in the 1940s, when several workers independently recognised the close analogy between these and the delocalised π-electrons of polyene dyes. The method was extended to many other classes of dyes, notably by Kuhn in the 1950s, but it has not found general acceptance for spectroscopic calculations, since it lacks adaptability by simple parameter adjustment.

The molecular orbital (MO) approach developed more slowly but was ultimately much more successful than the other approaches. Dewar (1950) was able to predict absorption maxima for various types of cyanine dyes in excellent agreement with experiment. A major advance was made in 1953 when a self-consistent molecular orbital method specifically taking into account antisymmetrisation and electron repulsion effects was developed by Pariser, Parr and Pople. The PPP-MO method established itself over the next two decades as the most useful and versatile technique for colour prediction, especially when the micro-electronics revolution provided facilities for overcoming the complexity of the necessary calculations.

Limitations of space preclude mention of more than a handful of recent examples where the PPP-MO method has been employed to predict the absorption properties of dyes from various classes. Simulation of the change in molecular geometry on excitation by iteration within the framework of the PPP-MO procedure has been used to calculate the fluorescence maxima of dyes with satisfactory accuracy to permit reliable predictions [34]. A technique for predicting absorption bandwidths has been devised, based on the linear relationship between the fluorescence Stokes shift of a dye and the absorption half-bandwidth. Theoretical Stokes shifts were computed using PPP-MO parameters for the various types of bands encountered in dye spectra. The predictive value of the method was tested on dyes from various chemical classes. The correlation between calculated and experimental bandwidths was good enough to predict brightness as well as colour [35]. Modification of the parameters for protonated N atoms enabled the visible spectral shift attributable to formation of the azonium cation (1.45) from *N,N*-diethylaminoazobenzene to be predicted reliably. Using these new parameters, halochromism could also be quantified in this way for more complex bis-azonium ions with insulated chromogens [36].

1.45
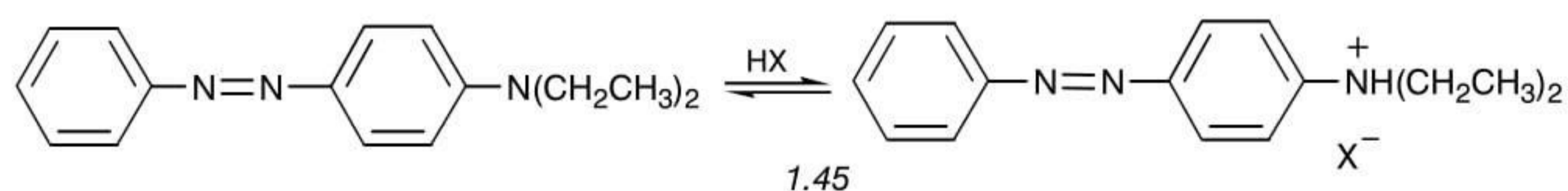
A striking feature of disperse dye development in recent decades has been the steady growth in bathochromic azo blue dyes to replace the tinctorially weaker and more costly anthraquinone blues. One approach is represented by heavily nuclei-substituted derivatives of *N,N*-disubstituted 4-aminoazobenzenes, in which electron donor groups (e.g. 2-acylamino-5-alkoxy) are introduced into the aniline coupler residue and acceptor groups (acetyl, cyano or nitro) into the 2,4,6-positions of the diazo component. A PPP-MO study of the mobility of substituent configurations in such systems demonstrated that coplanarity of the two aryl rings could only be maintained if at least one of the 2,6-substituents was cyano. Thus much commercial research effort was directed towards these more bathochromic *o*-cyano-substituted dyes.

A more important trend, however, has been the development of intensely bathochromic monoazo blues by replacing either one of the aryl rings in the aminoazobenzene chromogen by a heterocyclic ring, such as thiazole or thiophene. Study of a series of thiazolyl- and thienylazo dyes of this kind using the PPP-MO method and its CNDO/S refinement showed that their highly bathochromic intensity is not attributable to the 3d atomic orbitals on the sulphur atom of the heterocyclic ring [37]. New parameters for S-containing heterocyclic systems enabled good agreement between experimental and calculated spectral features to be obtained for a series of monoazo dyes derived from *N*-phenylpyrrolidine [38]. Spectral data for dyes prepared by coupling diazonium salts with 2-thioalkyl-4,6-diaminopyrimidine and with 3-cyano-1,4-dimethyl-6-hydroxypyrid-2-one indicated that the yellow to orange pyrimidine dyes exist in the azo tautomeric form (1.46), whereas the brighter yellow pyridone dyes exist as ketohydrazones (1.47). The spectral behaviour was predicted well by PPP-MO calculations, although steric effects intervened when a substituent in the diazo component was *ortho* to the azo group of a diaminopyrimidine dye [39].

1.46

1.47
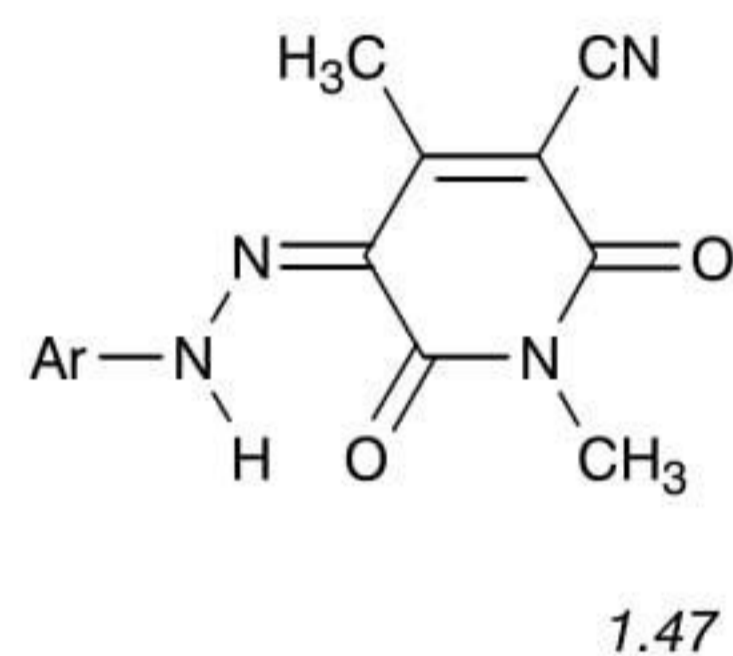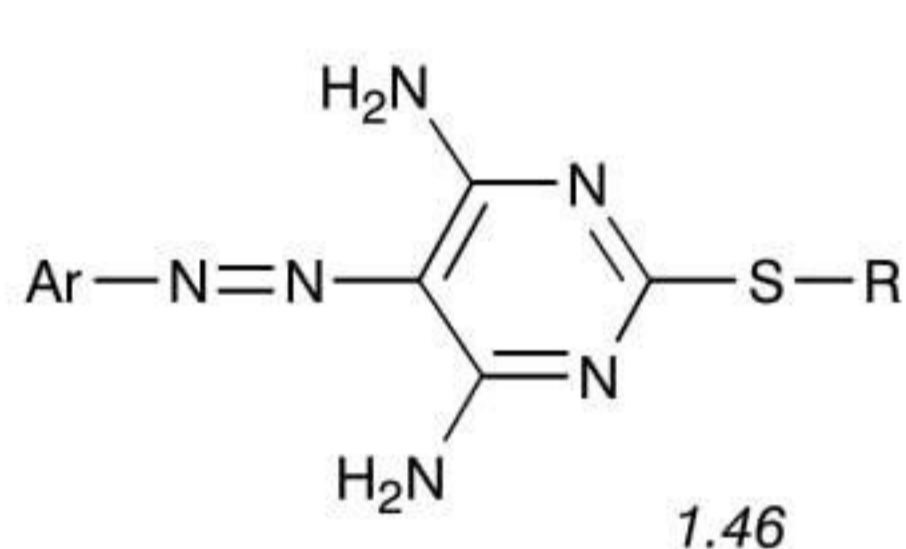
The peak wavelengths of some arylated diaminoanthrarufin disperse dyes calculated by the PPP-MO route agreed well with the observed values. The 1-arylamino-3-aryl-5-amino derivatives (1.48; X = Ar, Y = H) showed better dichroism and improved solubility in liquid crystals than their 1-amino-5-arylamino analogues (1.48; X = H, Y = Ar). The tris-arylated derivatives (1.48; X = Y = Ar) also had satisfactory dichroism and solubility. The presence of 1-arylamino and 3-aryl substituents in these deeply coloured anthraquinone dyes resulted in favourable orientation in liquid crystals, producing the desired properties [40]. A range of metal-free phthalocyanine colorants and their metal complexes were prepared and their spectral characteristics in solution were predicted by PPP-MO calculation. The influence of the central metal atom, substituents on the aryl rings and the type of solvent was examined. The nature of the electronic excitation processes was interpreted in terms of the calculated changes in π-electron charge density. Good agreement with experimental absorption maxima was obtained, except in the case of a tetranitro derivative [41].

1.48
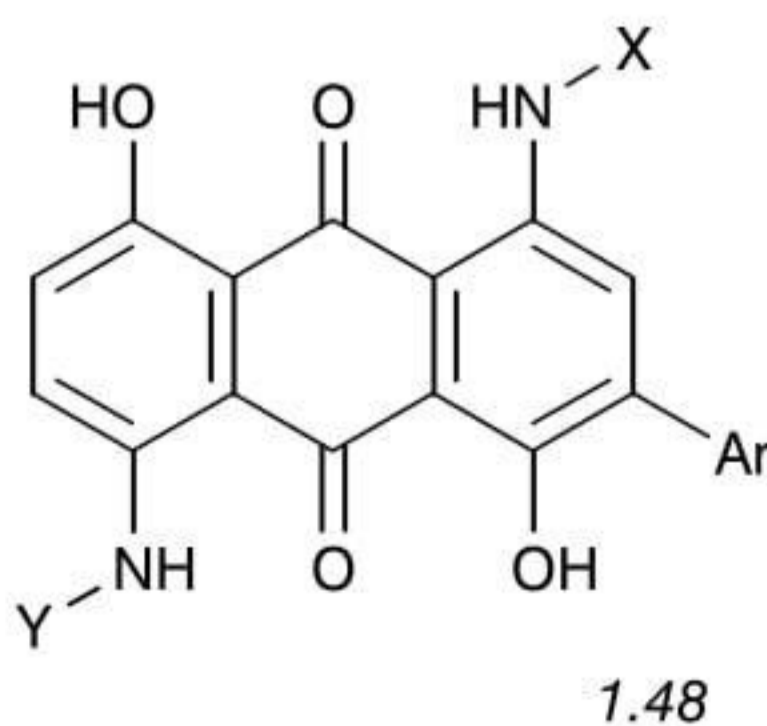
One of the most noteworthy consequences of the refinement of these quantitative treatments of colour-structure relationships has been the stimulus it has given to the search

for radically new chromogenic systems. The benzodifuranone chromogen (1.14) is a particularly interesting example. One of the remarkable properties of this system is the sensitivity of the absorption band to the strength of the electron-donating groups R. Thus the unsubstituted chromogen (1.14; R = H) absorbs at 460 nm, whereas the dimethoxy derivative (1.14; R = OCH$_3$) absorbs at 540 nm [23].

Another novel chromogen of high bathochromic intensity is the dihydrobenzothiophene-1,1-dioxide nucleus with an arylmethine group in the 2-position and a dicyanovinyl residue in the 3-position (1.49). This provides brilliant blues with molar absorption coefficients in the 70 000 region. Analogous dyes with carbonyl in place of the sulphonyl group are less intense, raising speculation about other applications of the sulphone acceptor group as part of a heterocyclic ring system.

1.49
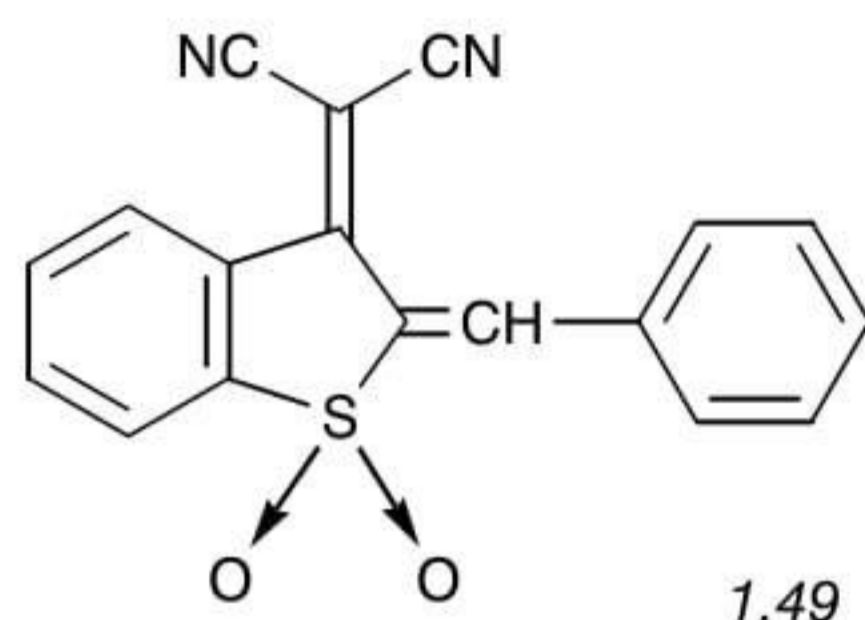
1.6 APPLICATION RANGES OF DYES AND PIGMENTS

As mentioned earlier, the nineteen application categories forming the respective series of CI generic names are not restricted to colorants. In the following discussion, however, the colorant ranges are emphasised because this is where the major variations in chemical class are found. Thus it is necessary to depart from the alphabetical order of listing in the *Colour Index*. The application ranges of most interest for dyeing cellulosic fibres (vat, sulphur, reactive and direct dyes) are discussed first, followed by those for synthetic fibres and wool (disperse, basic, acid and mordant dyes) and finally the non-textile colorants (leather dyes, food dyes, solvent dyes and pigments). The colorant precursors and uncoloured products listed form more homogeneous groups that are best discussed where relevant in the appropriate chapters of Volumes 1 and 2. There is much variety of chemical structure among fluorescent brighteners, but the characteristic classes represented are mostly different from those in colorants.

1.6.1 Vat dyes

A vat dye is a water-insoluble colorant containing two or more keto groups. It can thus be brought into aqueous solution by a reduction process (vatting), which converts the vat dye into its alkali-soluble enolic (leuco) form. As the soluble sodium enolate the leuco vat dye has substantivity for cellulose. The application of vat dyes to cellulosic fibres (virtually the only fibre type on which their outstanding fastness properties can be exploited) thus proceeds in four stages:

(a)   reduction and dissolution,
(b)   absorption by cellulose,
(c)   reoxidation and
(d)   association of the vat dye molecules within the fibre (Scheme 1.1).
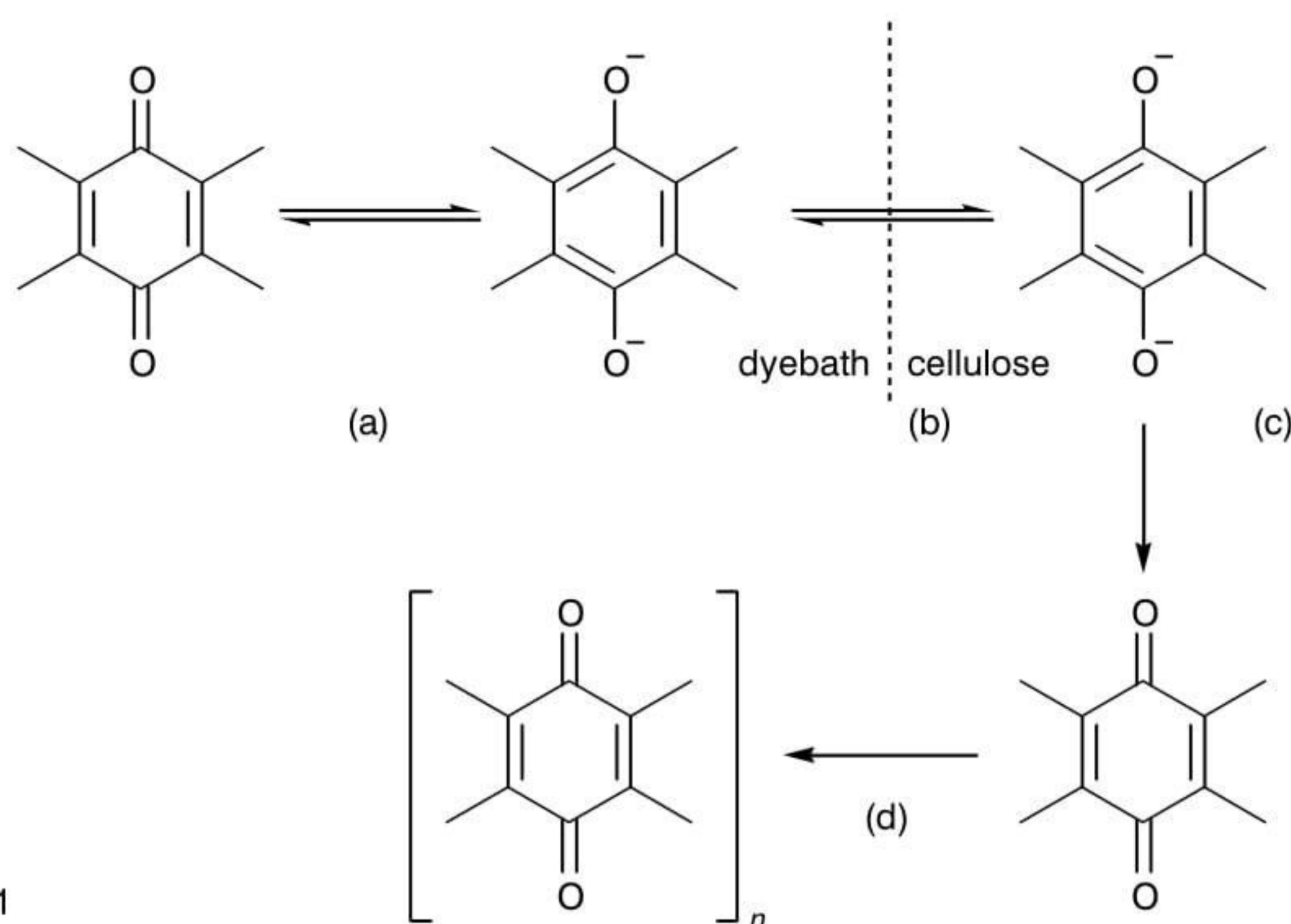
Scheme 1.1

Sodium dithionite is the traditional reducing agent used for vat dyeing but concern about environmental problems has aroused interest in less damaging alternatives, such as thiourea dioxide and the biodegradable and sulphur-free hydroxyacetone (section 12.9.1). Recycling is worthy of consideration for vat dyebaths because the redox process is reversible and only the dye absorbed by the cellulosic fibres is oxidised at a later stage of processing [42]. One of the dyehouses in North Carolina, USA, has been successfully recycling indigo dyebaths for many years [43].

Vat dyes are used to colour both components in pale depths on polyester/cellulosic fibre blends [44] but coloration of the polyester component in this case is more closely analogous to disperse dyeing (section 1.6.5). Anthraquinone disperse dyes resemble those vat dyes that are substituted anthraquinone derivatives and in both instances it is exclusively the virtually water-insoluble keto form that is absorbed by the polyester fibre.

Approximately 80% of all vat dyes belong to the anthraquinonoid class (see Table 1.2) and this certainly includes the leading products in all sectors of the colour gamut. Indigo and its derivatives as well as the sulphurised vat types contribute mainly to the navy blue sector, whereas thioindigoid and indolethianaphthene derivatives occupy the red to brown region. In this and succeeding tables, the figures again relate to all dyes of known chemical type listed and are given in percentage terms to permit easier comparison between the distributions in different hue sectors. The total number of dyes in each of the primary sectors (yellow, red or blue) is, of course, almost always larger than those in the non-primary sectors.

The vat dyes section of the *Colour Index* incorporates a subgroup called solubilised vat dyes. These are sodium salts of sulphuric acid esters of the parent leuco vat dyes, such as CI Solubilised Vat Blue 6 (1.50). In contrast to the leuco compounds, the vat leuco esters dissolve readily in water at neutral pH. They have relatively low substantivity for cellulose and thus have been used mainly in continuous dyeing and printing. In the presence of an oxidant in mineral acid solution (sodium nitrite and sulphuric acid, for example) the leuco ester is rapidly decomposed and the insoluble vat dye regenerated. Thus application of a vat leuco ester represents a simpler (but more costly and less versatile) alternative to conventional dyeing methods via the alkaline leuco compound.

Table 1.2 Percentage distribution of chemical classes in vat dye hue sectors

| Chemical class | Distribution in hue sector (%) | | | | | | | | % of all vat dyes |
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	
Anthraquinonoid	94	92	65	67	62	90	83	90	79
Indigoid			11		17		2		5
Thioindigoid		4	15	14			4		4
Indole-thianaphthene			2	14	5		2	10	4
Aminoketone	3		5			5	9		3
Sulphurised vat	3				11	5			3
Miscellaneous		4	2	5	5				2
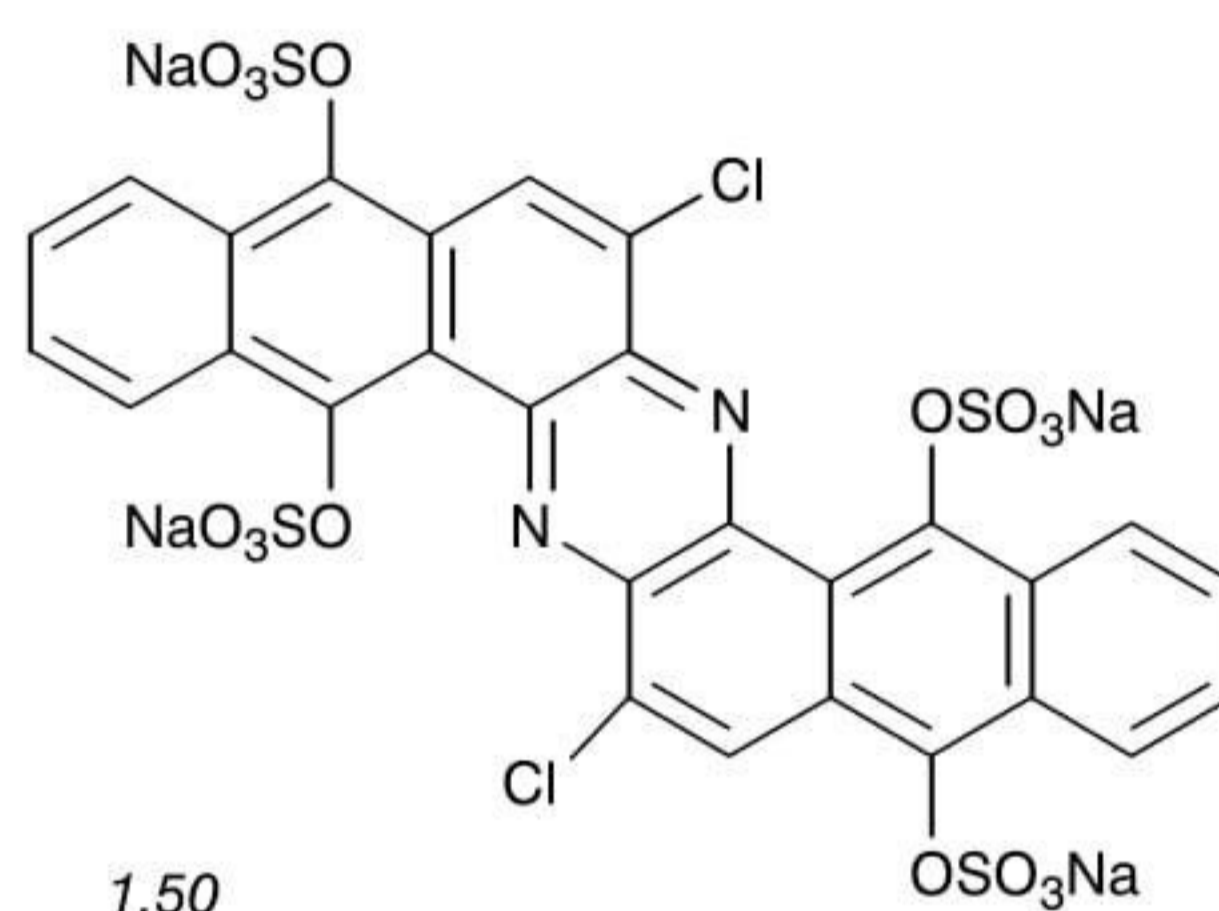
CI Solubilised Vat Blue 6

1.6.2 Sulphur dyes

These resemble the vat dyes in certain ways, although they are of indeterminate constitution and usually mixtures of different chemical species (section 6.4). The characteristic disulphide group (D‑S‑S‑D in Scheme 1.2) is always present in the insoluble form of a sulphur dye, which is brought into aqueous solution by reduction to the alkali‑soluble (leuco) form (D‑S⁻). The soluble sodium thiolate form of the leuco sulphur dye has substantivity for cellulose. Thus the application of sulphur dyes to cellulosic fibres is a three‑stage process (Scheme 1.2) broadly similar to that already outlined for vat dyes.
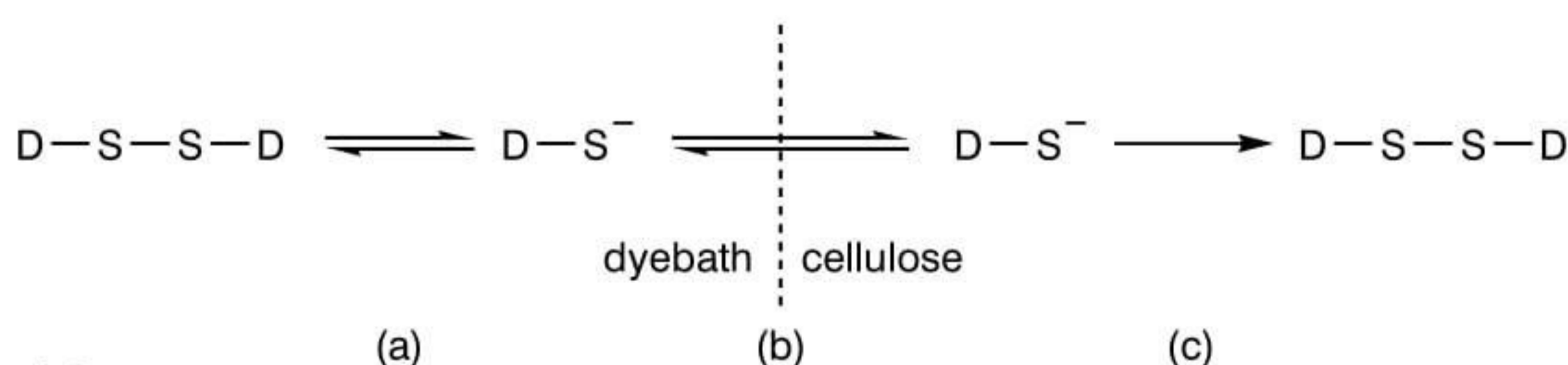
Scheme 1.2

In the *Colour Index* the sulphur dyes are classified into four subgroups. Conventional insoluble disulphide brands, taking the generic CI Sulphur dye designation, are converted to the leuco compound by adding sodium sulphide to a boiling aqueous dispersion of the parent

dye. CI Leuco Sulphur dyes are marketed as concentrated solutions (or dispersions) of the pre-reduced dye with a small excess of the reducing agent. They can be added directly to a dyebath prepared with additional reducing agent and are particularly convenient for continuous dyeing. CI Solubilised Sulphur dyes are sodium salts of thiosulphato derivatives of the parent dyes. Like the CI Solubilised Vat dyes they are highly soluble in water but low in substantivity for cellulose. Addition of alkali and reducing agent converts them to the leuco sulphur form. The *Colour Index* refers to a fourth subgroup, the CI Condense Sulphur dyes, but these are only of historical interest. They were water-soluble alkyl- or arylthiosulphato derivatives, mostly of phthalocyanine dyes. In the presence of an alkaline reducing agent (sodium sulphide or polysulphide) they underwent a polycendensation reaction to give an insoluble coloured polymer within the fibre, the chromogenic groupings being linked together via disulphide bridges as in conventional sulphur dyeings.

Improvements in dye synthesis, formulation and application in recent years have led to modern ranges of sulphur dyes with notable advantages: freedom from heavy metals, AOX or carcinogenic arylamines, high exhaustion and insolubility after reoxidation. Developments in application methods include exhaust dyeing under a nitrogen atmosphere, indirect electrochemical reduction and pad–steam dyeing with fixation in a flash ager [45].

Sulphur dye effluent from traditional dyeing systems contains sulphides and thiosulphates as well as the residual unfixed dyes. The discharge of sulphide liquors to drain is not normally permissible because of the toxicity of hydrogen sulphide vapour that would be released under acidic conditions. Corrosion of the sewerage system and damage to the treatment works would also occur. Stringent standards are required for consent and sulphide waste is normally treated by oxidation or precipitation separately from other effluent streams [46]. Sulphur-free biodegradable products such as glucose or hydroxyacetone have been evaluated as alternative reducing agents for sulphur dyes but they are more costly and less versatile than the traditional sulphide or hydrosulphide.

1.6.3 Reactive dyes

These dyes are capable of reacting chemically with a substrate under suitable application conditions to form a covalent dye-substrate bond.

The characteristic structural feature is thus the possession of one or more reactive groupings of various kinds (section 7.2). Almost always these may be categorised as either:

(a) an activated unsaturated vinyl group that reacts with cellulose by addition to the double bond, or

(b) an activated halogeno substituent (C1 or F) that undergoes nucleo-philic substitution by a cellulosate anion (section 7.3.1).

A marked trend in recent years has been the growth in availability and variety of ranges of dyes containing two or more reactive groups per molecule (section 7.4). Although more costly to manufacture, such structures react with greater efficiency, so that less dye is lost by hydrolysis.

The introduction of such a specific means of ensuring dye fixation freed the colour chemist from many of the structural limitations implicit in the design of most other ranges of dyes, so that virtually any chemical class may be employed as a chromogen [47]. In practice, however, the reactive dye chemist has relied heavily on the azo chromogen (see Table 1.3),

Table 1.3 Percentage distribution of chemical classes in reactive dye hue sectors

Chemical class	Distribution in hue sector (%)								% of all reactive dyes
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	
Unmetallised azo	97	90	90	63	20	16	57	42	66
Metal-complex azo	2	10	9	32	17	5	43	55	15
Anthraquinone				5	34	37		3	10
Phthalocyanine					27	42			8
Miscellaneous	1		1		2				1

usually unmetallised but sometimes as metal complexes in the duller hues, such as navy, brown and black. Anthraquinone, phthalocyanine, formazan and triphenodioxazine chromogens have made notable contributions in blue and turquoise hues but in all other hue sectors the azo dyes account for more than 95% of reactive dye structures.

Several instances of respiratory sensitisation resulting from exposure to reactive dyes have been reported. If an individual becomes sensitised to reactive dyes, it is essential that any future contact with these dyes or other respiratory allergens be avoided. Subsequent exposures may cause anaphylactic shock and can progress into convulsions, coma and death. As yet, there is no animal test that can be used to predict reliably the potential of a reactive dye to cause respiratory sensitisation [1].

Reactive groups in dye molecules that fail to react with the substrate are hydrolysed during dyeing or discharge of the residual dyebath. Recycling is therefore not a viable option in the case of reactive dyeings [42]. Bioelimination (the sorptive removal of dyes during biological treatment of effluent) is also ineffective for reactive dyes, which show little adsorption in this way. This behaviour is independent of the degree of sulphonation or the ease of hydrolysis of the reactive dye molecules. The use of cationic flocculants for removal of reactive dye hydrolysates is of considerable interest [48].

By far the most important application segment for reactive dyes is the dyeing and printing of cellulosic fibres. Their impact in wool dyeing has been less dramatic but the exceptionally high wet fastness requirements of machine-washable knitwear, for example, do justify the use of reactive dyes, in spite of their higher cost relative to conventional dyes for wool. Reactive dyes are suitable for dyeing glove leather, silk and similar materials where resistance to water and cleaning aids is essential.

1.6.4 Direct dyes

These are defined as anionic dyes with substantivity for cellulosic fibres applied from an aqueous dyebath containing an electrolyte. The forces that operate between a direct dye and cellulose include hydrogen bonding, dipolar forces and non-specific hydrophobic interaction, depending on the chemical structure and polarity of the dye. Apparently multiple attachments are important, since linearity and coplanarity of molecular structure seem to be desirable features (section 3.2.1). The sorption process is reversible and numerous attempts have been made to minimise desorption by suitable aftertreatments (section 10.9.5). The two most significant non-textile outlets for direct dyes are the batchwise dyeing of leather and the continuous coloration of paper.

In every hue sector, at least 70% of direct dyes are unmetallised azo structures (see Table 1.4). In contrast to all other application ranges, the great majority of them are disazo or polyazo types, the former predominating in the brighter yellow to blue sectors and the latter in the duller greens, browns, greys and blacks. The copper-complex direct dyes are mostly duller violets, navies and blacks derived from the disezo and polyazo subclasses. Stilbene and thiazole dyes, the only non-azo contributors in the yellow to red sector, bear certain similarities to the disazo and polyazo structures (sections 1.4.1 to 1.4.3). The dioxazine and phthalocyanine chromogens are represented in bright blue direct dyes of high light fastness.

Table 1.4 Percentage distribution of chemical classes in direct dye hue sectors

Chemical class	Distribution in hue sector (%)								% of all direct dyes
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	
Monoazo	4	7	14	4		8	3		5
Disazo	58	53	71	83	52	21	22	23	49
Polyazo	8	16	10	3	31	64	67	68	33
Copper-complex azo			3	9	12	4	1	8	5
Stilbene	17	23	2			1	7	1	5
Thiazole	13	1							1
Dioxazine				1	3				1
Phthalocyanine					2	2			1

As there is no chemical change of direct dyes during orthodox application, their exhaust dyebaths are eminently suitable for recycling. Membrane processes have been used successfully to remove direct dyes from dyehouse effluents. There are possible cost savings associated with reuse of the electrolyte, depending on the rejection properties of the membrane [42]. High adsorption of direct dyes occurs during biological treatment of dyehouse waste liquors containing them. This effect is not dependent on the degree of sulphonation of the direct dye molecules [48]. Oxidation with ozone or precipitation using cationic flocculants are effective ways of eliminating direct dye residues.

1.6.5 Disperse dyes

These dyes have affinity for one or, usually, more types of hydrophobic fibre and they are normally applied by exhaustion from fine aqueous dispersion. Although pure disperse dyes have extremely low solubility in cold water, such dyes nevertheless do dissolve to a limited extent in aqueous surfactant solutions at typical dyeing temperatures. The fibre is believed to sorb dye from this dilute aqueous solution phase, which is continuously replenished by rapid dissolution of particles from suspension. Alternatively, hydrophobic fibres can absorb disperse dyes from the vapour phase. This mechanism is the basis of many continuous dyeing and printing methods of application of these dyes. The requirements and limitations of disperse dyes on cellulose acetate, triacetate, polyester, nylon and other synthetic fibres will be discussed more fully in Chapter 3. Similar products have been employed in the surface coloration of certain thermoplastics, including cellulose acetate, poly(methyl methacrylate) and polystyrene.

Table 1.5 Percentage distribution of chemical classes in disperse dye hue sectors

Chemical class	Distribution in hue sector (%)								% of all disperse dyes
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	
Azo	48	92	73	47	27	30	100	100	59
Anthraquinone	6	2	25	53	72	65			32
Nitro	16	3							3
Aminoketone	8	2	1		1	5			2
Methine	14								2
Quinophthalone	4								1
Miscellaneous	4	1	1						1

Yellow disperse dyes are known from a wide range of chemical classes (see Table 1.5) but azo dyes derived from heterocyclic coupling components are particularly important for economic reasons. The monoazo subclass dominates throughout the disperse dye range and there are no metal-complex disperse dyes designed for the ester fibres, although they do exist as a subgroup of 'acid dyes' for wool. Anthraquinone derivatives traditionally dominated the bright red to bright green series but here again cost considerations have favoured the introduction of new monoazo dyes, often with heterocyclic amines as diazo components, for the dyeing of polyester fibres [49]. Browns and blacks on polyester and acetate fibres have always been provided almost entirely by azo disperse dyes. The disperse range contains relatively few homogeneous green, brown or black dyes, however. Many of the commercial navy, green, brown and black products are in fact mixtures of two or more components (section 3.2.3).

Disperse dyes from the monoazo and anthraquinone classes have been implicated in cases of contact dermatitis. Circumstances common to such cases appear to be heavy depths of these dyes on nylon rather than polyester and occurring in articles of clothing that are in direct contact with the skin, often in areas that are likely to become moistened by perspiration. Hosiery, socks, blouses and close-fitting athletic or fashion wear, such as velvet leggings, are representative of the types of garment where this problem has arisen [1].

There is no chemical change of disperse dyes during orthodox application, so their exhaust dyebaths are suitable for recycling. Such dyes were successfully removed from an effluent stream by a microfiltration membrane module on an industrial scale [50]. In this trial the permeate was reused but not the dyes, although other work has demonstrated that recycling of disperse dyes is possible [51]. Moderate to high adsorption of disperse dyes takes place during biological treatment of dyehouse effluent. Although dispersible but insoluble in watercourses, disperse dyes released to the aquatic environment have shown no evidence of bioaccumulation in fish [48].

1.6.6 Basic dyes

Controversy has arisen at times [52] regarding the apparent synonymity of the terms 'basic dye' and 'cationic dye'. The Society of Dyers and Colourists defines a basic dye as 'characterised by its substantivity for the acidic types of acrylic fibres and for tannin-mordanted cotton', whereas a cationic dye is defined as one 'that dissociates in aqueous

solution to give a positively charged coloured ion'. Since the second of these describes a chemical feature rather than an application property, the term 'basic dyes' is adopted in this book for this range, as in the *Colour Index*. This category includes those weakly basic dyes (1.51) that are essentially uncharged under neutral or alkaline conditions and only form a cation by protonation in acidic solution, such as chrysoidine (CI Basic Orange 2). The powerful dye-fibre forces responsible for the excellent exhaustion and high wet fastness of basic dyes on acrylic fibres are believed to include electrostatic attraction to anionic sites in the fibre and non-specific hydrophobic interaction.

1.51

Chrysoidine
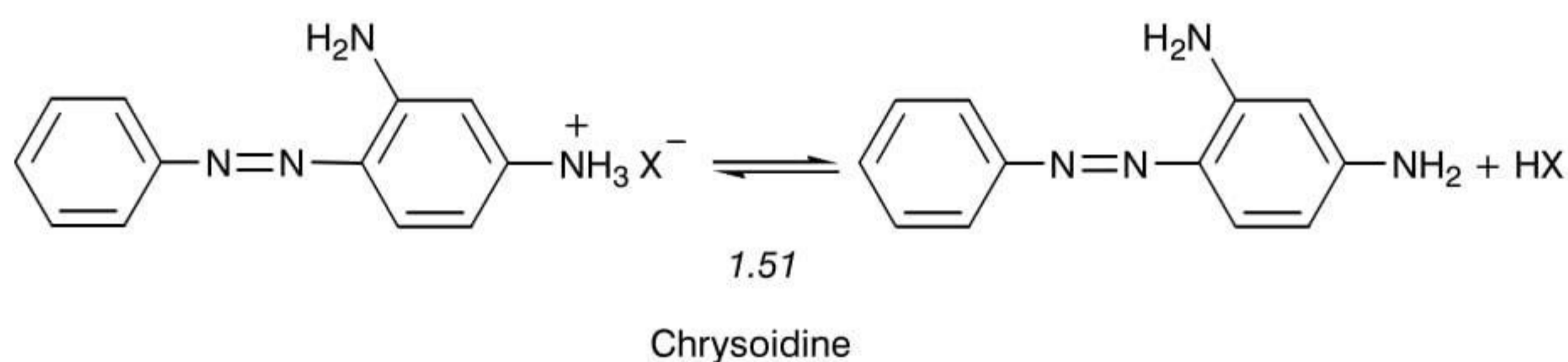
Many brilliantly coloured and tinctorially strong basic dyes for silk and tannin-mordanted cotton were developed in the early decades of the synthetic dye industry. Most of these belonged to the acridine, azine, oxazine, triarylmethane, xanthene and related chemical classes; their molecules are usually characterised by one delocalised positive charge. Thus in crystal violet (1.29) the cationic charge is shared between the three equivalent methylated *p*-amino nitrogen atoms. A few of these 'traditional basic' dyes are still of some interest in the dyeing of acrylic fibres, notably as components of cheap mixture navies and blacks, but many 'modified basic' dyes were introduced from the 1950s onwards for acrylic and modacrylic fibres, as well as for basic-dyeable variants of nylon and polyester [44].

Most of these products are azo or anthraquinone types, often with a localised quaternary ammonium group isolated from the chromogen by a saturated alkyl chain, as in CI Basic Red 18 (1.52). Such products often exhibit higher light fastness than the traditional delocalised types. Improved azomethine, methine and polymethine basic dyes of good light fastness are also available. In contrast to the more specialised traditional classes, the azo and methine dyes have contributed to the basic dye range across the entire spectrum of hues (see Table 1.6) and now account for a clear majority of all basic dyes listed in the *Colour Index*.

Basic dyes do not undergo chemical change during dyeing, but the proportion remaining in the exhausted dyebath is low (typically 2–3%) and scarcely justifies isolation for reuse. Recycling of the process water, however, may allow recovery of the inorganic salts and other auxiliary chemicals present [42]. There is normally a high degree of sorptive removal of residual basic dyes during biological treatment of effluent. This is important, because basic dyes tend to exhibit toxicity to aquatic organisms. In a survey of 3000 dyes in common use, 98% of
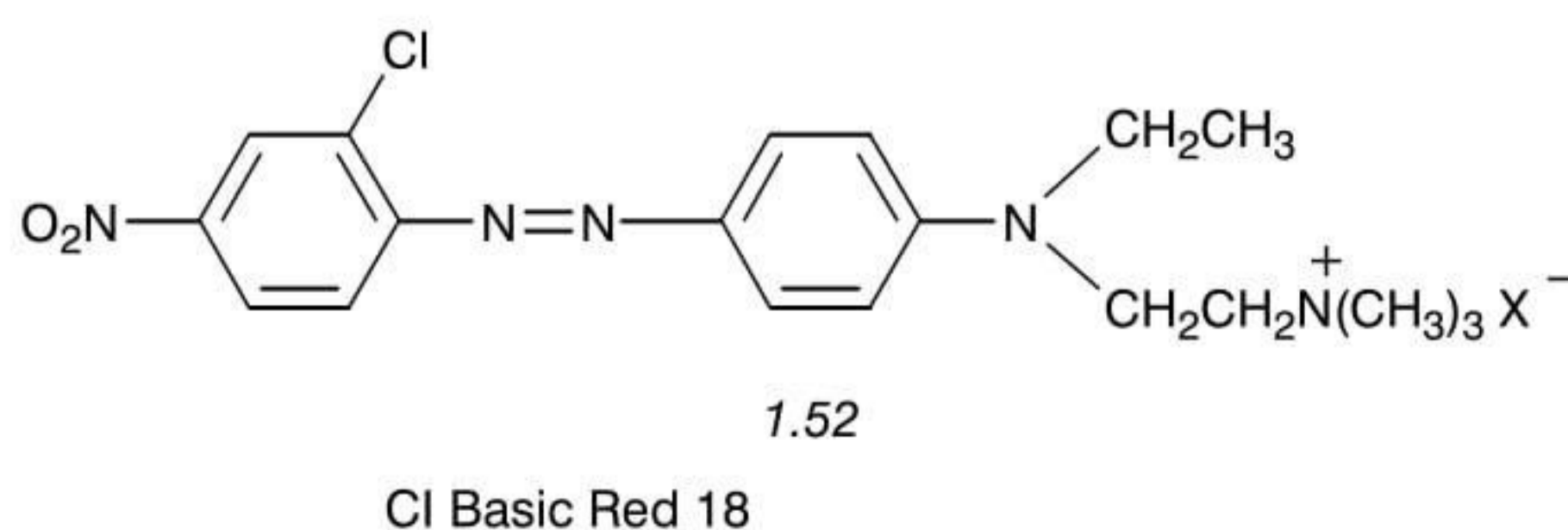

1.52

CI Basic Red 18

Table 1.6 Percentage distribution of chemical classes in basic dye hue sectors

Chemical class	Distribution in hue sector (%)								% of all basic dyes
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	
Azo	33	51	55	38	34	12	100	60	43
Methine	41	13	23	21	2	10			17
Triarylmethane			5	18	23	56			11
Acridine	12	36							7
Anthraquinone				5	15				5
Azine			6	13	5			20	5
Oxazine					11			20	3
Xanthene			11	5					3
Miscellaneous	14				10	22			6

them showed low toxicity to fish (LC_{50} > 1 mg/l). In 27 instances, however, 16 of them basic dyes and 10 of these triphenylmethane types, the LC_{50} was of the order of 0.05 mg/l [53]. A study by the American Dye Manufacturers' Institute (ADMI) of the effects of 56 dyes on the growth of green algae, 15 of them inhibited algal growth and 13 of these were basic dyes. In screening tests designed to determine whether dyes have an adverse effect on waste water bacteria and hence on the operation of effluent treatment plants, only 18 of the 202 dyes examined gave an LC_{50} value less than 100 mg/l and all of these were basic dyes [53].

1.6.7 Acid dyes

These are defined as anionic dyes characterised by substantivity for protein fibres. Levelling acid dyes and 1:1 metal-complex dyes are normally applied to wool from strongly acidic solutions, but the 1:2 metal complexes and many milling acid dyes have considerable substantivity even from neutral dyebaths (section 3.2.2). Wool, silk and nylon contain basic groups and the uptake of levelling acid dyes by nylon at acidic pH can usually be related to the amine end group content of the fibre. Under neutral dyeing conditions, however, non-specific hydrophobic interaction makes a considerable contribution, reinforcing the electrostatic bonding between such fibres and acid dyes of higher wet fastness.

Azo acid dyes represent the biggest single segment in the *Colour Index*, about two-fifths of them being metal-complex types (see Table 1.7). Monoazo dyes are supreme in all hue sectors of the azo acid range except the unmetallised browns and blacks, where disazo structures are more numerous. Anthraquinone and triarylmethane acid dyes traditionally provided most of the brilliant violet to green members of this range but demand for them declined, especially the triarylmethane types, as bright azo alternatives were developed. The significance of nitro yellows and browns, xanthene reds and violets and the phthalocyanine blues has always been marginal in the acid dye range.

The first acid dye, Orange I (1.53; CI Acid Orange 20), was discovered in 1876. All but a handful of the acid dyes developed since then were evaluated initially with wool dyeing in mind. In terms of adaptability to the coloration of other substrates, however, acid dyes have proved pre-eminent. This is the main reason for their number and variety. As well as the dyeing and printing of nylon and protein fibres, acid dyes are important for the coloration of leather, paper, jute, wood and anodised aluminium. Most of the permitted dyes for food and

Table 1.7 Percentage distribution of chemical classes in acid dye hue sectors

Chemical class	Distribution in hue sector (%)								% of all acid dyes
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	
Unmetallised azo	65	55	64	22	17	15	79	47	48
Metal-complex azo	31	42	29	44	21	39	13	46	31
Anthraquinone			2	18	36	22	3	3	10
Triarylmethane				12	16	16			5
Xanthene	1	1	4	3					2
Azine		1	1	1	4			1	1
Phthalocyanine					5	1			1
Nitro	1	1					5		1
Miscellaneous	2				1	7		3	1
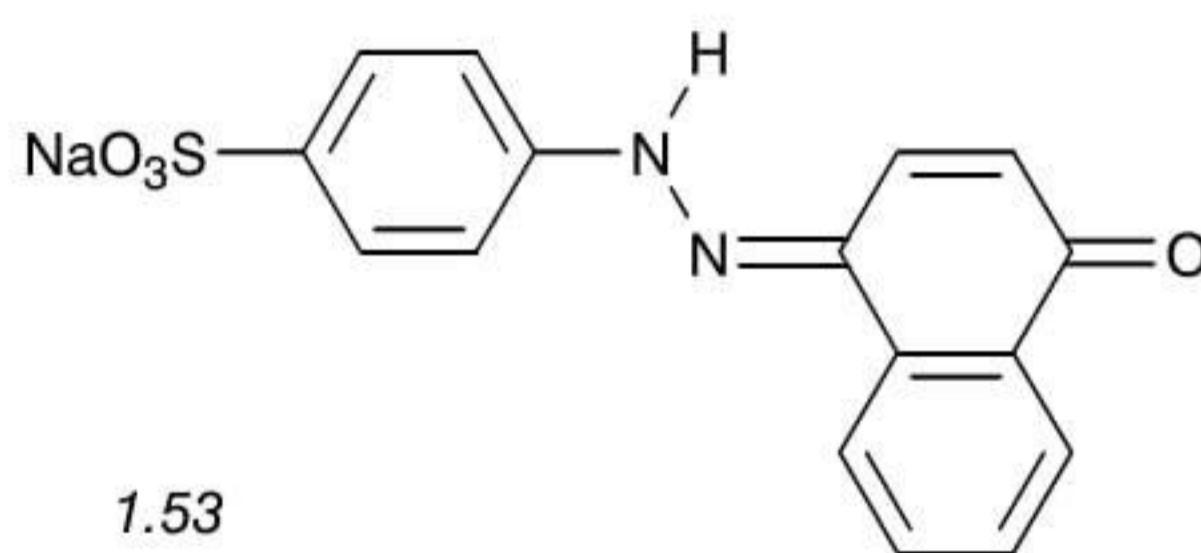
1.53

CI Acid Orange 20

cosmetics were originally marketed long ago for the dyeing of wool. Some solvent-soluble dyes are formed by co-precipitation of acid dyes and basic dyes. Concentrated monoazo acid dyes, often unmetallised bright yellows and reds, can be precipitated as their water-insoluble metal salts for use as pigments (section 2.2.1).

Acid dyes are highly suitable for reuse because they do not undergo chemical change during dyeing. Removal of acid dyes from dyehouse effluent has been achieved by membrane processing on an industrial scale. The process water and auxiliary chemicals are also suitable for recycling to the dyebath [42]. The sorptive removal of acid dyes during biological treatment of effluent varies with their degree of sulphonation. Levelling acid dyes of high solubility exhibit low sorption, whereas the more hydrophobic neutral-dyeing dyes are bioeliminated to a much greater extent [48]. As in the case of reactive dyes, flocculation with cationic agents is an effective method of removing the highly sulphonated acid dyes. Electrochemical coagulation of acid dyes is a viable alternative, with values of 55–85% colour removal from carpet dyeing waste waters being reported [54]. Reuse of the permeate from a reverse-osmosis membrane process on dyebath effluent containing premetallised acid dyes has been achieved [50].

1.6.8 Mordant dyes

The somewhat ambiguous term 'mordant dye' is defined as a dye that is fixed with a 'mordant'. A mordant is itself defined as 'a substance, usually a metallic compound, applied to a substrate to form a complex with a dye which is retained by the substrate more firmly than the dye itself'. Unfortunately, the mordant dyes category in the *Colour Index* follows

the more restricted convention of excluding both chelatable direct dyes capable of complexing with copper salts and those traditional basic dyes that were formerly applied to tannin-mordanted cotton, both of which subgroups conform to the above less than precise definition. A more logical generic name for those chelatable anionic dyes capable of being fixed to wool by aftertreatment with a dichromate would be the more popular term 'chrome dyes' or 'chrome mordant dyes', but the designation CI Mordant dye is well entrenched. Since the range has been steadily declining for many years, the ambiguity is of decreasing significance too. In all hue sectors except violet and blue, where triarylmethane, anthraquinone and oxazine dyes make notable contributions, 80% or more of chrome dyes are of the o,o′-dihydroxymonoazo type (1.54; CI Mordant Violet 5). Although most chrome dyes are only of interest for wool dyeing, a minority are applicable to most of those other substrates where acid dyes are found useful.

1.54

CI Mordant Violet 5
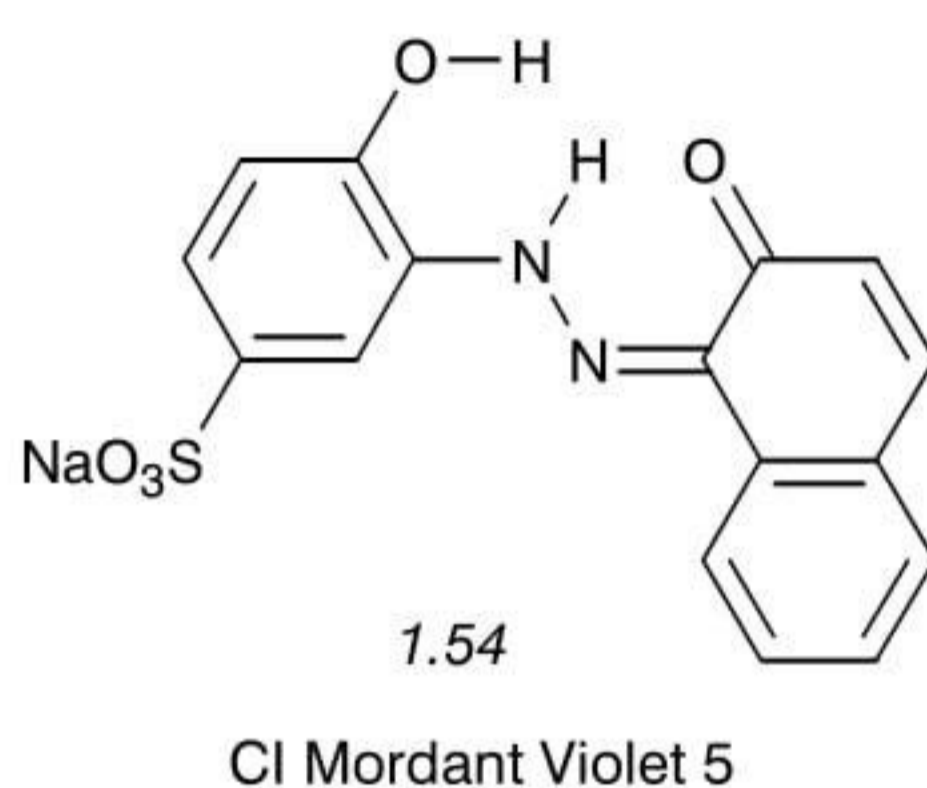
The complex formed when a mordant dyeing is aftertreated in a dichromate solution is retained by the wool in preference to the unmetallised mordant dye, which may desorb to some extent during the treatment. The latter is rather unstable in an oxidising solution and quinonoid by-products are often formed. If the chromium complex of the dye is formed from the desorbed dye in solution, this will further complicate the composition of the aftertreatment liquor. Thus reuse of mordant dyeing and aftertreatment baths is not an option. Furthermore, 100% rejection of dichromate ions would be required if the permeate of a membrane process treating the effluent was to be recycled [42].

1.6.9 Leather dyes

The application range designated by this generic name in the *Colour Index* incorporates those acid, direct and mordant dyes with substantivity for leather and satisfactory fastness on that substrate [55]. It is a commercially important sector, the number of products listed being exceeded only by the complete acid or direct dye ranges. As expected from the sources of this selection, about 85% of leather dyes are azo compounds (35% disazo, 30% monoazo, 20% metal-complex monoazo) and the remainder are mainly yellow to orange stilbene dyes and anthraquinone or triarylmethane types in the violet to green sectors.

There is growing concern over the potential risks to human health and the environment arising from leather goods. Dye manufacturers and tanneries are concerned about effluent, air pollution, containers and packaging [56]. In the light of the relatively important contribution to leather dyeing of azo dyes that can yield hazardous arylamines on reduction, careful guidance on the selection of dyes for leather is essential, with emphasis on procurement from reliable sources and the utilisation of liquid formulations to minimise

effluent treatment [57]. Based on theoretical considerations of dye structure and application properties, a range of compatible dyes that give deep colours of good fastness on leather has been developed [58].

For the reasons already outlined, only selected dyebath wastes from leather dyeing will be suitable for recycling (providing mordant dyes are absent). Bioelimination of the disazo direct dyes and monoazo metal-complex dyes will be relatively high. Flocculation using cationic precipitants should be an effective way of dealing with the residual dyes remaining in leather dyeing effluents. It is also necessary to consider methods for the disposal of leather goods at the end of their useful life. Dyed leather in itself, however, is not regarded as posing a hazard to humans, nor is it considered harmful to the environment [56].

1.6.10 Food dyes

Increasing legislation over the last fifty years has been imposed to control additives such as colorants that might enter foodstuffs directly or by migration from food containers or packages. Similar criteria cover the composition of drugs and cosmetics, but the cosmetics regulations tend to be less stringent in terms of chronic toxicity because skin represents an effective barrier to many chemicals.

Freedom from toxicity is clearly the primary consideration for dyes used in foods, drugs and cosmetics, followed by high solubility and chemical stability in the appropriate medium of incorporation. The possibility that they may affect consumers adversely has caused growing concern [59,60]. Legislation over many years has increasingly restricted the usage of synthetic colorants to certain permitted products that have shown no harmful effects when tested rigorously.

There is as yet no agreed international list of permitted food colours. Thus a food dye that is permitted in one country may be considered unacceptable in another. The synthetic food colorants permitted in the European Union are listed in Table 1.8 [60]. All were originally introduced as acid dyes for wool many years ago. Furthermore, more than thirty colorants of natural origin are permitted in most countries. The natural carotenoid dyes are of outstanding importance for colouring edible fats and oils. These yellow to red methine dye structures occur in many families of plants and animals, including vegetables, berries,

Table 1.8 Synthetic colorants permitted for use in food in the European Union (EU)

EU No	Colorant	CI Food	CI Acid	Chemical class
E102	Tartrazine	Yellow 4	Yellow 23	Monoazo
E104	Quinoline Yellow	Yellow 13	Yellow 3	Quinophthalone
E110	Sunset Yellow	Yellow 3		Monoazo
E122	Carmoisine	Red 3	Red 14	Monoazo
E123	Amaranth	Red 9	Red 27	Monoazo
E124	Ponceau 4R	Red 7	Red 18	Monoazo
E127	Erythrosine	Red 14	Red 51	Xanthene
E131	Patent Blue V	Blue 5	Blue 1	Triarylmethane
E132	Indigo Carmine	Blue 1	Blue 74	Indigoid
E142	Green S	Green 4	Green 50	Triarylmethane
E151	Black PN	Black 1		Disazo

fungi, insects, bacteria, feathers and egg yolks [61]. In general, the regulations governing the use of permitted additives such as those added directly in food manufacture are applied similarly in different member countries of the EU. There is greater variation, however, with regard to the indirect contamination of food by transfer of additives from packaging materials.

1.6.11 Solvent dyes

Solvent dyes are characterised by their solubility in one or more organic solvents. Numerous media are of interest in practice, the most significant being alcohols, ethers, esters, ketones, chlorinated solvents, hydrocarbons, oils, fats and waxes. The many practical applications in which the specific solubilities of these dyes are exploited have been outlined elsewhere (section 2.12). More than half of the solvent dyes listed in the *Colour Index* are unsulphonated azo compounds (27% monoazo, 18% monoazo metal-complex, 9% disazo) and a further 7% are complexes formed by co-precipitation of acid dyes with basic dyes, mostly yellows and reds. Unsulphonated anthraquinones lead the field in the bright violet to green sectors (17%). Xanthene reds (5%) and triarylmethane blues (5%) are the other noteworthy segments represented, together with a miscellany (12%) drawn from almost all other chemical classes. Some simple yellow solvent dyes used widely in the past, such as 4-aminoazobenzene (CI Solvent Yellow 1), are now known to be carcinogenic.

1.6.12 Pigments

In contrast to solvent dyes, pigments are substances in particulate form. They are essentially insoluble in the media into which they are incorporated, and are mechanically dispersed therein in order to modify the colour and/or light-scattering properties of such media. These characteristics of low solubility in water and organic solvents, which are obligatory for the satisfactory technical performance of pigments, also mean that their bioavailability is unusually low. This is certainly the prime reason for the remarkably low toxicity of organic pigments [1]. In many cases, the solubilities in n-octanol and water are so low that the experimental determination of solubility poses serious difficulties, so that calculation procedures are adopted in assessing the toxicological hazards of pigments [62].

The complete range of pigments may be conveniently divided into three main groups on the basis of their chemical constitution and mode of preparation for use:
(a)   Organic pigments (approximately 60% of the total number of products) are concentrated nonionic colorants from various chemical classes,
(b)   Water-soluble dyes (approximately 20%) that are rendered insoluble by various techniques of precipitation,
(c)   Inorganic pigments (approximately 20%) are coloured insoluble materials from inorganic sources.

Monoazo and disazo compounds form by far the largest subgroup among the organic pigments, mainly occupying the yellow-orange-brown-red sectors of the colour gamut. This class may be subdivided further into metal-free structures with inherently negligible solubility in water and those containing potentially ionisable groups that must be converted to their heavy-metal salts (section 2.3). Anthraquinonoid pigments are analogous to vat

dyes in their keto forms (section 1.6.1) and they provide mostly red-violet-blue colours of high light fastness. Further chromogens represented include isoindolinones (yellow-orange), quinacridones (red-violet) and phthalocyanines (blue-green).

Conventional basic dyes (section 1.6.6) can be rendered insoluble by precipitation using phosphomolybdic or phosphotungstic acids, or alternatively copper(II) hexacyanoferrate. These complexes exhibit higher light fastness than the parent basic dyes on a traditional tannate mordant. Concentrated anionic monoazo dyes (mainly yellows, oranges and especially reds) can be precipitated as their insoluble metal salts, typically those of barium, aluminium or calcium. These processes of converting soluble dyes into pigments by precipitation, often in the presence of an inert substrate such as the so-called alumina hydrate, are now of declining importance.

The inorganic group of pigments represents the naturally occurring coloured minerals that have been widely used throughout recorded history to colour ceramics, glass and many other artefacts. This class includes coloured metal salts such as lead chromate (CI Pigment Yellow 34), complex salts such as Prussian blue (CI Pigment Blue 27) and ultramarine (CI Pigment Blue 29), metal oxides such as titanium dioxide (CI Pigment White 6) and free elements such as carbon black (CI Pigment Black 6).

1.6.13 Azoic components and compositions

These are the only ranges of precursor products in the *Colour Index* that are still commercially significant. Azoic dyes have a close formal relationship to those monoazo pigments derived from BON acid or from acetoacetanilides (section 2.3.1) and some are chemically identical with them, although they are used in a totally different way. Azoic components are applied to produce insoluble azo dyes within the textile substrate, which is almost always cotton. Corresponding azoic components for the dyeing of cellulose acetate, triacetate and polyester fibres were once commercially important, but are now obsolete because of environmental hazards and the time-consuming application procedure.

In dyeing with azoic components, an insoluble azo compound is produced within the fibre by the coupling of an azoic diazo component (a diazotised arylamine) with an azoic coupling component (usually an arylide of BON acid or a related naphthol). Azoic dyes provide only relatively dull violets and navy blues, costly greens, and browns or blacks of limited versatility, but are tinctorially strong, bright and economical in the orange to red sectors. Some of the diazotisable amines of former importance in this range, such as 4-chloro-2-methylaniline (CI Azoic Diazo Component 11) or 3,3'-dimethoxybenzidine (CI Azoic Diazo Component 48) are now known to be carcinogenic.

The two types of component form separate generic series in the *Colour Index*. There is also a third series, designated CI Azoic compositions. Now obsolescent, these prepared mixtures of an azoic coupling component and a stabilised diazo component were intended mainly for textile printing. The stabilisation prevented coupling until the printed fabric was steamed under appropriate conditions to regenerate the active diazonium salt and promote formation of the azoic dye. When dyeing with azoic components it is difficult to prevent some desorption of coupling component into the developing bath containing the diazo salt. The latter is also inherently unstable, releasing nitrogen to leave the phenolic analogue of the original arylamine. Thus recycling is not a realistic option for residual azoic dyebaths because of their complex composition [42].

1.6.14 Developers

This short range of simple coupling components, comprising phenols, naphthols and 1-phenyl-3-methylpyrazol-5-one, is seldom used nowadays. Developers were once used as aftertreatments to enhance the wet fastness of certain direct dyes for cellulosic fibres or disperse dyes for cellulose acetate. Each of these dyes contained a primary arylamine grouping that was capable of diazotisation and coupling to the developer molecule. This application technique was prolonged, however, and the improvement in fastness performance was disappointingly slight. The usage of developers in this way has fallen to negligible levels.

1.6.15 Oxidation bases

Like azoic components, these are precursors of a distinct chemical class of colorant as well as an application category, but they are too restricted in attainable hues to be described as a 'range'. This cheap but unpleasant method of continuous coloration, once popular for cotton printing in visually attractive illuminated resist styles under aniline black or paramine brown colours, has been superseded by environmentally more acceptable and controllable alternative processes. Oxidation dyeing was simply the *in situ* formation of a polymeric black or dark brown azine colorant of indeterminate constitution by acidic oxidation of a simple arylamine such as aniline or *p*-phenylenediamine on the fibre, using a chlorate or dichromate as oxidant and a copper salt catalyst. Although no longer significant in textile dyeing or printing, coloration techniques of a similar kind have remained the primary method of colouring human hair, feathers and natural furs.

1.6.16 Ingrain dyes

This is another somewhat ambiguous category in the context of the *Colour Index* classification, but fortunately it is now merely of historical interest. An 'ingrain' dyeing process is defined as the formation of a colorant '*in situ* in the substrate by the development and coupling of one or more intermediate compounds'. This imprecise description clearly embraces azoic dyeing and the application of oxidation bases, but the generic term 'CI Ingrain dye' is limited to a third small group of now obsolete colorant precursors, again too restricted in hue to be regarded as a 'range'.

   They were introduced in the late 1940s for the textile printing of cellulosic fabrics under the trade names Alcian (ICI) and Phthalogen (BAY). Both types resulted in the insolubilisation of copper phthalocyanine or related pigments within the fibre, although the respective application techniques differed considerably. Reactive phthalocyanine dyes in the 1960s superseded these early approaches to the attainment of fast bright blues and turquoises on cellulosic fabrics [63].

1.6.17 Fluorescent brightening agents

These essentially colourless compounds have been defined as substances 'that, when added to an uncoloured or a coloured substrate, increase the reflectance of the substrate in the visible region by converting UV radiation into visible light and so increase the whiteness or brightness of the substrate'. The air of uncertainty in the final clause of this definition

reflects the general indecision among practitioners in this field about whether to call them 'fluorescent brightening agents' (or FBAs), as in the *Colour Index*, 'fluorescent whiteners' (FWs) or 'optical whiteners' (OWs).

Since their commercial introduction during the 1940s as components of proprietary detergents and laundry preparations, these products have found extensive usage in the whitening of paper and textile materials. Disperse FBAs are available for whitening hydrophobic fibres and solvent-soluble FBAs impart fluorescence to oils, paints, varnishes and waxes. Approximately 75% of commercially established FBAs are stilbene derivatives with inherent substantivity for paper and cellulosic textiles, but the remainder come from about twenty different chemical classes. These include aminocoumarins (6%), naphthalimides (3%), pyrazoles and pyrazolines (each about 2%), acenaphthenes, benzidine sulphones, stilbene-naphthotriazoles, thiazoles and xanthenes (each about 1%). FBAs of these and other chemical types are discussed in detail in Chapter 11 of Volume 2.

1.6.18 Reducing agents

As noted earlier, the specific inclusion in the *Colour Index* of a group of textile auxiliaries under this generic name seems anomalous, if not aberrant. The justification claimed is that they are indispensable for the application of vat dyes and in discharge printing or stripping processes. A similar level of interdependency could be claimed for certain other classes of auxiliaries, as is discussed particularly in Chapters 10 and 12 of Volume 2. One has only to visualise textile printing without thickeners or emulsifying agents to realise this. In future plans for further development of the *Colour Index*, however, there seems to be no scope for extending coverage to other groups of auxiliary products used in colorant application processes [13].

1.7 COLORANTS AND THE ENVIRONMENT

Health and safety were absent from the list of priorities in the early decades of the synthetic dyes industry. Practical experience in the primitive working conditions of the time [64] no doubt made workers aware of the more obvious dangers, such as corrosive acids, flammable solvents and potentially explosive nitro compounds. Accidents must have occurred frequently, reminding victims and supervisors alike of the penalties suffered if hazardous chemicals were handled carelessly.

More insidious, however, were the potential health risks resulting from longer-term exposure to certain organic and inorganic chemicals. Operatives were expected to provide and wash their own working clothes. These must have become heavily contaminated with chemical stains, putting the worker's family also at risk of exposure to hazardous vapours [65]. It was not until the 1940s that the connection was made between the high incidence of bladder cancer in employees of dye-making and dye-using firms and their exposure to certain arylamines, following epidemiological studies of individuals who had spent their working lives in these industries. Compounds now recognised as highly carcinogenic, notably 2-naphthylamine and benzidine, had been widely used as dye intermediates since the 1880s. Even if such causal links had been suspected over the intervening decades, it is difficult to see how they could have been demonstrated in any other way.

Following a period of unprecedented growth and optimism in the chemical industries

worldwide during the 1950s and 1960s, a sociopolitical reaction set in during and after the oil crises of the 1970s. Public demand, often fuelled by media misinformation and speculation [60,66], became insistent that the manufacture and use of industrial chemicals should be more closely regulated and monitored. A series of tragic incidents occurred over this period, involving cyclohexane at Flixborough (UK), dioxins at Seveso (Italy), mercury compounds at Minamata (Japan) and methyl isocyanate at Bhopal (India). These were followed in 1986 by the Chernobyl (USSR) nuclear explosion that polluted much of Northern Europe and the Schweizerhalle (Switzerland) fire that polluted the Rhine basin in the heart of Europe, reinforcing this trend towards a political climate of reform and control.

1.7.1 Risk evaluation and prevention

Indispensable to the management of risk by reduction or avoidance is a knowledge of the risk and the controlling factors determining its magnitude. Risk in this context is a function of the potentially harmful effects arising from inherent toxicological properties of the chemical and the extent of its bioavailability to the organism exposed. Risk is also a function of degree of exposure and the probability of its occurrence. Obviously, the risk of experiencing harmful effects can be lowered by limiting the degree of exposure and this approach affords a means of improving safety [67]. Industry has a substantial interest in helping the risk assessment approach to work. Failure to do so will encourage regulation based on hazard considerations alone. There is already a tendency in favour of the precautionary principle and the introduction of various 'black-lists'. Such discriminatory actions undermine the agreed basis for chemicals control and warrant an unreserved rejection by the chemical industry [68].

Thus two components, exposure and hazard, must be evaluated together in determining the level of risk posed by a given colorant or other chemical. Risk management may therefore be regarded as a series of interdependent steps:
(1) Exposure assessment
(2) Hazard assessment
(3) Risk evaluation
(4) Risk prevention

The process of risk evaluation for personnel working with dyes and textile chemicals has been discussed in detail [69]. The more extensive the database covering toxicological, physical, chemical and application properties of the product, the easier it is to assess the risks involved.

Although exposure levels are just as important as hazard potential for the risk assessment, the quality of the exposure data is often the weak point in the data available. Consequently, in many instances it is not possible to be fully confident of the reliability of the risk assessment, which may tend to be in error on the side of overestimation. Particular attention should be given to improving aspects of exposure assessment (occupational exposure, consumer exposure, environmental release) [70]. The widespread use of colorants creates a great diversity of exposure situations. The most serious exposure potential exists for operatives in colorant manufacture and those employees of dye user firms engaged in weighing and dispensing dyes. Dust particles less than 7 μm in size can gain access into the lungs and pose the greatest problem. It is not feasible to market all colorants in liquid form

and considerable efforts have been devoted to the development of low-dusting solid forms. The monitoring of amine excretion in the urine of individuals exposed to arylamines, or dyes expected to be metabolised in the body to such amines, offers a possibility of checking the adequacy of safety precautions [67].

The conventional classification of organic colorants into broad chemical classes or application ranges is of limited help in hazard assessment. It is not possible to generalise about the toxicological properties of entire groups like these. Biological activity can vary dramatically in spite of close structural relationships. Nevertheless, an observed toxic effect can often be attributed to a specific structural feature within a narrow subclass of colorants, or to a specific metabolite produced from them as in the formation of benzidine from its parent disazo dyes. Organic colorants generally exhibit relatively low acute toxicity. This is especially true of organic pigments because of their extremely low bioavailability. Of major concern, however, are the potential carcinogenic and allergic effects.

As a basis for the determination of risk it must be assumed that the colorants are properly handled and applied. It is not appropriate to estimate risk primarily on the basis of exposure values obtained under improper working conditions, or where appropriate plant and equipment are not available. Ensuring satisfactory operating conditions and training of operatives to handle products correctly is essential nowadays for technological success as well as for health and safety requirements. In this way, exposure levels can be kept below the threshold of unacceptable risk. It is reasonable to accept that for practical purposes levels of exposure exist below which the risk becomes trivial [67].

The various measures to reduce risk are an integral part of risk management. A state of 'zero risk' cannot be reached, but efforts to maintain exposure levels below the threshold of unacceptability must be unremitting, in order to increase the margin of safety. An essential prerequisite for effective risk control is the provision of readily accessible hazard information on computer disc, in safety data sheets and on warning labels. It is prudent to minimise exposure to all chemicals through good working practice. Respiratory protection by approved equipment must be worn wherever dusts or aerosols are being generated or disturbed. A constructive approach to reducing risk is the replacement of hazardous products by safer ones. This cannot be achieved quickly in most instances, because of the complex profile of technical and economic requirements that governs selection of a colorant for a specific purpose [71].

Over recent years there has been an extraordinary growth of ecolabelling schemes worldwide, but notably in Europe. The term 'ecolabel' has been defined as an EU scheme to promote products with reduced environmental impact during their life cycle [72]. These schemes build upon increasing public awareness of environmental issues, offering an opportunity to increase and sustain consumer interest in reducing the environmental impact, as well as opening up new marketing opportunities. The chemical industry's stance has been supportive of these objectives but somewhat sceptical and concerned at the multitude of different schemes [68,70].

As a basis for evaluating individual schemes, the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) concluded that a satisfactory scheme should meet the following criteria:
(1) Objective criteria must be provided
(2) The approach should be risk-based, not hazard-based
(3) Consumer goods should be specified, rather than the colorants used to colour them

(4) Dye selection should only be necessary if there is real environmental benefit
(5) European or international schemes are preferable, rather than a proliferation of national ecolabels.

The main deficiency of existing schemes is that they focus on the exclusion of certain hazardous dyes but do not take into account that it is the conditions of manufacture and application that are the most important determinants of environmental impact [68,70].

1.7.2 Sensitisation, toxicity and carcinogenicity

Allergic contact dermatitis or skin sensitisation by dyes or other chemicals manifests itself as a persistent irritating rash. The presence of certain dye stains on the skin has been known to accelerate the reddening effect of sunlight exposure (erythema). The causation of skin sensitisation by dyes, both in animal tests and in exposed workers or the general public, has been reviewed [73,74]. Cases of occupational skin sensitisation attributable to dyes are uncommon [75], even in those workplaces where inadequate handling precautions have been taken. Occasionally, reports of organic pigments causing skin sensitisation have arisen but such cases appear to be due to the presence of soluble impurities. Instances of contact dermatitis linked to the wearing of close-fitting garments often seem to be associated with nylon dyed with certain disperse dyes of low fastness in full depths (section 1.6.5). A list of nine such dyes that may be sensitising has been drawn up: CI Disperse Yellow 3, Orange 3, 37 and 76, Red 1 and Blue 1, 35, 106 and 124. Garments containing any of these dyes should carry a hazard warning label and for contact clothing such as hosiery they should not be used. The possible mechanism of sensitisation in the case of azo dyes is thought to be the production of the quinonimine derivative by reduction and oxidation [75].

Sensitisation of the respiratory tract by inhaling dust particles from various chemicals has frequently been reported in industry. It is likely to result in symptoms of respiratory disease or distress when the sensitised individual is exposed to a specific allergen. Respiratory allergy is the clinical manifestation of this state, with bronchial asthma or allergic rhinitis (resembling hay fever) constituting typical disease symptoms. It is believed that relatively high exposure levels are important in the induction phase. There is also evidence that a predisposition to respiratory allergy may be caused by genetic or other factors.

Instances of severe sensitisation to the dust from reactive dyes have been reported [76]. These prompted the UK Health and Safety Executive to initiate a study involving about 440 workers in 51 dyehouses who were in contact with reactive dye powders. About 15% of them showed work-related respiratory or nasal symptoms. In 21 individuals their allergic reactions could be attributed to contact with one or more specific reactive dyes [77]. Reactive dyes are able to react with amino, hydroxy and thiol groups in proteins. Such a reaction seems to be the initial step of the sensitisation process. The reactive dye may react with human serum albumin (HSA) to form a dye-HSA conjugate, which behaves as an antigen. This in turn gives rise to specific antibodies and these, through the release of mediators such as histamine, produce the allergic symptoms [67,77].

Acute toxicity refers to effects that occur within a brief time after a short-term exposure, such as a simple oral administration. The generally low acute oral toxicity of colorants is well-established [78–81]. This is normally expressed in terms of the LD_{50} value, a

statistically derived dose that is expected to cause death in 50% of treated animals (typically rats) when administered over a prescribed period in the test. In 1974 ETAD began a programme to generate a systematic toxicological database. More than 80% of commercial dyes have an LD_{50} value (rat, oral) greater than 5000 mg/kg.

In response to an EEC Council Directive of 1979 (6th amendment) regarding the labelling of dangerous substances, ETAD in 1986 decided to publish a list of twelve colorants that have been classified as toxic on the basis of their acute peroral LD_{50} values [82]. These varied within the range 25 mg/kg (CI Basic Red 12) to 205 mg/kg (CI Basic Blue 81) and the list included six basic dyes, three azoic diazo components, two acid dyes and one direct dye. Although such data provide an essential basis for advice on safe handling procedures, long-established experience indicates that dyes, and even more so organic pigments, present few acute toxicological risks providing good working practices are followed.

In the debate about the toxic effects of dyes and chemicals, there is no doubt that carcinogenic effects are perceived by the general public as the most threatening. Chemicals remain a focus for this concern in spite of the weight of evidence that they make only a minor contribution to the incidence of cancer [60,67,83]. The generally accepted estimate of cancer causation, based on mortality statistics, indicates that only 4% of all cancer deaths are attributable to occupational exposure. Another 2% are considered to arise from environmental causes and 1% from other forms of exposure to industrial products.

As by far the largest chemical class, it is perhaps not surprising that azo dyes have attracted most attention with regard to carcinogenicity. Some structure-carcinogenicity trends for azo dyes and their metabolites have been discussed with a view to the prediction of dye carcinogenicity [84,85]. If an azo dye is carcinogenic and is relatively stable in the hydroxyazo tautomeric form, the dye itself is likely to be the active carcinogen. In contrast, those dyes that exist predominantly in the ketohydrazone form are more readily reduced to metabolites. In this case, the pro-carcinogen is likely to be an arylamine and the ultimate carcinogenic potential can then be deduced from the availability of a suitable active site on the metabolite. Azo pigments, because of their extreme insolubility and low bioavailability, are unlikely to be metabolised even if they exist preferentially in the hydrazone form [84]. A large majority of water-soluble azo dyes do not form carcinogenic arylamines when reductively cleaved. In most cases, the reduction products are arylaminesulphonic acids, which have little or no carcinogenic potential.

Epidemiological studies first alerted the colorants industries to the causal links between certain manufacturing operations and an increased risk of bladder cancer among workers [1,60,86]. Regulations were passed in the 1960s that placed a virtual ban on the importation and use of certain dye intermediates, such as benzidine and 2-naphthylamine, and certain processes, including auramine (1.28) manufacture [87]. Most responsible colorant manufacturers in Europe, Japan and the USA ceased production of benzidine-based dyes in the early 1970s due to inability to ensure their safe handling in dyehouses. However, owing to the attractive economic and technical merits of such dyes on leather and cellulosic fibres, manufacture continued in other parts of the world (for example, Latin America, India and the Asia Pacific region). The risk to workers in manufacturing and dyeing plants in these areas is of concern because of the poor conditions of occupational hygiene that often exist [1].

1.7.3 Colorants in waste waters

The high visibility of water-soluble dyes released to the environment ensures that only extremely low concentrations in watercourses would not be noticed. A typical visibility limit in a river would be about 0.1 to 1 mg/l, but this varies with the colour, illumination and degree of clarity of the water. The human eye can detect a reactive dye concentration as low as 0.005 mg/l in pure water, particularly in the red to violet hue sector [88]. There is considerable debate, however, about what level of environmental hazard is represented *per se* by colour in effluent. The view has been expressed that dyestuffs should not be regarded as water pollutants because at concentrations of the same order of magnitude as these visibility limits their harmful effects are negligible [89]. Nevertheless, even though this colour problem is mainly if not entirely an aesthetic one, the fact is that the general public will not tolerate coloured amenity water and the problem therefore has to be addressed and rectified [90,91,92].

The main consideration regarding the environmental impact of dye residues is concerned with toxicity to aquatic organisms. This is normally expressed in terms of the LC_{50} value, which represents the concentration of the substance under test that is required to kill 50% of the organisms exposed. With the exception of a small minority (about 2%, mainly basic dyes), organic dyes generally show only low toxicity to fish and other organisms such as *Daphnia magna* [48]. Bioaccumulation is also important, defined as the factor $F = C_a/C_e$, where C_a is the concentration of the pollutant in the fish species and C_e that for the general environment [93]. The partition coefficient (P) of the colorant in an n-octanol/water mixture is used as an indicator of bioaccumulation. If P is less than 1000 it can be predicted that F in fish will be less than 100, at which level no problems are foreseen. Water-soluble dyes do not bioaccumulate and even those disperse dyes and pigments that give P values above 1000 still show no evidence of bioaccumulation in fish [48].

Algae are an important part of the aquatic ecosystem, with algal photosynthesis a critical source of oxygen. The adverse effects of dyes in inhibiting the growth of green algae do not parallel the effects on fish, so that no conclusions about the one can be drawn from the other. Nevertheless, those basic dyes that yield low LC_{50} values in fish toxicity tests also tend to inhibit algal growth at concentrations as low as 1 mg/l. It is also true that a majority of basic dyes have an inhibitory effect on waste water bacteria, having LC_{50} values of less than 100 mg/l, so that they tend to have a deleterious effect on the operation of effluent treatment plants (section 1.6.6).

In view of the good to excellent fastness of most colorants, it is not surprising that they are not readily biodegradable. Biodegradability may be defined as the degree of decomposition of an organic contaminant after biological treatment under specified conditions [94]. With the brief retention times normally prevailing in effluent plants, there is practically no evidence of biodegradation of colorants under aerobic conditions [53]. Bioelimination includes removal of the colorant by adsorption on the biomass as well as that undergoing biochemical decomposition. A large majority of dyes are adsorbed by the biomass to the extent of 40–80%. High adsorption occurs with basic dyes, direct dyes, disperse dyes and most of the premetallised and milling acid dyes [48,95,96]. The only dye types that are not substantially adsorbed during biological treatment are the highly soluble multisulphonated levelling acid dyes and virtually all reactive dyes, which share similar characteristics.

1.7.4 Hazardous arylamines

Anaerobic conditions, such as apply when digesting sewage sludge or when residual colorants are present in river sediments, favour biodegradative reactions. Under these circumstances the biodegradation of dye chromogens is a primary cause of colour removal. Dyes are quite readily absorbed by sludge, suspended solids or sedimental matter. With azo colorants these conditions render the azo group susceptible to reductive cleavage, giving rise to arylamines as breakdown products [97,98]. There is concern that arylamine metabolites formed under such anaerobic conditions could be desorbed later into the aquatic aerobic environment and thus represent a hazard. The arylamines, however, are generally susceptible to aerobic degradation. Aniline and its monosubstituted derivatives, such as anisidines, phenetidines and toluidines, are readily biodegraded. Diaminobiphenyls, namely benzidine, dianisidine, dichlorobenzidine and tolidine, are more resistant but still inherently biodegradable [99]. A wider selection of arylamine metabolites from azo dyes, including arylaminesulphonic acids, gave broadly similar results [100].

The voluntary cessation of manufacture of benzidine and the dyes derived from it by major dyemakers in the early 1970s created a series of research targets to find replacements with corresponding technical properties. Alternative non-mutagenic diamines were sought and found to yield dyes exhibiting satisfactory performance [101]. Unfortunately, these were almost always substantially less cost-effective than the analogous benzidine-based products they were intended to replace and which were still commercially available from non-traditional suppliers. Following the emergence in the early l990s of conclusive evidence of animal carcinogenicity from CI Acid Red 114 (1.55) derived from o-tolidine and CI Direct Blue 15 (1.56) derived from o-dianisidine, several dye manufacturers ceased production of these and other dyes made from these two diamines.

1.55

CI Acid Red 114

1.56

CI Direct Blue 15
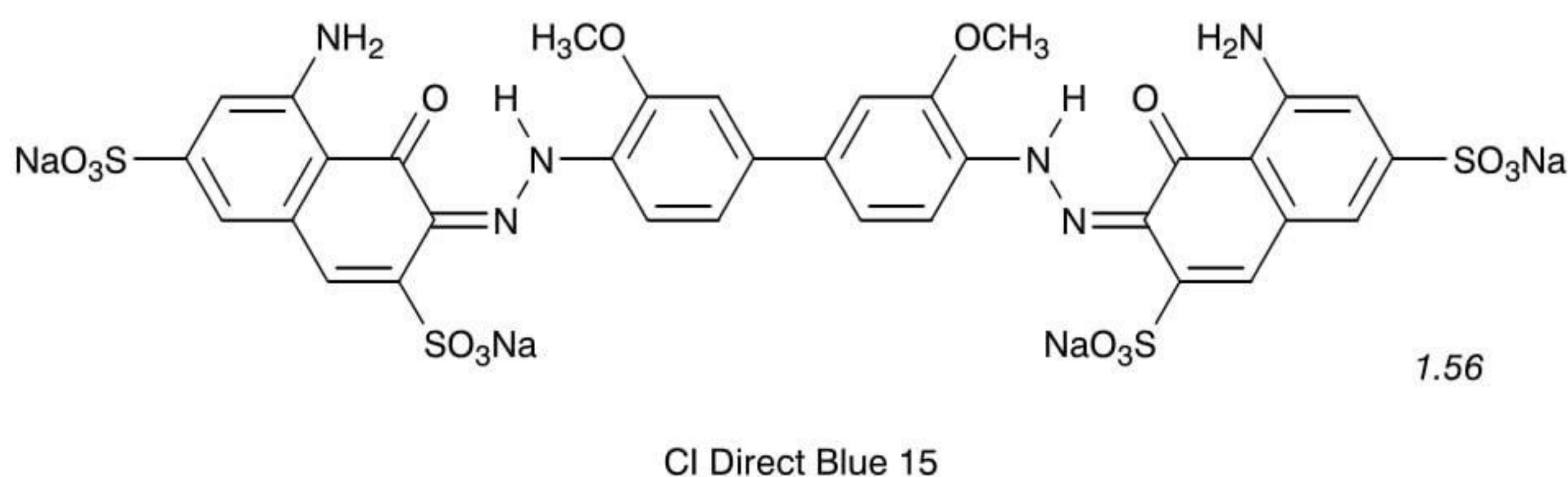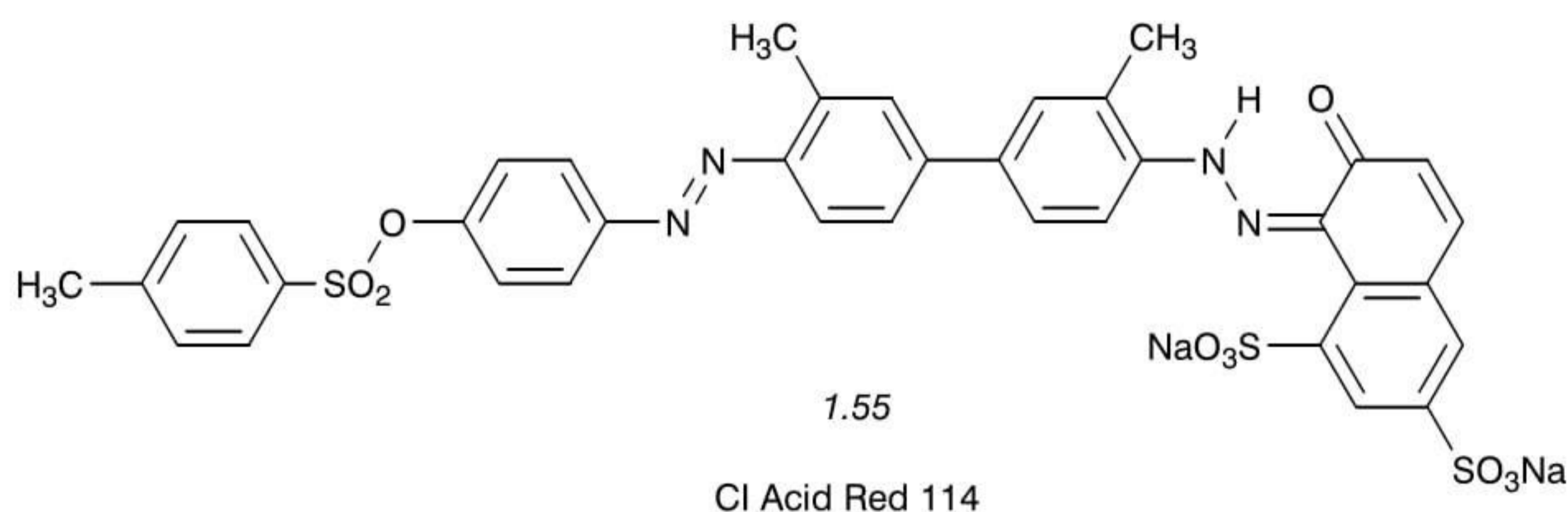
The German government issued in July 1994 an amended regulation concerning consumer goods involved in direct body contact, including clothing, shoes and bedlinen. This banned the use of azo colorants that could be reduced to give any of twenty specified arylamines. These amines have been classified by the German MAK commission as substances that have been unequivocally proved to be carcinogenic. This regulation embraces the concept that an azo dye that can cleave to yield a carcinogenic arylamine is itself a carcinogen [70]. It is estimated [1] that about 150 commercial azo colorants are carcinogenic according to this definition. Since the German ban, ecolabelling schemes within the EU have adopted the same list of twenty arylamines and added two more that have been classified by the EU as Category 2 carcinogens [102]. A full list of these specified arylamines is given in Chapter 4 (Table 4.1).

Since the implications of this unilateral ban by the German authorities began to be realised, it seems to have developed into a prime example of how not to enact legislation in such a commercially and technically complex area. There was an immediate and substantial impact on certain sectors of industry, notably textiles and leather. The globalisation of trade in the 1990s ensured that there were many repercussions both inside and outside the EU. No risk analysis had been carried out and there was no consultation with interested parties outside Germany before the ban, in spite of notification procedures required by EU regulations [103]. The Netherlands later enacted a similar ban and several other EU member states [70] are intending to introduce regulations concerning consumer goods involved in direct body contact.

Although the 1994 regulation specified consumer goods, suppliers were asked by German retailers to guarantee that all materials supplied were free from the banned dyes. Thus companies higher up the supply chain became involved, if their goods containing such dyes were to be imported into Germany. A major stumbling-block was the lack of an official list of dyes to be banned [104]. Member firms of ETAD quickly undertook to inform their customers and other interested parties if they supplied any of the azo dyes implicated in this legislation [105]. This still left dye users and others uncertain about supplies from elsewhere, especially from colorant merchants who do not manufacture the products that they sell. Until 1997, there was no officially recognised test method [106] to isolate and identify the specified amines from textiles or leather.

Analysis was sometimes undertaken by organisations lacking the necessary skills or expertise. It was not surprising, therefore, that spurious results (false positives) were sometimes obtained [103,105]. The early tests carried out with alkaline dithionite at temperatures above 70 °C could give rise to banned amines by reactions other than azo reduction, including reduction of nitro groups [107], hydrolysis of amides and desulphonation of water-soluble amines [108]. In order to minimise the misleading results obtained under these conditions, methods of reduction using buffered dithionite at 70 °C or lower temperatures were developed [108,109].

1.7.5 Halogenated colorants

During the 1990s, several environmental agencies and activist groups have argued that the banning of chlorine and all chlorinated organic chemicals will be necessary to protect the environment. The impact of such a ban would be immense, particularly for those organic dyes and pigments that are predominantly dependent on chlorine-containing intermediates leading

to their manufacture. Approximately 40% of all organic pigments contain chlorine in the pigment itself, although this corresponds to only 0.02% of total chlorine usage. Interestingly, organofluorine compounds do not fall into the AOX classification since the fluoride ion liberated as soluble silver fluoride according to the test protocol is not detected [25].

In the EU and Japan, controls on the discharge of absorbable organohalogen compounds are becoming increasingly severe. Insect-proofing agents for wool, trichlorobenzene carriers for polyester dyeing and reactive dyes of the chloroheterocyclic types certainly fall into this category [65,110]. It seems likely that reactive dyes containing vinylsulphone or fluoroheterocyclic groups will become increasingly important [25]. Many direct, disperse and vat dyes also contain chloro-substituted aryl nuclei [111]. It is to be hoped that rational evaluation of the available evidence will convince regulatory authorities that the mere presence of an inert chloro substituent in a molecule does not mean that it will pose an environmental risk [1].

1.7.6 Heavy-metal contaminants

Heavy metals are widely used as catalysts in the manufacture of anthraquinonoid dyes. Mercury is used when sulphonating anthraquinones and copper when reacting arylamines with bromoanthraquinones. Much effort has been devoted to minimising the trace metal content of such colorants and in effluents from dyemaking plants. Metal salts are used as reactants in dye synthesis, particularly in the ranges of premetallised acid, direct or reactive dyes, which usually contain copper, chromium, nickel or cobalt. These structures are described in detail in Chapter 5, where the implications in terms of environmental problems are also discussed. Certain basic dyes and stabilised azoic diazo components (Fast Salts) are marketed in the form of tetrachlorozincate complex salts. The environmental impact of the heavy metal salts used in dye application processes is dealt with in Volume 2.

The toxic effects of trace metals towards animals or aquatic life are highly dependent on the physical and chemical form of the contaminant [112]. For example, dissolved copper(II) or chromium(III) ions are highly toxic, whereas the same atoms coordinated within stable organic ligands such as dye molecules are not harmful. Unfortunately this is not widely acknowledged in setting limits for consent conditions, where the total metal content is often specified rather than the forms in which it is present. The permitted levels for trace metals in dyehouse effluents vary from one country to another and even between different areas in the same country [65,94,113]. Improved dyeing methods that have been developed to minimise release of residual chromium when applying chrome dyes to wool are outlined elsewhere (section 5.8.2).

When restrictions on the contamination of effluent by chromium residues were imposed in the 1970s, the initial reaction in the wool dyeing industry was to predict the rapid demise of chrome dyes. This forecast decline did not materialise because of the outstanding fastness of chrome dyeings and the efforts made to minimise effluent pollution [25,65]. In 1996 member firms of the GuT carpet ecolabelling scheme in the EU introduced a voluntary ban against the use of metal-complex dyes on certain nylon floorcoverings. Extension of this ban to all carpets made from nylon, wool or their blends has been predicted [104]. Ecolabelling schemes covering apparel and household textiles must also take account of the presence of premetallised dyes because of the obvious risk that extraction into perspiration or saliva can take place from dyeings of inadequate wet fastness [114].

1.7.7 Natural and synthetic dyes

In Germany during the 1970s there was a growing demand by supporters of the Green movement for greater use of natural dyes of vegetable origin to dye natural fibres such as wool, silk and cotton. This trend has been taken up enthusiastically in tropical countries with climates suitable for growing such dye-yielding plants [115,116], including woad [117], lac dye [118], lichens [119] and even tea plants [120,121]. Research has been carried out with a view to minimising the amounts of mordanting chemicals necessary to apply natural dyes [122–124], in order to offset criticism that such processes would be as polluting as the use of premetallised synthetic dyes.

Contamination of effluent streams with residual heavy metals from mordanting [125,126] is by no means the only drawback of a return to colouring methods that prevailed before the discovery of synthetic dyes [127,128]. Natural dyes are tinctorially weaker and duller, are often difficult to dye level and show inferior fastness to light and washing compared with their synthetic counterparts. Although applicable to natural fibres with the aid of mordant chemicals, important synthetic polymers such as polyester or acrylic fibres cannot be dyed using these products [126,129]. Calculations show that about 400 kg of cultivated dye plants are required to dye to the same depth as given by 1 kg of synthetic dye on cotton or wool, at a cost ratio of about 100:1. Furthermore, if the worldwide consumption of dyed cotton were coloured with natural vegetable dyes rather than synthetic ones, approximately 30% of the world's agricultural land would be needed for the cultivation [125,127]. This is more than 13 times the area currently in use to grow the cotton and does not take into account what would be required if the other textile fibres, paper and leather were also to be coloured in the same way.

The extraction of natural dyes from animal sources is just as wasteful of resources, time-consuming and by no means environmentally friendly. To obtain 1 kg of cochineal scarlet requires the harvesting of 150 000 insects reared on cactus plants. The living insects are swept off the leaves into bowls or cloths and executed by immersion in steam or hot water, then dried by long exposure to sunlight. If production of the classical dye Tyrian purple were to be restored on a large scale, isolation of only 1 kg of this colorant would demand the slaughter of about 10 million specimens of a Mediterranean mollusc (*Murex brandaris* – now rare). Vast quantities of these discarded shells that develop an obnoxious odour when exposed to the sun would become unsightly spoilheaps, extremely offensive to the coastal environment [104,127].

REFERENCES

1. E A Clarke and D Steinle, *Rev. Prog. Coloration*, **25** (1995) 1.
2. P F Gordon and P Gregory, *Organic chemistry in colour*, (Berlin: Springer-Verlag, 1983).
3. P F Gordon and P Gregory, *Developments in the chemistry and technology of organic dyes*, Ed J Griffiths (Oxford: Blackwell Scientific Publications, 1984) 66.
4. H Zollinger, *Color chemistry* 2nd Edn, (Weinheim: VCH Publishers, 1991).
5. J Griffiths, *J.S.D.C.*, **104** (1988) 416.
6. *Colour chemistry: Design and synthesis of organic dyes and pigments*, Eds A T Peters and H S Freeman (Glasgow: Blackie, 1991).
7. *Modern colorants: Synthesis and structure*, Eds A T Peters and H S Freeman (Glasgow: Blackie, 1994).
8. G W Gray, *Chimia*, **34** (1980) 47.
9. M Okawara et al., *Organic colorants: A handbook of data of selected dyes for electro-optical applications*, (Oxford: Elsevier, 1988).
10. *Infrared absorbing dyes*, Ed M Matsuoka (New York: Plenum, 1990).

11. J T Guthrie, Macromolecular dyes in *Encyclopaedia of polymer science and engineering*, Vol 5 (1986) 277.
12. B C Burdett, *J.S.D.C.*, **98** (1982) 114.
13. P M Dinsdale, *J.S.D.C.*, **112** (1996) 38.
14. J W Slater, *Manual of colours and dyewares*, (London: 1870).
15. W R Richardson, *J.S.D.C.*, **1** (1885) 251.
16. *Colour Index International*, Pigments and solvent dyes Edn (Bradford: SDC 1998).
17. A Abel, *J Oil Colour Chem. Assoc.*, **81** (1998) 77.
18. H Wolfson, *J.S.D.C.*, **112** (1996) 347.
19. N Ward, private communication.
20. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985).
21. G Hallas and A H M Renfrew, *J.S.D.C.*, **112** (1996) 207.
22. J Shore, *Textilveredlung*, **12** (1986) 207.
23. C W Greenhalgh, J L Carey and D F Newton, *Dyes and Pigments*, **1** (1980) 103.
24. C W Greenhalgh *et al.*, *J.S.D.C.*, **110** (1994) 178.
25. D M Lewis, *Rev. Prog. Coloration*, **29** (1999) 23.
26. F H Moser and A L Thomas, *Phthalocyanine compounds*, (New York: Reinhold, 1963).
27. N Sekar, *Colourage*, **45** (Aug 1998) 47.
28. A Albert, *The acridines*, 2nd Edn. (London: Edward Arnold, 1967).
29   A H M Renfrew, *Rev. Prog. Coloration*, **15** (1985) 15.
30. J Griffiths, *Colour and constitution of organic molecules*, (London: Academic Press, 1976).
31. J Fabian and H Hartmann, *Light absorption of organic colorants*, (Berlin: Springer-Verlag, 1980).
32. J Griffiths, *Rev. Prog. Coloration*, **11** (1981) 37; **14** (1984) 21; Chem. Brit, **22** (1986) 997.
33. M Matsuoka, *J.S.D.C.*, **105** (1989) 167.
34. W Fabian, *Dyes and Pigments*, **6**, No 5 (1985) 341.
35. C Lubai *et al.*, *Dyes and Pigments*, **10**, No 2 (1989) 123.
36. J Griffiths, J Hill and B Fishwick, *Dyes and Pigments*, **15**, No 4 (1991) 307.
37. Y Kogo, *Dyes and Pigments*, **6**, No 1 (1985) 31.
38. G Hallas and R Marsden, *Dyes and Pigments*, **6**, No 6 (1985) 463.
39. C Lubai *et al.*, *Dyes and Pigments*, **7**, No 5 (1986) 373.
40. S Yasui, M Matsuoka and T Kitao, *Dyes and Pigments*, **11**, No 2 (1989) 81.
41. R M Christie and B G Freer, *Dyes and Pigments*, **24** (1994) 113, 259; **27** (1995) 35.
42. C Diaper, V M Correia and S J Judd, *J.S.D.C.*, **112** (1996) 273.
43. J J Porter, *Am. Dyestuff Rep.*, **22** (Jun 1990) 21.
44. J Shore, *Blends Dyeing*, (Bradford: SDC, 1998).
45. O Annen, *Melliand Textilber.*, **79** (1998) 752.
46. James Robinson Ltd., *J.S.D.C.*, **111** (1995) 172.
47. I D Rattee, *J.S.D.C.*, **85** (1969) 23.
48. I G Laing, *Rev. Prog. Coloration*, **21** (1991) 56.
49. J F Dawson, *Rev.Prog.Coloration*, **14** (1984) 90; *J.S.D.C.*, **99** (1983) 183; **107** (1991) 395.
50. C A Buckley, *Water Sci. Tech.*, **25** (1992) 203.
51. J J Porter and G A Goodman, *Desalination*, **49** (1984) 185.
52. H Zollinger, *J.S.D.C.*, **88** (1972) 447.
53. R Anliker, IFATCC Congress, Budapest (Jun 1981) lecture.
54. W C Tincher, *Text. Chem. Colorist*, **21** (1989) 33.
55. K Eitel, E Rau and J Westphal, *Rev. Prog. Coloration*, **14** (1984) 119.
56. A G Puntener, *J. Soc. Leather Tech. Chem.*, **82** (1998) 1.
57. H Gardere, *J. Amer. Leather Chem. Assoc.*, **93** (1998) 215.
58. J Berenguer, M Dien and J Rocas, *J. Soc. Leather Tech. Chem.*, **82** (1998) 154.
59. *Developments in food colours*, Ed.J Walford (London: Elsevier) Vol 1 (1980) Vol 2 (1984).
60. A J Hinton, *Rev. Prog. Coloration*, **18** (1988) 1.
61. N Sekar, *Colourage*, **45** (Oct 1998) 55.
62. R Anliker and P Moser, *Ecotox. Environ. Safety*, **13** (1987) 43.
63. J Shore, *Dyer*, **167** (Jun 1982) 28.
64. M R Fox, *Dyemakers of Great Britain 1856–1976*, (Manchester: ICI, 1987).
65. D M Lewis, *J.S.D.C.*, **105** (1989) 119.
66. R H Horning, *Text. Chem. Colorist*, **18** (Jan 1986) 17.
67. R Anliker and D Steinle, *J.S.D.C.*, **104** (1988) 377.
68. E A Clarke, *J.S.D.C.*, **114** (1998) 348.
69. J A LoMenzo, Risk assessment's role in dye safety, Proc. AATCC Symp., (Mar 1984) 18.
70. H Motschi and E A Clarke, *Rev. Prog. Coloration*, **28** (1998) 71.
71. J Park and J Shore, *Rev. Prog.Coloration*, **12** (1982) 1.

72. B J McCarthy and B C Burdett, *Rev. Prog. Coloration*, **28** (1998) 61.
73. F Klaschka, *Melliand Textilber.*, **75** (1994) 193.
74. K L Hatch, *Text. Chem. Colorist*, **30** (Mar 1998) 22.
75. V A Shenai, *Colourage*, **45** (Oct/Nov 1998) 62.
76. J M Wattie, *J.S.D.C.*, **103** (1987) 304.
77. *Clinical and immunological investigations of respiratory disease in workers using reactive dyes* (London: HSE, Aug 1986).
78. E A Clarke and R Anliker, *The handbook of environmental chemistry*, Vol 3A, Ed O Hutzinger (Berlin: Springer-Verlag, 1980) 181.
79. E A Clarke and R Anliker, *Rev. Prog. Coloration*, **14** (1984) 84.
80. R Anliker in *Toxic hazard assessment of chemicals*, Ed M L Richardson (London: Royal Society of Chemistry, 1986) 116.
81. V A Shenai, *Toxicity of dyes and intermediates*, (Bombay: Mirachem Industries, 1996).
82. R Anliker *et al.*, *J.S.D.C.*, **104** (1988) 223.
83. J H Duffus, *Cancer and workplace chemicals*, (Leeds: H & H Scientific Consultants, 1995).
84. P Gregory, *Dyes and Pigments*, **7**, No 1 (1986) 45.
85. K Hunger, *Chimia*, **48** (1994) 520.
86. C E Searle, *Chem. Brit.*, **22** (1986) 211.
87. Carcinogenic Substances Regulations 1967 (London: HMSO, 1967).
88. J H Pierce, *J.S.D.C.*, **110** (1994) 131.
89. W Beckmann and U Sewekow, *Textil Praxis*, **46** (1991) 346.
90. P Cooper, *J.S.D.C.*, **109** (1993) 97.
91. *Colour in dyehouse effluent*, Ed P Cooper (Bradford: SDC, 1995).
92. *Environmental chemistry of dyes and pigments*, Eds A Reife and H S Freeman (New York: Wiley-Interscience, 1996)
93. F Moriarty, *Chem. Ind.*, (1986) 737.
94. J Park and J Shore, *J.S.D.C.*, **100** (1984) 383.
95. H R Hitz, W Huber and R H Reed, *J.S.D.C.*, **94** (1978) 71.
96. A J Greaves, D A S Phillips and J A Taylor, *J.S.D.C.*, **115** (1999) 363.
97. K Wührmann, K Mechsner and T Kappeler, *Eur. J. Appl. Microbiol. Biotechnol.*, **9** (1980) 325.
98. V A Shenai, *Colourage*, **44** (Dec 1997) 41.
99. D Brown and P Laboureur, *Chemosphere*, **12** (1983) 405.
100. D Brown and B Hamburger, *Chemosphere*, **16** (1987) 1539.
101. V G Yadav, *Colourage*, **45** (Jan 1998) 53.
102. P A Turner, *J.S.D.C.*, **111** (1995) 53.
103. K T W Alexander, *J.S.D.C.*, **112** (1996) 341.
104. B C Burdett, *Dyer*, **180** (Sep 1995) 16.
105. ETAD, *J.S.D.C.*, **111** (1995) 97.
106. K Hübner, E Schmelz and V Rossbach, *Melliand Textilber.*, **78** (1997) 720.
107. C T Page and J Fennen, *J. Soc. Leather Tech. Chem.*, **82 (1998) 75.**
108. W B Achwal, *Colourage*, **44** (May 1997) 29.
109. F Planelles et al, *J. Soc. Leather Tech. Chem.*, **82** (1998) 45.
110. B M Müller, *Rev. Prog. Coloration*, **22** (1992) 14.
111. W D Kermer, *Melliand Textilber.*, **69** (1988) 586.
112. G M P Morrison, G E Batley and T M Florence, *Chem. Ind.*, (1989) 791.
113. W D Kermer and I Steenken-Richter, *Melliand Textilber.*, **76** (1995) 433.
114. U Sewakow, *Text. Chem. Colorist*, **28** (1996) 21.
115. S I Ali, *J.S.D.C.*, **109** (1993) 13.
116. P M Chan, C W M Yuan and K W Yeung, *Text. Asia*, **29** (May 1998) 59.
117. M Ryder, *Wool Record*, **157** (May 1998) 41.
118. Eco-Fab, *Colourage*, **45** (May 1998) 79.
119. K D Casselman, *Wool Record*, **157** (Oct 1998) 57.
120. P M Chan, C W M Yuan and K W Yeung, *Text. Asia*, **28** (Oct 1997) 58.
121. H T Deo and B K Desai, *J.S.D.C.*, **115** (1999) 224
122. G Dalby, *J.S.D.C.*, **109** (1993) 9.
123. U Sewekow, *Melliand Textilber.*, **76** (1995) 330.
124. H Bürger, *Melliand Textilber.*, **76** (1995) 910.
125. B Glover, *J.S.D.C.*, **114** (1998) 4.
126. V A Shenai, *Colourage*, **45** (Jan 1998) 19.
127. B Glover and J H Pierce, *J.S.D.C.*, **109** (1993) 5.
128. B Glover, *Text. Chem. Colorist*, **27** (Apr 1995) 17.
129. W B Achwal, *Colourage*, **45** (Jan 1998) 45.