CHAPTER 6

Chemistry of anthraquinonoid, polycyclic and miscellaneous colorants

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6.1 ANTHRAQUINONE ACID, DISPERSE, BASIC AND REACTIVE DYES

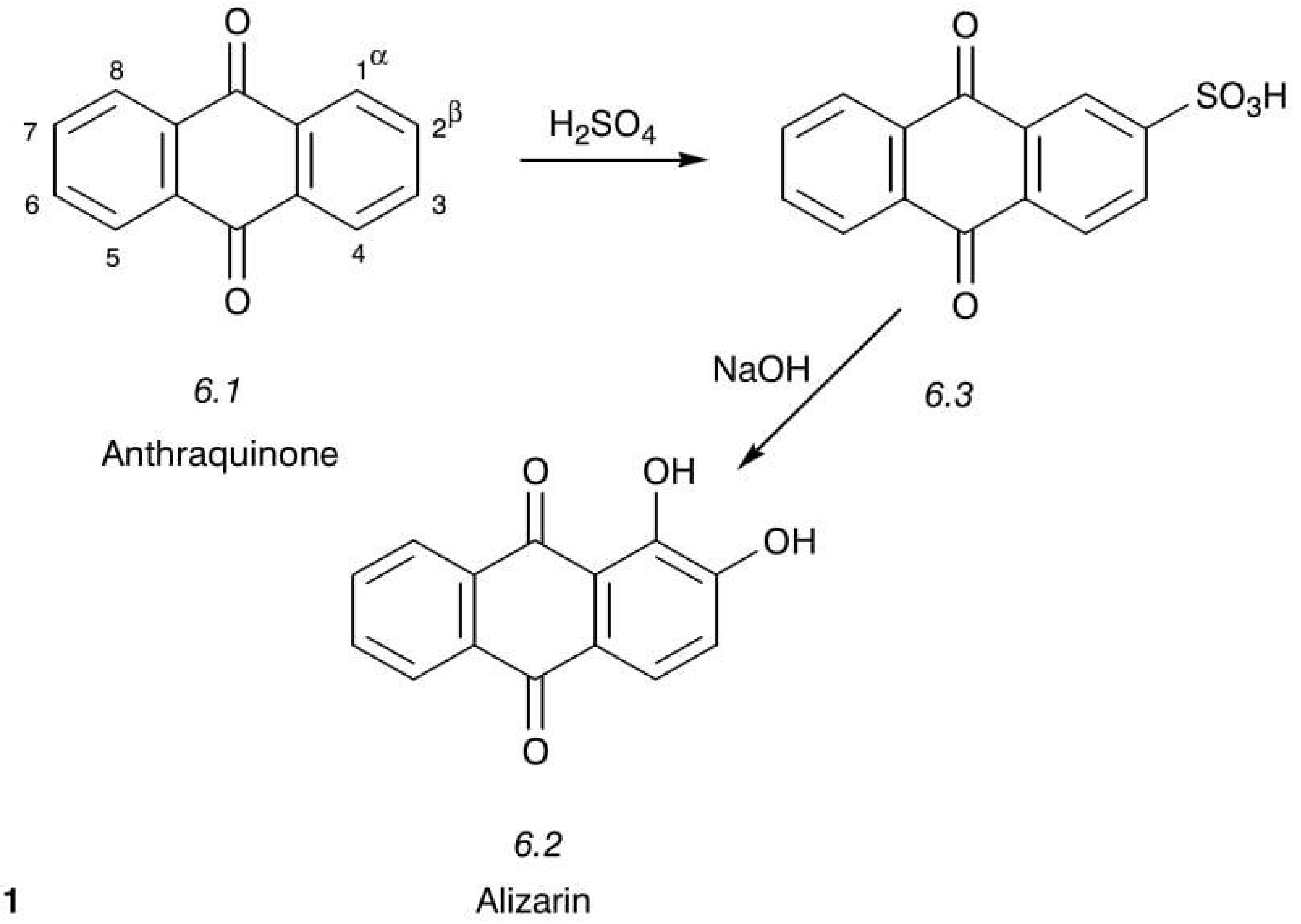
It was pointed out in Chapter 1 that, after the azo class, anthraquinone derivatives form the next most important group of organic colorants listed in the *Colour Index*. The major application groups are vat dyes, disperse dyes and acid dyes (Table 1.1).

Of the various anthracenedione isomers, only the 9,10-compound is used for the synthesis of dyes; it is usually referred to simply as anthraquinone (6.1). The parent compound is pale yellow in colour, having a weak absorption band in the visible region ($n \rightarrow \pi^*$ transition). The presence of one or more electron-donating substituents leads to significant bathochromic effects so that relatively simple derivatives are of commercial importance as dyes. The colour of such compounds, which usually contain amino or hydroxy groups, can be attributed to the existence of a charge-transfer absorption band [1].

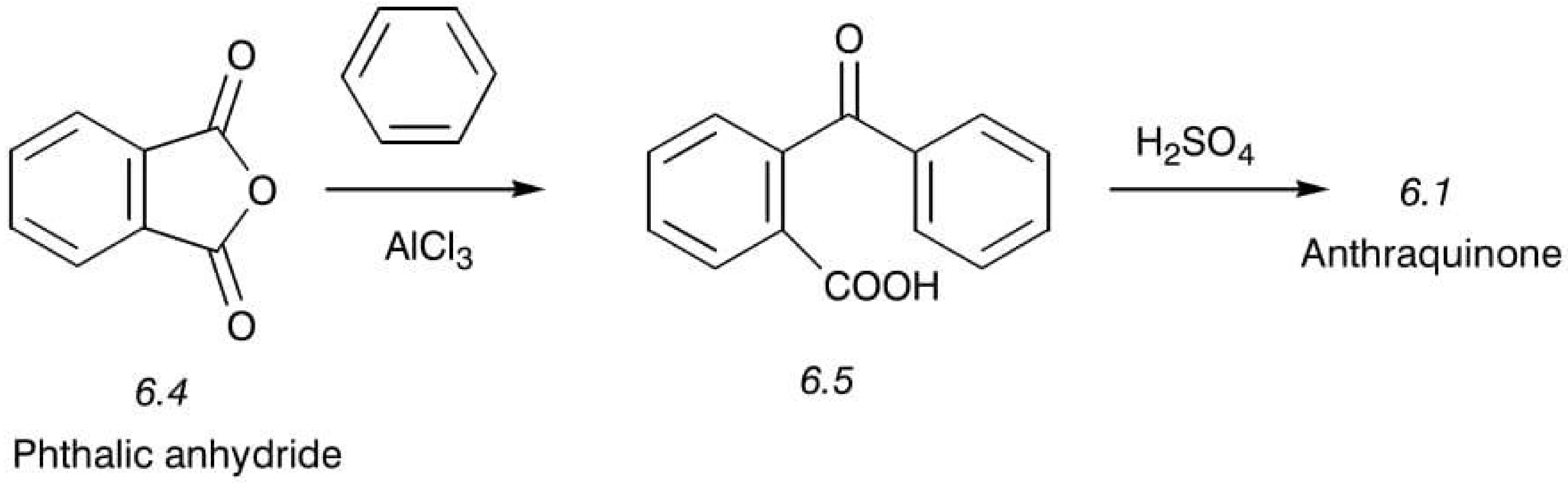
From a historical viewpoint, the advent of synthetic anthraquinone dyes can be traced to the elucidation of the structure of the important naturally occurring compound 1,2-dihydroxyanthraquinone (6.2; alizarin) by Graebe and Liebermann in 1868 [2]. Natural alizarin is the colouring matter of madder and was the source of the then valuable mordant dye Turkey red (CI Mordant Red 11), an aluminium–calcium complex. In the following year Caro and Perkin independently discovered a commercially viable route to alizarin from anthraquinone via the 2-sulphonic acid (6.3) Treatment of the sodium salt of anthraquinone-2-sulphonic acid (called 'silver salt', from its appearance) with aqueous sodium hydroxide under pressure at an elevated temperature in the presence of an oxidising agent gives the disodium salt of alizarin as the main product (Scheme 6.1). Perkin soon devised a more efficient and cheaper route that involved chlorination of anthracene to give 9,10-dichloroanthracene, which was then sulphonated, oxidised and fused with sodium hydroxide to yield alizarin [3].

6.1.1 Methods of synthesis

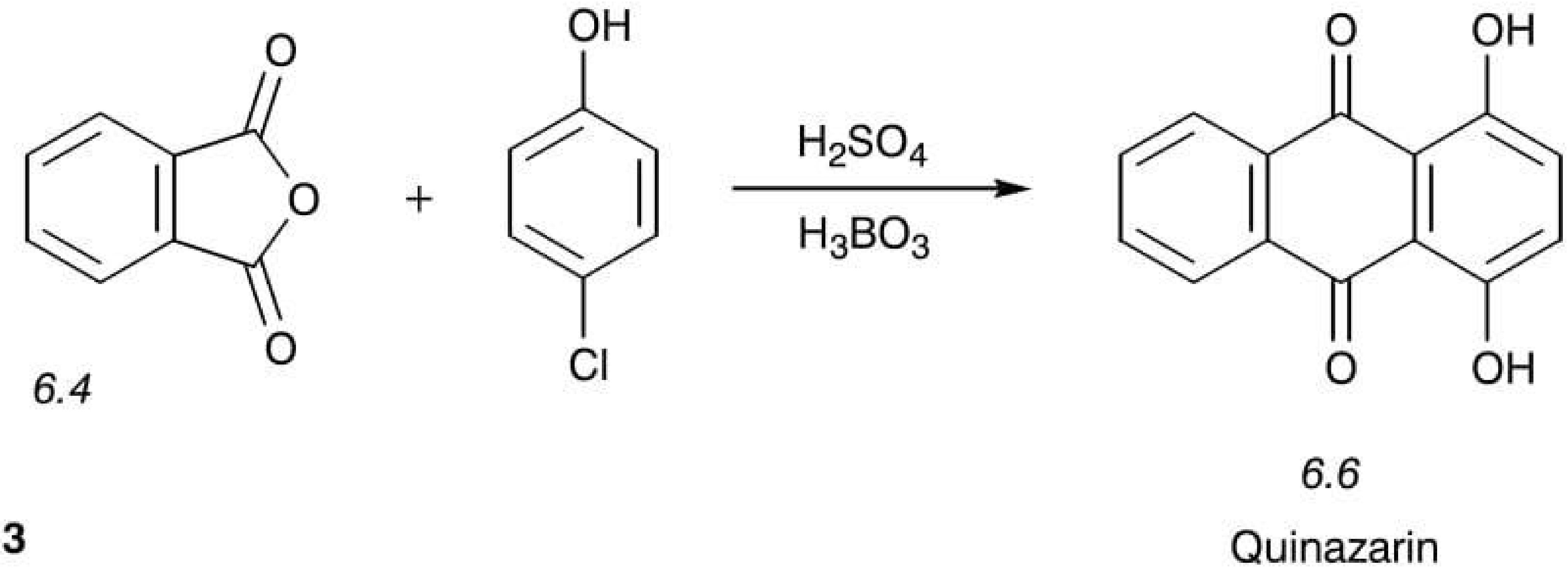
Anthraquinone itself is traditionally available from the anthracene of coal tar by oxidation, often with chromic acid or nitric acid; a more modern alternative method is that of air oxidation using vanadium(V) oxide as catalyst. Anthraquinone is also produced in the reaction of benzene with benzene-1,2-dicarboxylic anhydride (6.4; phthalic anhydride) using a Lewis acid catalyst, typically aluminium chloride. This Friedel–Crafts acylation gives *o*-benzoylbenzoic acid (6.5) which undergoes cyclodehydration when heated in concentrated sulphuric acid (Scheme 6.2). Phthalic anhydride is readily available from naphthalene or from 1,2-dimethylbenzene (*o*-xylene) by catalytic air oxidation.



Scheme 6.1



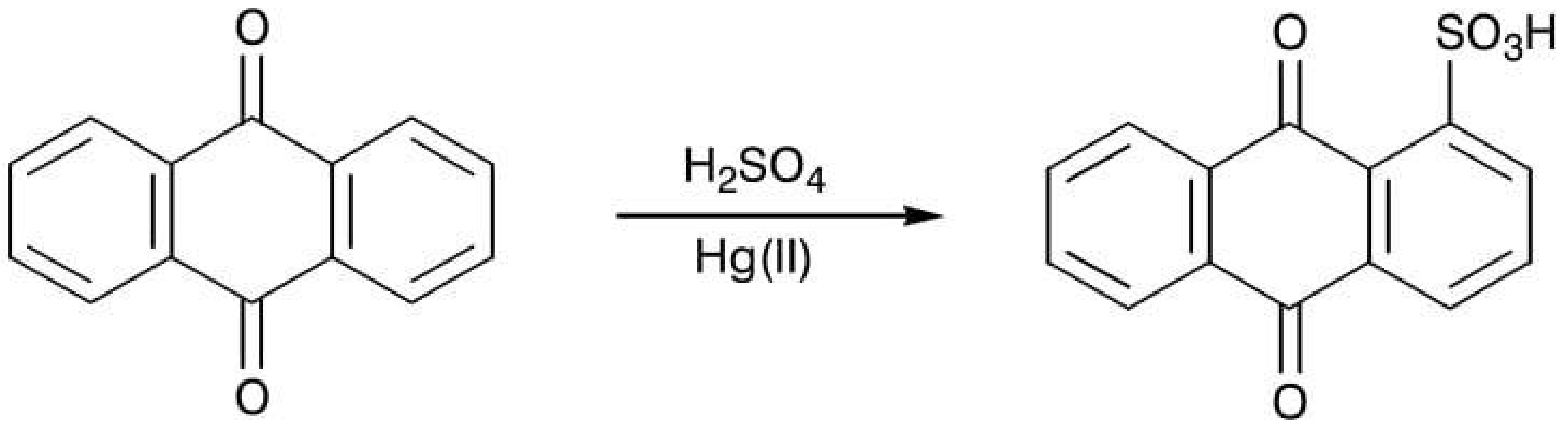
Scheme 6.2



Scheme 6.3

Although anthraquinone is the starting point for the preparation of many derivatives, involving substitution and replacement reactions, certain compounds are obtained directly by varying the components in the above synthesis. Thus, for example, replacement of benzene with methylbenzene (toluene) leads to the formation of 2-methylanthraquinone. A particularly important variation on the phthalic anhydride route is the synthesis of 1,4-dihydroxyanthraquinone (6.6; quinizarin) using 4-chlorophenol with sulphuric acid and boric acid as catalyst (Scheme 6.3). The absence of aluminium chloride permits hydrolysis of the chloro substituent to take place.

Electrophilic substitution at the anthraquinone ring system is difficult due to deactivation (electron withdrawal) by the carbonyl groups. Although the 1-position in anthraquinone is rather more susceptible to electrophilic attack than is the 2-position, as indicated by π-electron localisation energies [4], direct sulphonation with oleum produces the 2-sulphonic acid (6.3). The severity of the reaction conditions ensures that the thermodynamically favoured 2-isomer, which is not subject to steric hindrance from an adjacent carbonyl group, is formed. However, the more synthetically useful 1-isomer (6.7) can be obtained by sulphonation of anthraquinone in the presence of a mercury(II) salt (Scheme 6.4). It appears that mercuration first takes place at the 1-position followed by displacement. Some disulphonation occurs, leading to the formation of the 2,6- and 2,7- or the 1,5- and 1,8-disulphonic acids, respectively. Separation of the various compounds can be achieved without too much difficulty. Sulphonation of anthraquinone derivatives is also of some importance.

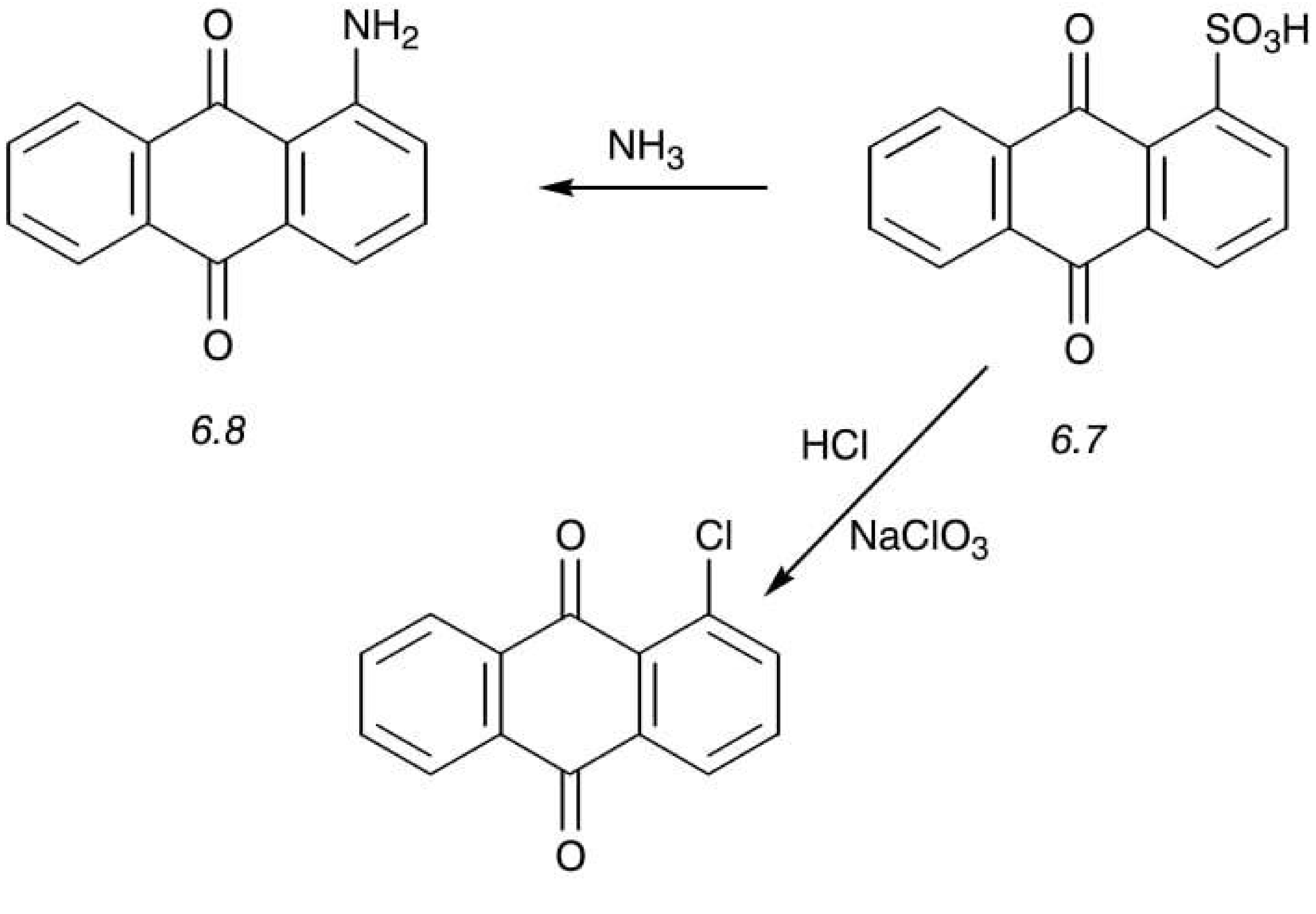


6.1 *6.7*

Scheme 6.4

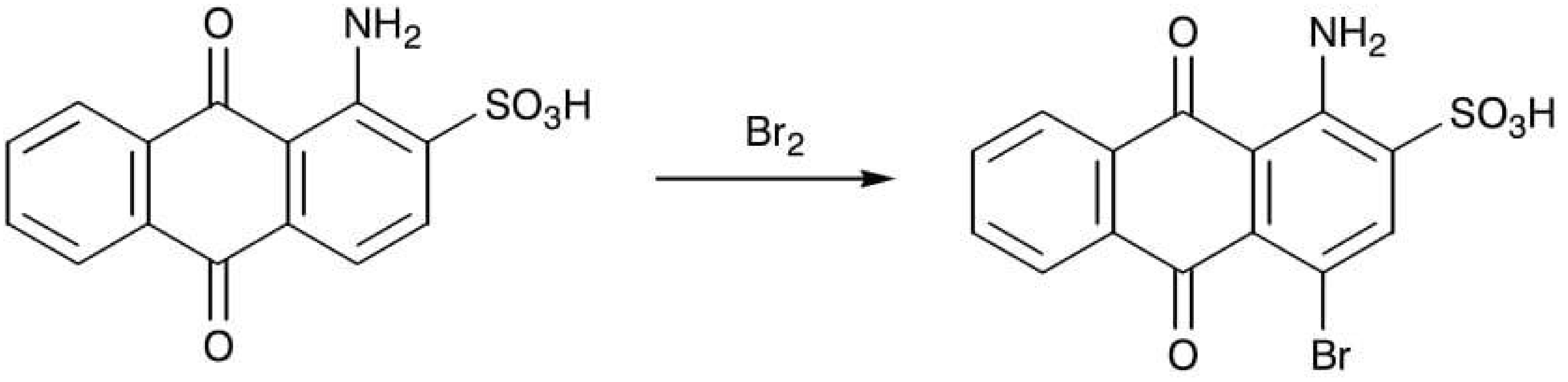
Anthraquinone-1-sulphonic acid is the traditional precursor of 1-aminoanthraquinone (6.8), the most important anthraquinone intermediate. Since it is expensive to eliminate mercury(II) ions from waste water, an alternative route via 1-nitroanthraquinone has been investigated. Nitration of anthraquinone gives, as well as the desired 1-nitro derivative, significant amounts of the 2-isomer together with 1,5- and 1,8-dinitroanthraquinones. Nevertheless, chemists at Sumitomo in Japan have optimised the nitration procedure with respect to both yield and purity of the 1-nitro compound. In particular, nitration is stopped when 80% of the anthraquinone has been substituted [5]. Nitration of anthraquinone derivatives is also of some significance.

Direct halogenation is normally carried out only on derivatives of anthraquinone. The importance of chloro or bromo derivatives lies mainly in the displacement of the halogen by nucleophiles, especially amines. Simple derivatives, such as 1-chloroanthraquinone (6.9), are available from the appropriate sulphonic acid by replacement (Scheme 6.5). 1-Amino-4-bromoanthraquinone-2-sulphonic acid (6.10; bromamine acid) is a very useful intermediate in the synthesis of dyes derived from 1,4-diaminoanthraquinone. Bromamine acid is obtained from 1-aminoanthraquinone (6.8) by sulphonation to give the 2-sulphonic acid (6.11), which is then brominated (Scheme 6.6). Direct bromination of 1-aminoanthraquinone affords the 2,4-dibromo derivative. Hydroxyanthraquinones are also susceptible to halogenation. In the case of alizarin (6.2), for example, the 1-hydroxy group is involved in intramolecular hydrogen bonding with the adjacent carbonyl group so that bromination takes place at the 3-position (6.12), which is both *ortho* to the 2-hydroxy group and *meta* to the other carbonyl group (Scheme 6.7).



6.8 6.7 6.9

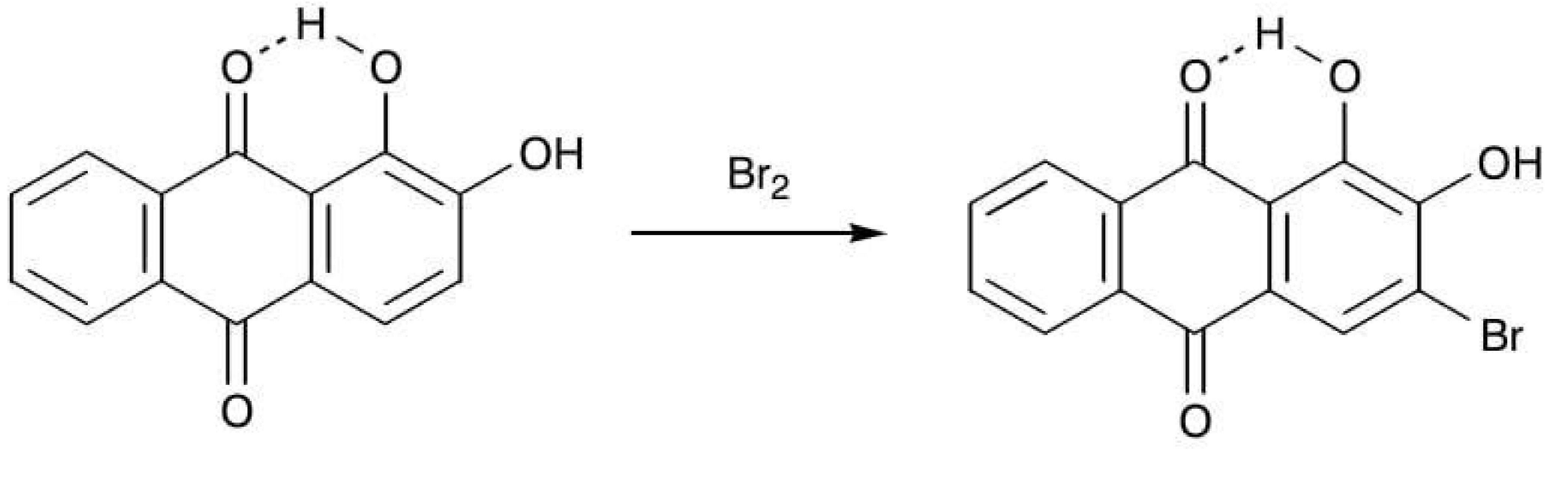
Scheme 6.5



6.11

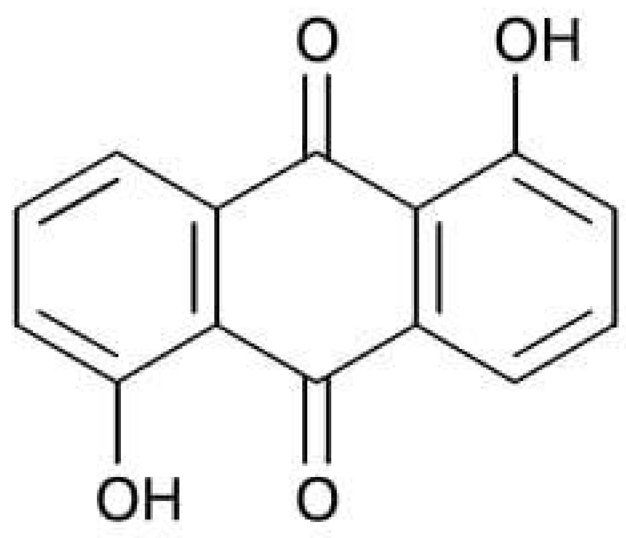
6.10
Bromamine acid

Scheme 6.6



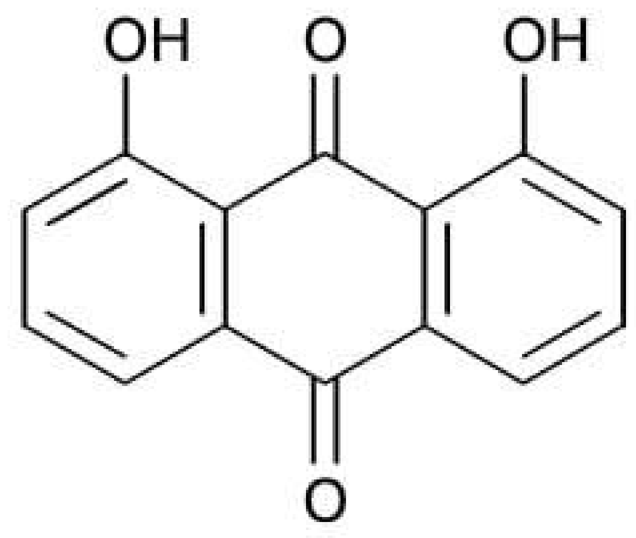
Scheme 6.7 6.2 6.12

Although some hydroxyanthraquinones, such as quinizarin (6.6), are available by direct synthesis, most hydroxy derivatives are produced by nucleophilic displacement of sulphonic acid groups or halogen atoms. Thus 1,5-dihydroxyanthraquinone (6.13; anthrarufin) and the 1,8-isomer (6.14; chrysazin) are obtained by alkaline hydrolysis of the corresponding disulphonic acids using calcium hydroxide or dilute sodium hydroxide. Under such relatively mild conditions additional hydroxy groups are not introduced. In the case of anthraquinone-2-sulphonic acid (6.3), as pointed out earlier, hydroxylation as well as displacement can take place to produce alizarin (6.2). From a mechanistic point of view it seems likely that the reaction first involves hydroxylation to produce a hydroquinone (6.15), which is then oxidised to 1-hydroxyanthraquinone-2-sulphonic acid (6.16) before nucleophilic displacement of the sulphonic acid group takes place (Scheme 6.8).



6.13

Anthrarufin



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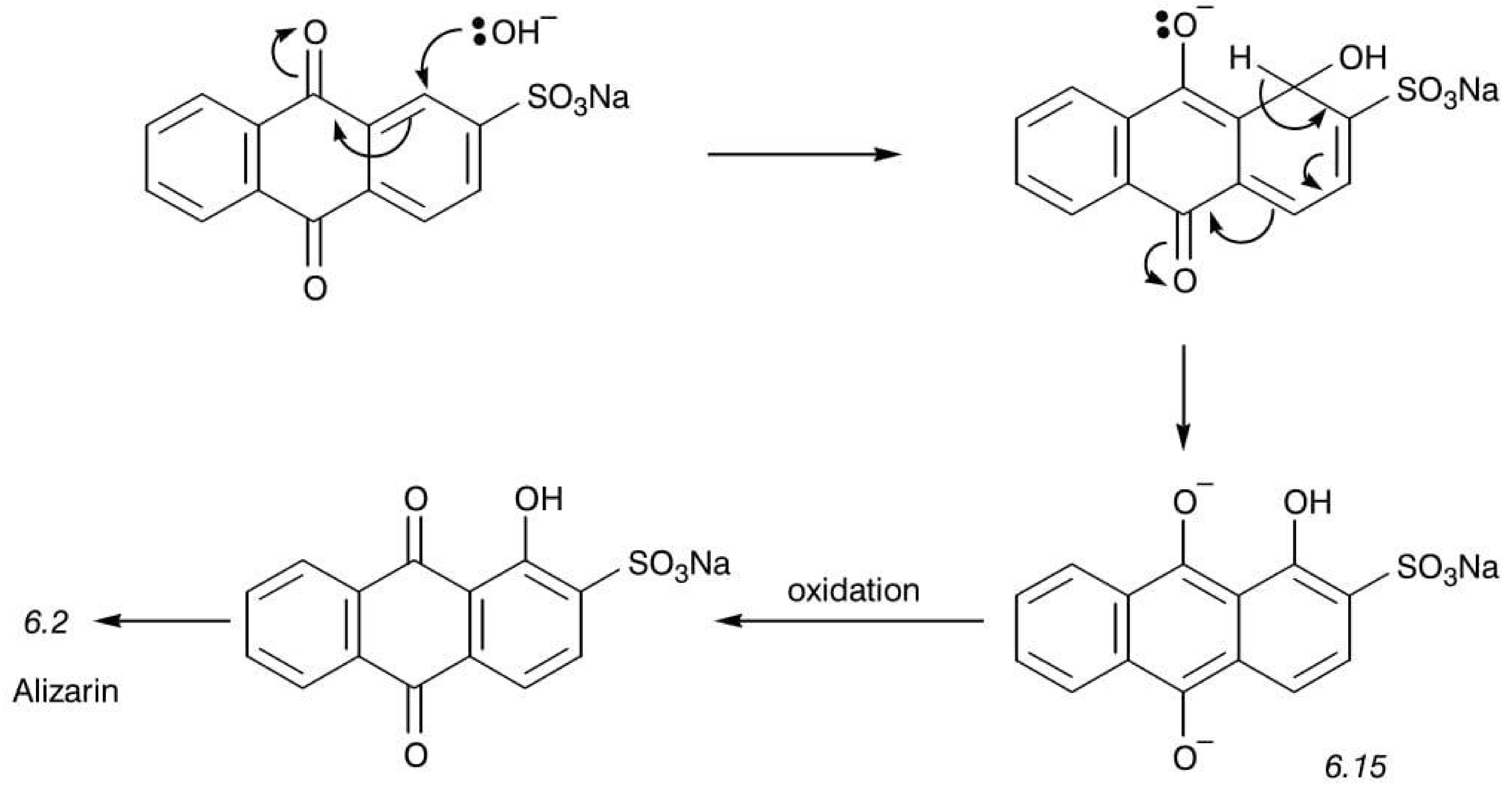
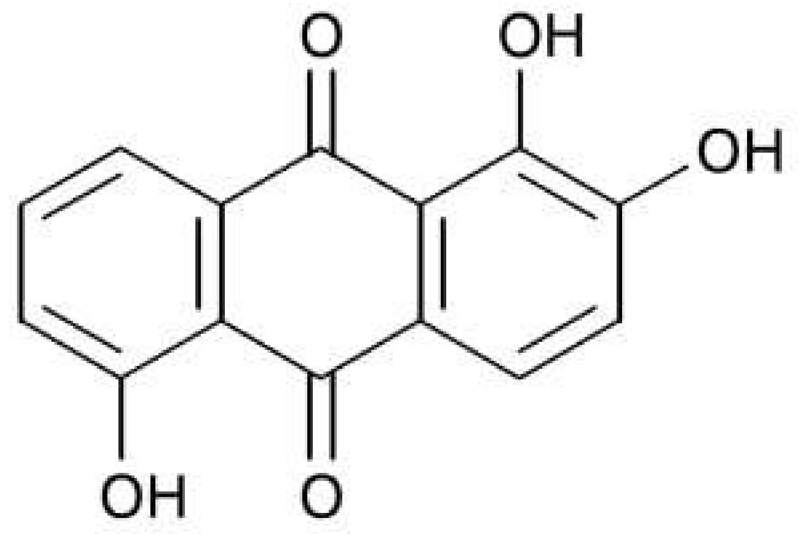
Chrysazin



Scheme 6.8

Polyhydroxyanthraquinone derivatives can be obtained by means of the Bohn–Schmidt reaction, in which hydroxyanthraquinones containing at least one α-hydroxy group react with fuming sulphuric acid; thus, for example, alizarin can be converted into 1,2,5-trihydroxyanthraquinone (6.17). The presence of boric acid leads to the formation of mixed anhydrides with sulphuric acid and to cyclic intermediates. The substitution mechanisms are complex but it has been established [6] that sulphur trioxide can interact with the 1-hydroxy group and the adjacent carbonyl group to form esters containing six-membered rings, exemplified by structure 6.18. The sulphuric acid esters are readily hydrolysed to hydroxy compounds during work-up. Sulphonation and subsequent desulphonation can also take place. The Bohn–Schmidt procedure is also applicable to aminoanthraquinones. Thus 1,4-diaminoanthraquinone (6.19) can be converted into 1,4-diamino-5,8-dihydroxyanthraquinone (6.20).

Nucleophilic displacement of halogen by amines is an important method of introducing amino groups into the anthraquinone ring system. In the Ullmann reaction the displacement is catalysed by metallic copper or by copper ions so that relatively mild conditions can be used. Mechanistic studies suggest that copper(I) ions exert a catalytic effect via complex formation. Derivatives of 1,4-diaminoanthraquinone are of considerable industrial significance. Many compounds are prepared from the reduced form of quinizarin (6.6).



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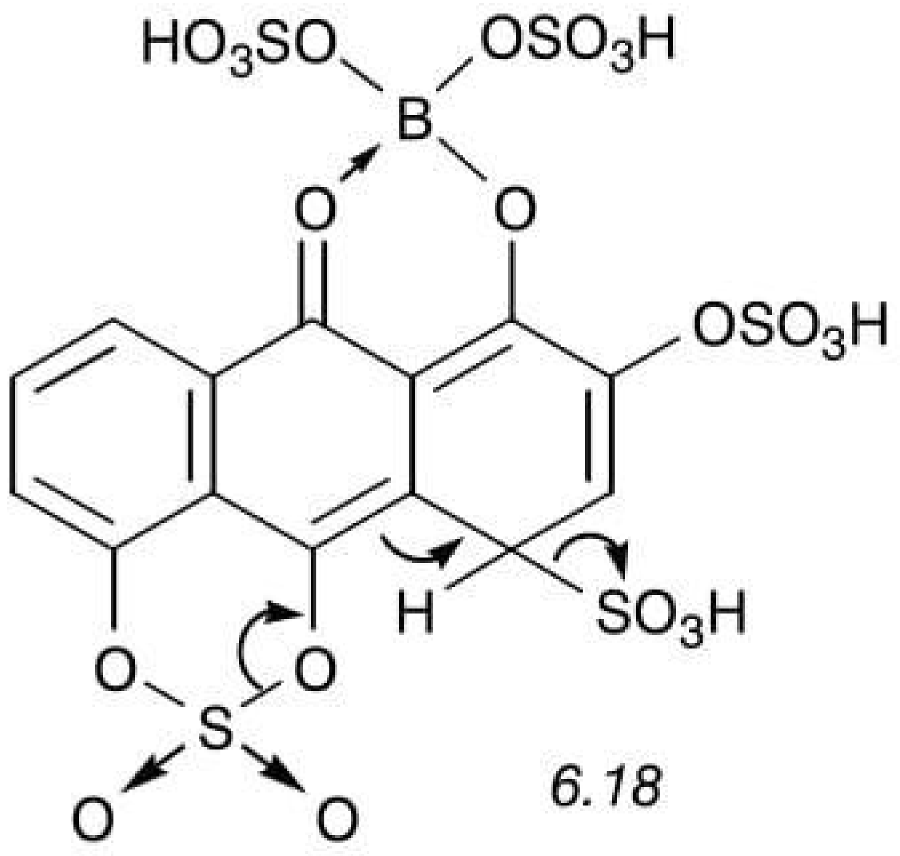

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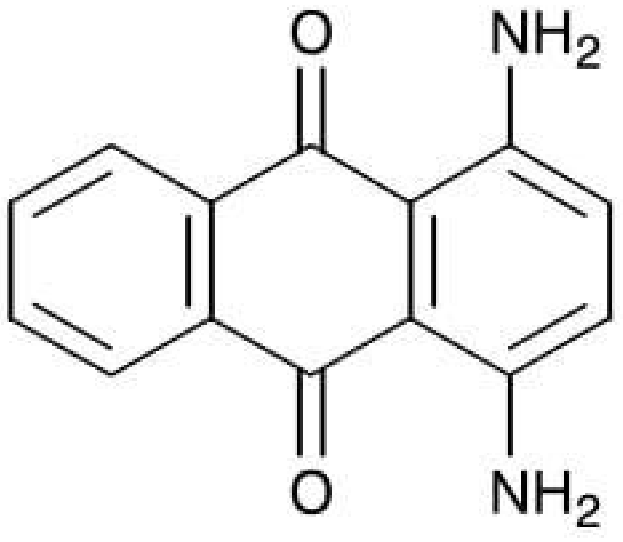
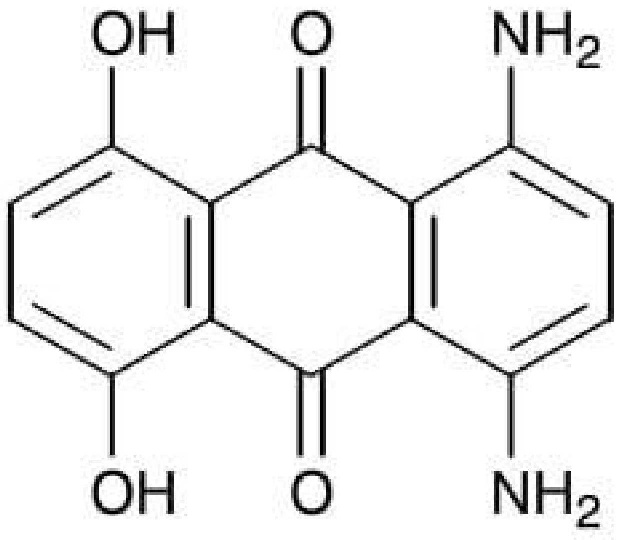


6.19

CI Disperse Violet 1



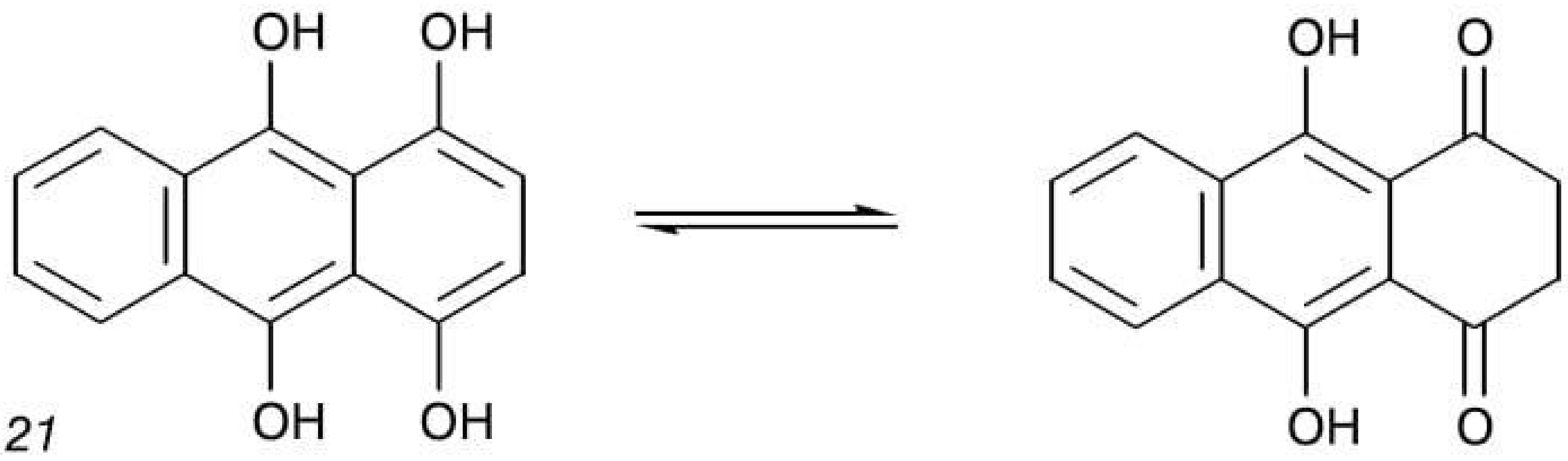
6.20

Leucoquinizarin can be represented by various tautomers such as structures 6.21 and 6.22; however, ^1H- and ^{13}C-n.m.r. have shown the dominant species to be the 2,3-dihydro tautomer (6.22) [7]. Alkylamines react with leucoquinizarin in a stepwise manner to give the corresponding 1,4-dialkylamino derivative (6.23) after air oxidation (Scheme 6.9). The less nucleophilic arylamines do not react unless boric acid is present as a catalyst. The complex thus formed (6.24) is more susceptible to nucleophilic attack at the 1- and 4-positions than is leucoquinizarin. Unsymmetrical 1,4-diaminoanthraquinones can be synthesised by using two different amines; the corresponding symmetrical dyes are also formed to a certain extent.

6.1.2 Acid, disperse, basic and reactive dyes

Anthraquinone dyes tend to predominate in the violet, blue and green hue sectors. Although they have the advantages of brightness and chemical stability, they are more expensive to manufacture than are azo dyes, which are also tinctorially stronger.

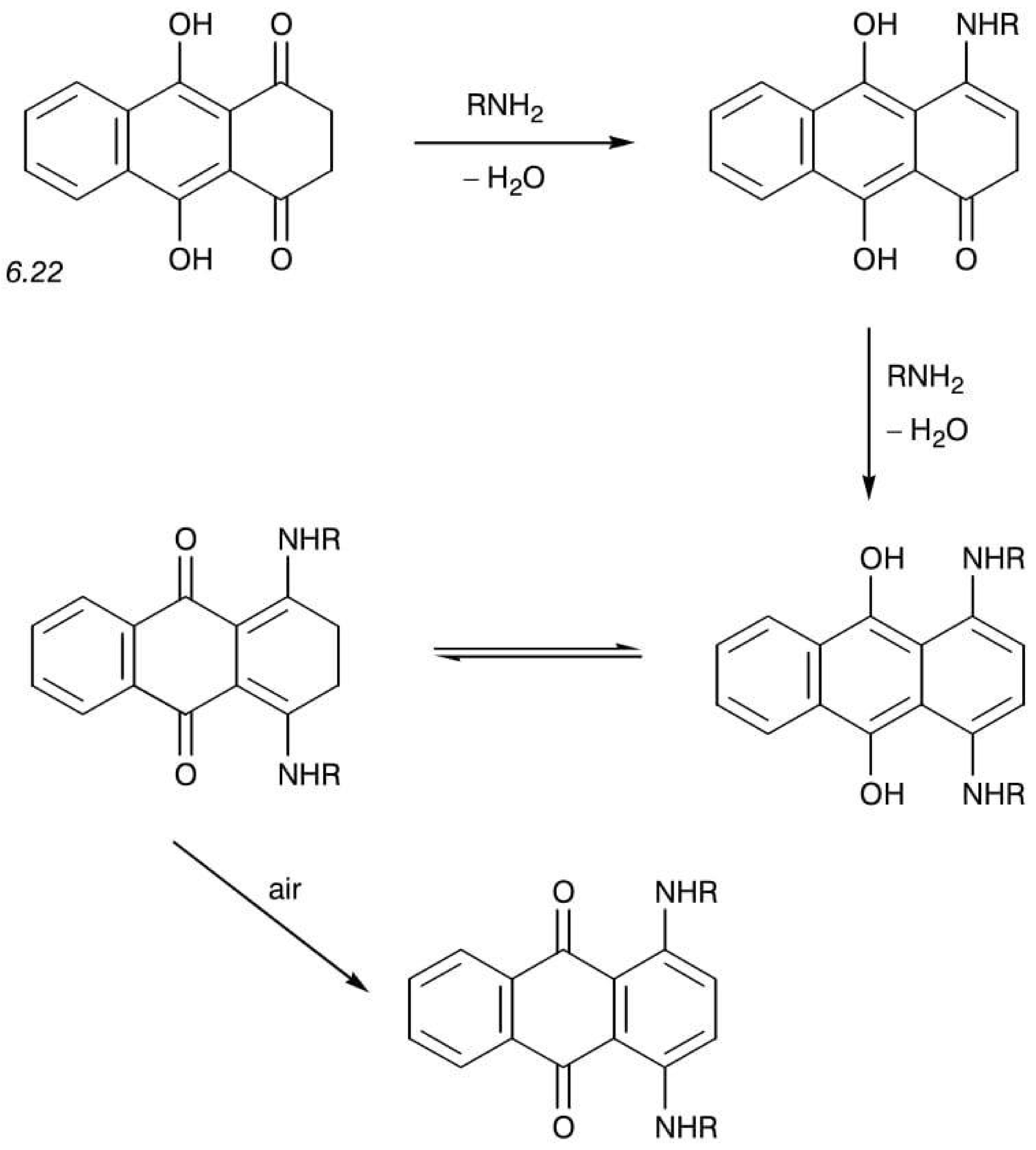
In general, 1-substituted derivatives of anthraquinone are more bathochromic than the corresponding 2-substituted isomers, in accordance with PPP-MO calculations [1]. Intramolecular hydrogen bonding is not possible between the carbonyl group and a 2-



6.21

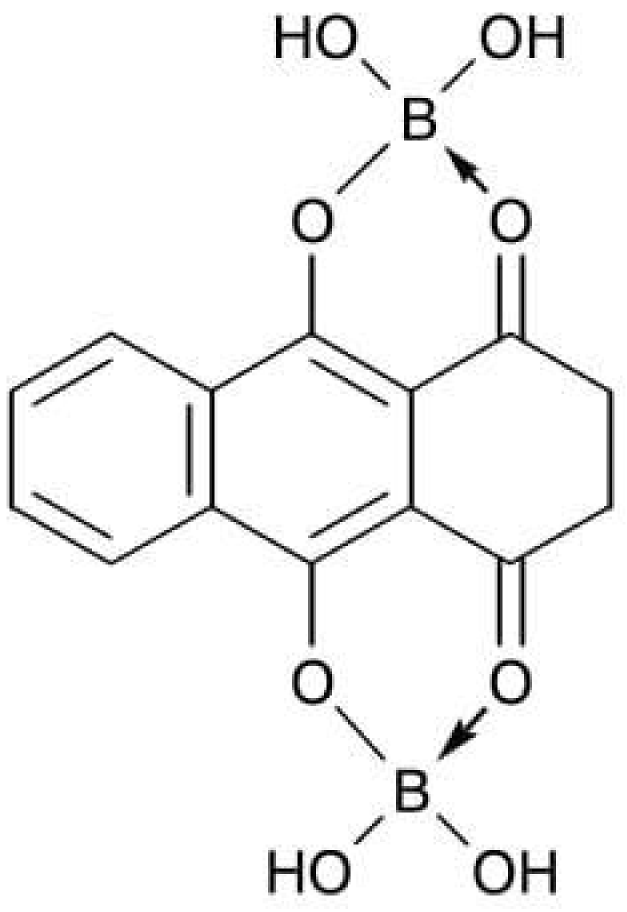
6.22

Leucoquinizarin



Scheme 6.9

6.23



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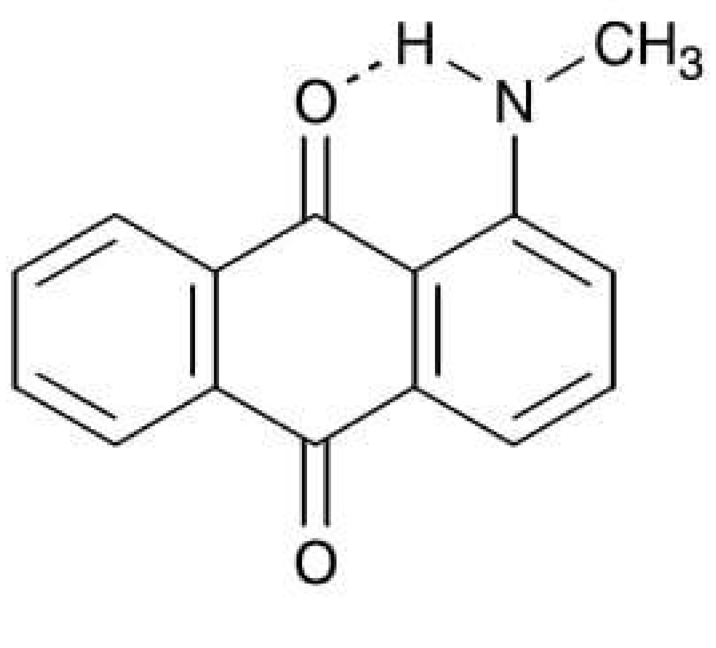
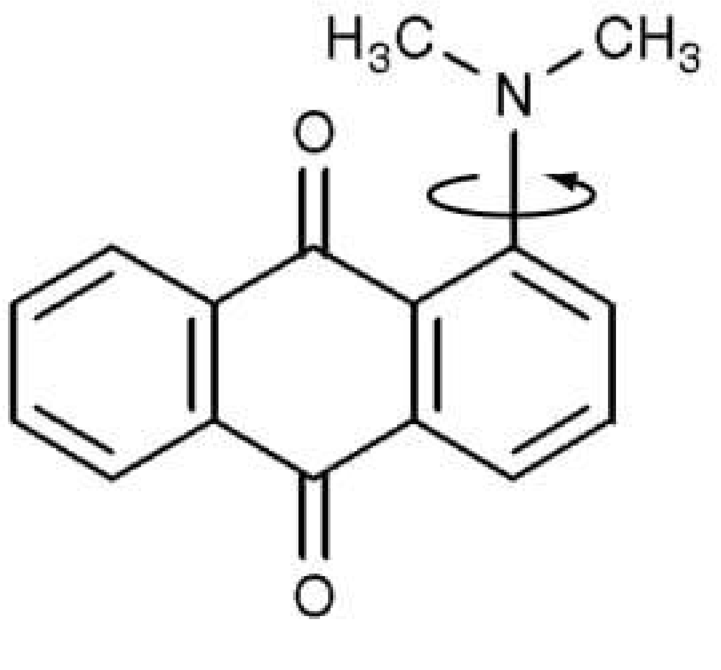


6.25



6.26

substituent and, in the 2-substituted series, the bathochromic shift increases with electron-donor power in the sequence: OH < OCH_3 < $NHCOCH_3$ < NH_2 < $NHCH_3$ < $N(CH_3)_2$. An enhanced bathochromic effect is observed when a 1-substituent, such as hydroxy or methylamino (6.25), is able to hydrogen-bond with the adjacent carbonyl group and thereby assist the conjugation of the donor lone pair of electrons with the anthraquinone ring system; for example, a methylamino group is a more effective donor than is a dimethylamino group in the 1-substituted series. Moreover, the latter group is unable to conjugate fully due to steric hindrance between the bulky substituent and the adjacent carbonyl group, which decreases the bathochromic effect and reduces the tinctorial strength (intensity). Steric interaction is minimised by rotation of the dimethylamino group out of the plane of the anthraquinone ring system (6.26). Some illustrative spectral data are given in Table 6.1 [8]. Significant crowding effects can also arise from the presence of *ortho* groups, as in 1,2-disubstituted anthraquinones.

Table 6.1 Spectral data for some monosubstituted anthraquinones in methanol [8]

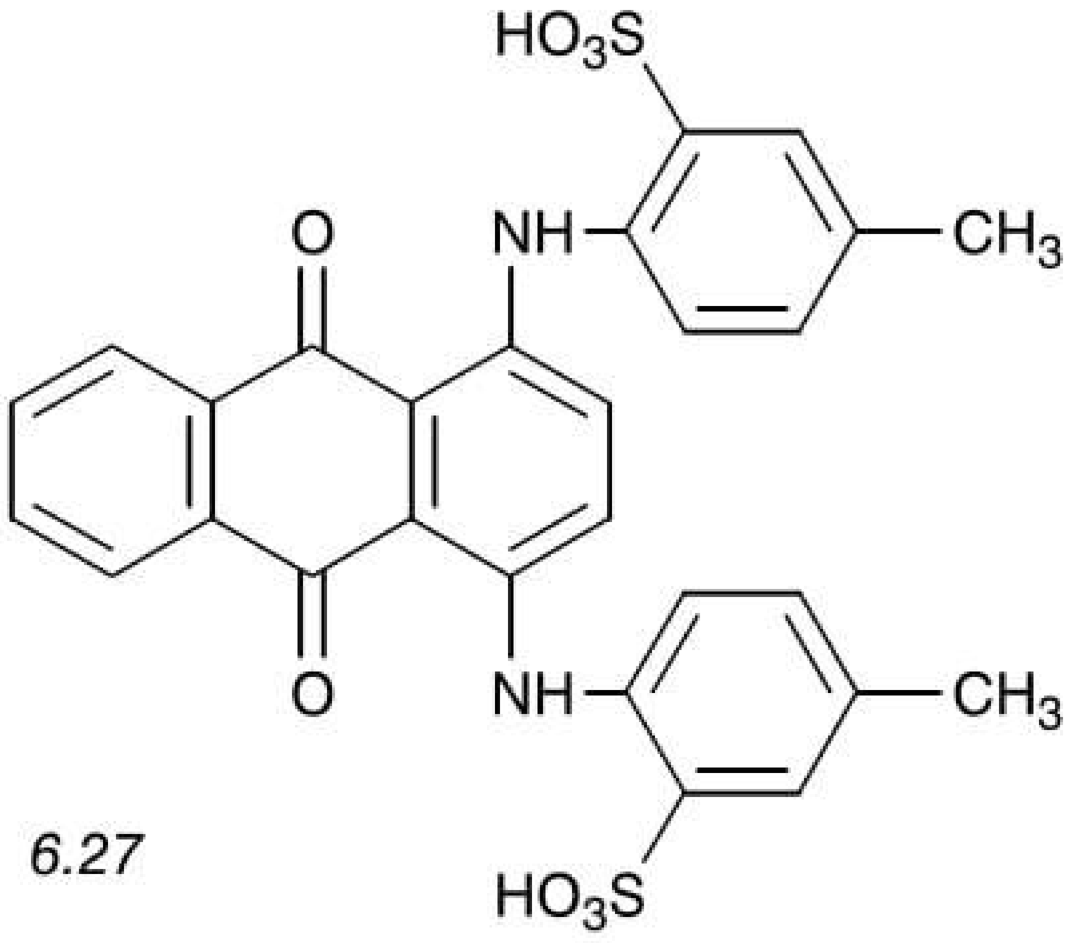
	1-position		2-position	
Substituent	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
OH	402	5500	368	3900
OCH_3	378	5200	363	3950
$NHCOCH_3$	400	5600	367	4200
NH_2	475	6300	440	4500
$NHCH_3$	503	7100	462	5700
NHC_6H_5	500	7250	467	7100
$N(CH_3)_2$	503	4900	472	5900

Table 6.2 Spectral data for some disubstituted anthraquinones in methanol [8]

Substituents	λ_{max} (nm)	ε_{max}
1,4-diOH	470	17 000
1,5-diOH	425	10 000
1,8-diOH	430	10 960
1,4-diNH_2	550, 590	15 850, 15 850
1,5-diNH_2	487	12 600
1,8-diNH_2	507	10 000

Anthraquinone itself can be regarded approximately as consisting of two *ortho*-interlinked benzoyl groups [9]. Thus, the introduction of a second group into the unsubstituted ring of a monosubstituted anthraquinone effectively doubles the extinction coefficient (compare ε_{max} values for α-hydroxy and α-amino substitution in Tables 6.1 and 6.2). However, the presence of two donor groups in the 1,4-positions gives rise to a pronounced increase in intensity, together with a significant bathochromic shift (Table 6.2) [8]. These enhanced effects have been widely exploited in commercial dyes. The order of bathochromicity for amino-substituted anthraquinones is: $2 < 1 < 1,5 < 1,8 < 1,2 < 1,4 < 1,4,5,8$. This sequence can be explained by VB theory [9] as well as by PPP-MO calculations [1], but only the latter approach can account for variations in tinctorial strength. The twin absorption peaks of 1,4-diaminoanthraquinones are thought to be caused by vibrational fine structure associated with one electronic transition in the visible region. 1,4-Bis(alkylamino)-anthraquinones are generally blue. The introduction of arylamino substituents into the 1,4-

positions gives rise to an additional absorption band in the 400 nm region that imparts a yellow component to the dominant blue colour. A good example is CI Acid Green 25 (6.27), which in aqueous solution absorbs at 410, 608 and 646 nm [10].

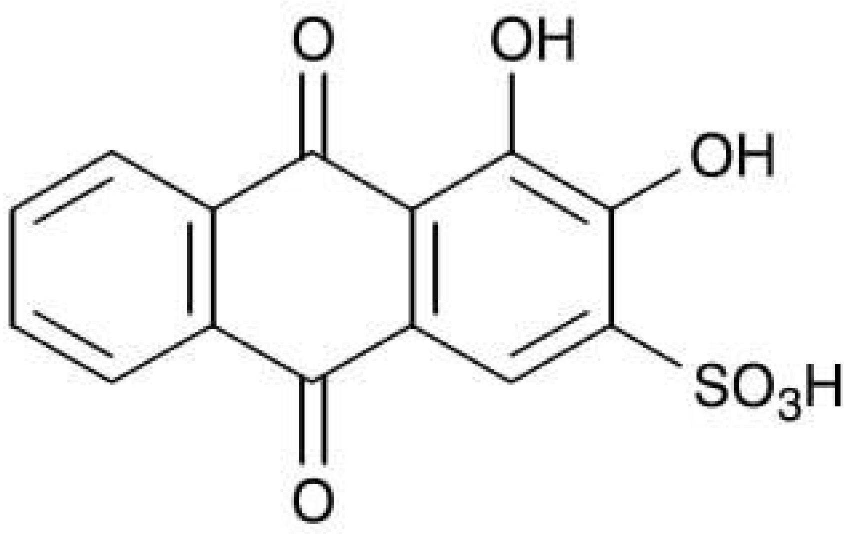


6.27

CI Acid Green 25

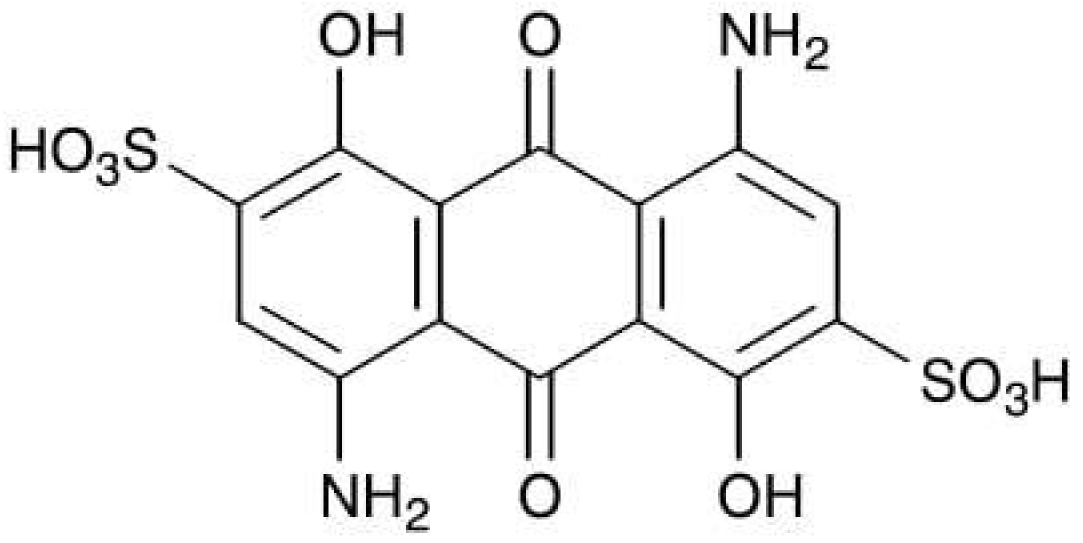
Acid dyes

In 1871 Graebe and Liebermann discovered that alizarin (6.2) could be applied to wool by mordant dyeing after sulphonation to produce the 3-sulphonic acid (6.28). This dye is still listed in the latest revision of the *Colour Index* as a commercial product [11]. Although many sulphonated polyhydroxyanthraquinones have been examined, few remain in current use. Another, and more important, classic dye that continues in commercial use as an acid dye is CI Acid Blue 45 (6.29). This dye was discovered in 1897 by Schmidt and can be made from anthrarufin (6.13) by disulphonation, subsequent dinitration and reduction. The dye gives an attractive blue on wool with good all-round fastness properties.



6.28

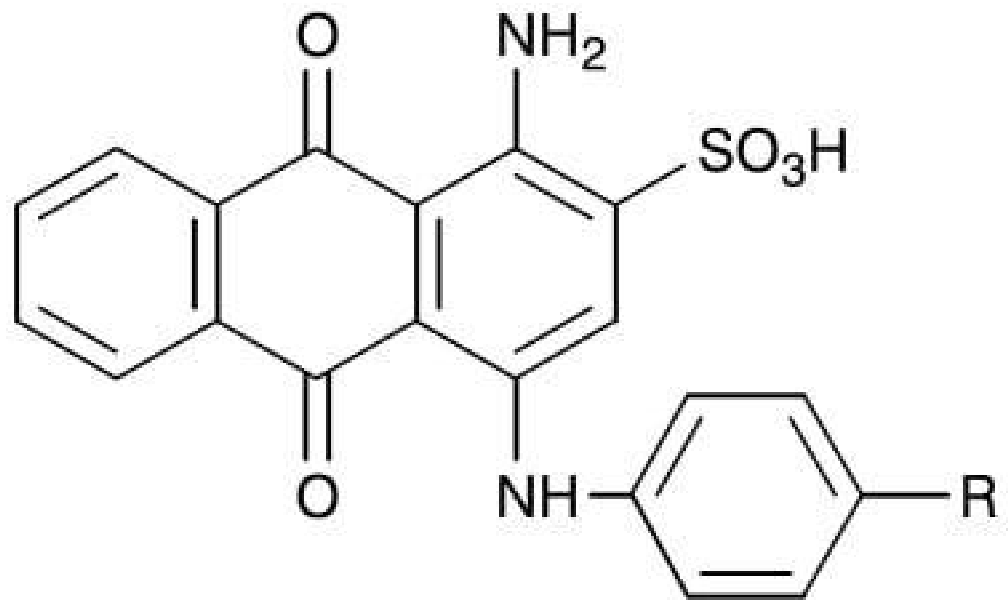
CI Mordant Red 3



6.29

CI Acid Blue 45

Many blue acid dyes have been derived from bromamine acid (6.10) by nucleophilic displacement of the halogen atom using arylamines of varying complexity in the presence of a copper catalyst. Simple examples include CI Acid Blue 25 (6.30; R = H) and the analogous cyclohexyl derivative CI Acid Blue 62 (6.31). Reaction with *p*-butylaniline gives CI Acid Blue 230 (6.30; R = butyl), which possesses good washing fastness owing to hydrophobic interaction with the substrate. Somewhat more complex structures are illustrated by CI Acid Blue 40 (6.32) and CI Acid Blue 129 (6.33). CI Acid Blue 40 is greener than the parent dye (6.30; R = H) due to the electronic effect of the acetylamino substituent.



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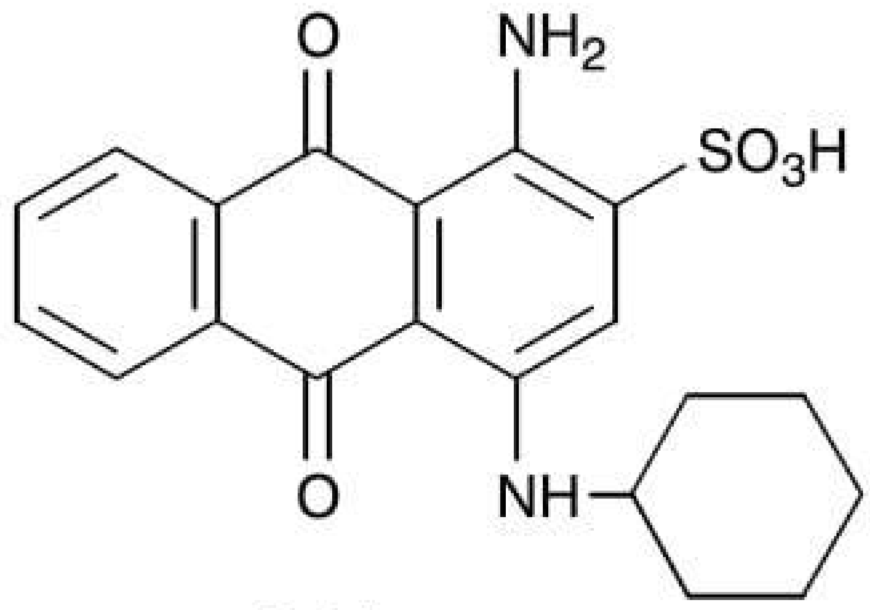
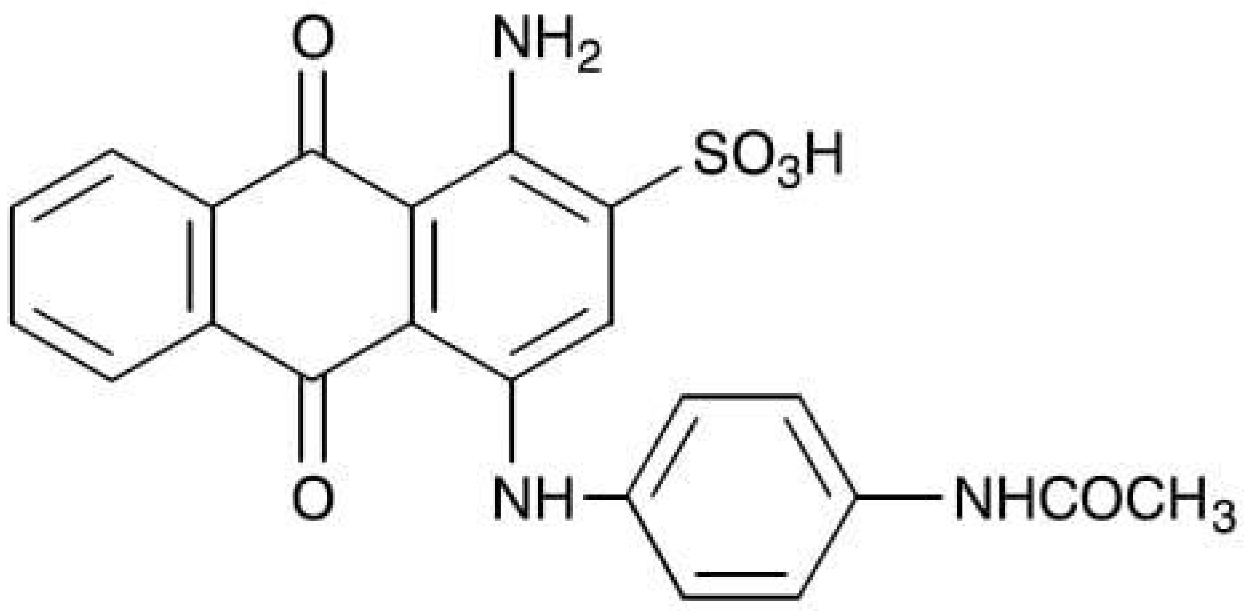


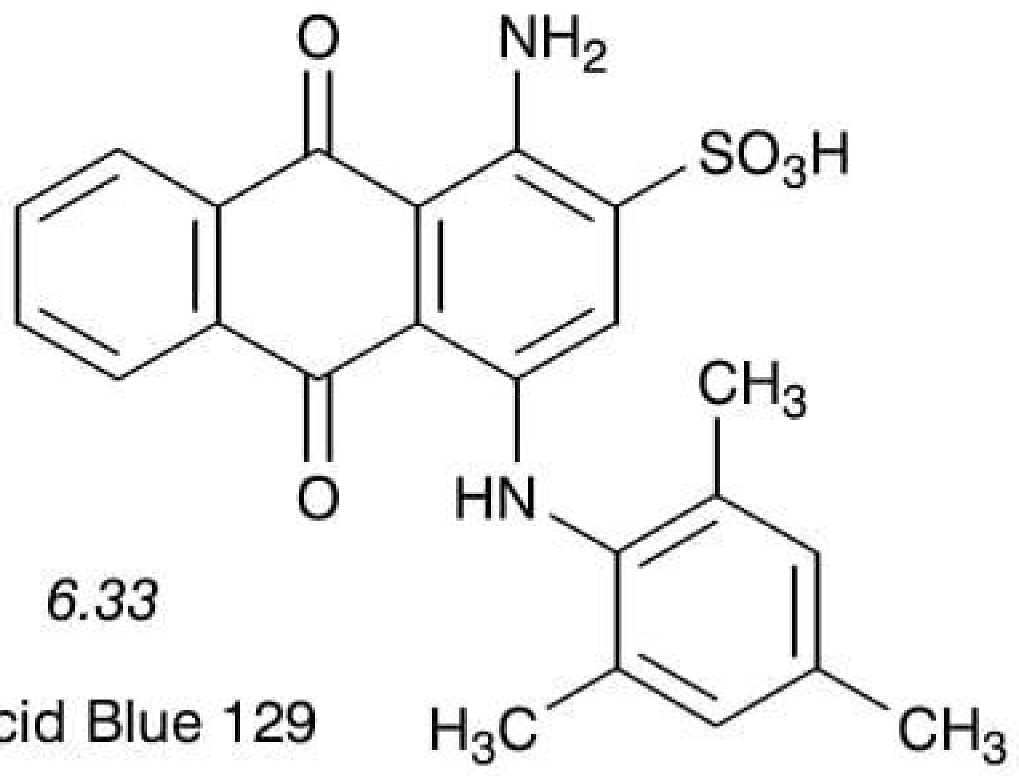
6.31

CI Acid Blue 62



6.32

CI Acid Blue 40

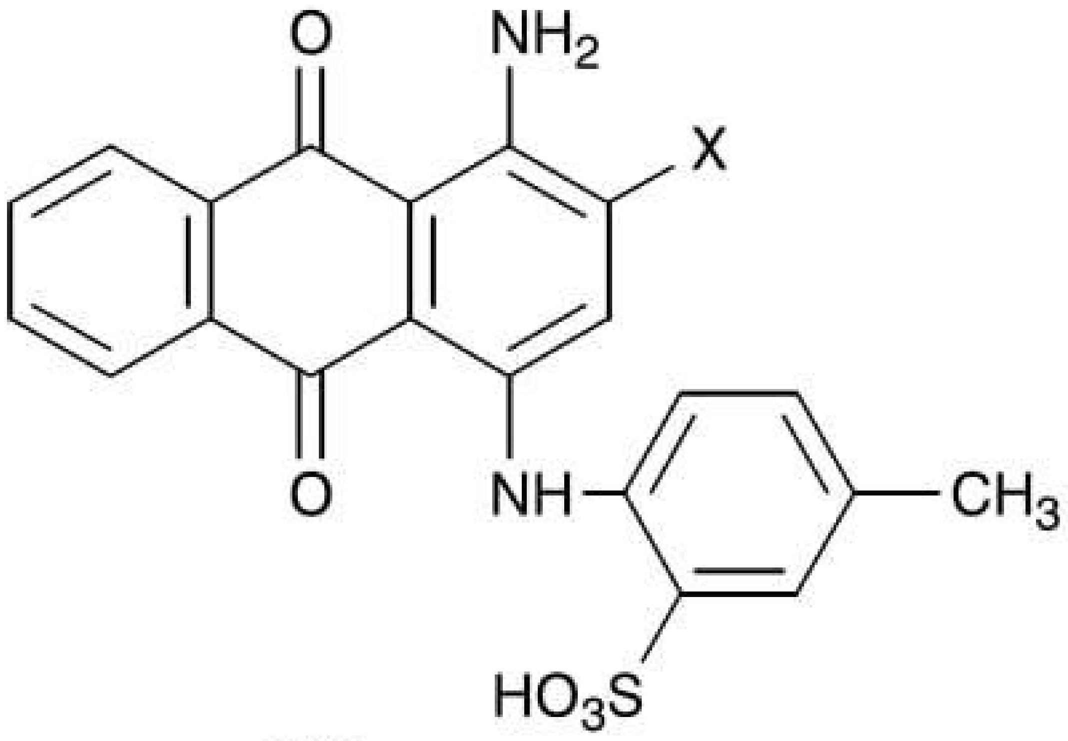


6.33

CI Acid Blue 129

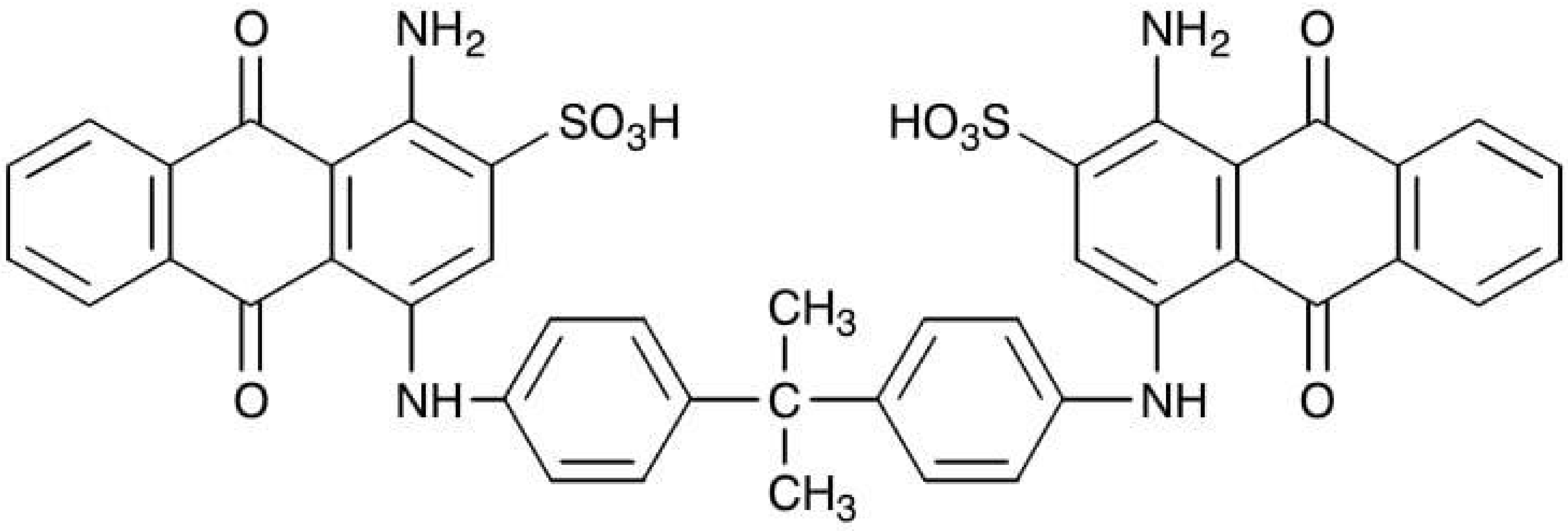
The progressive introduction of methyl groups into the pendant phenyl ring of CI Acid Blue 25 (6.30; R = H) leads to an increase in dye uptake and to improved wet fastness properties on wool [12]. Steric crowding in the case of CI Acid Blue 129 (6.33) reduces the conjugation of the 4-substituent with the remainder of the system and results in a reddish blue hue. The aliphatic cyclohexyl ring in CI Acid Blue 62 (6.31) has a similar effect on the hue.

Use of the intermediates 1-amino-2,4-dibromoanthraquinone and 1-amino-4-bromo-2-methylanthraquinone leads to similar dyes, exemplified by CI Acid Blue 78 (6.34; X = Br) and CI Acid Blue 47 (6.34; X = CH_3) respectively; in the production of these two dyes, sulphonation is the final step.



6.34

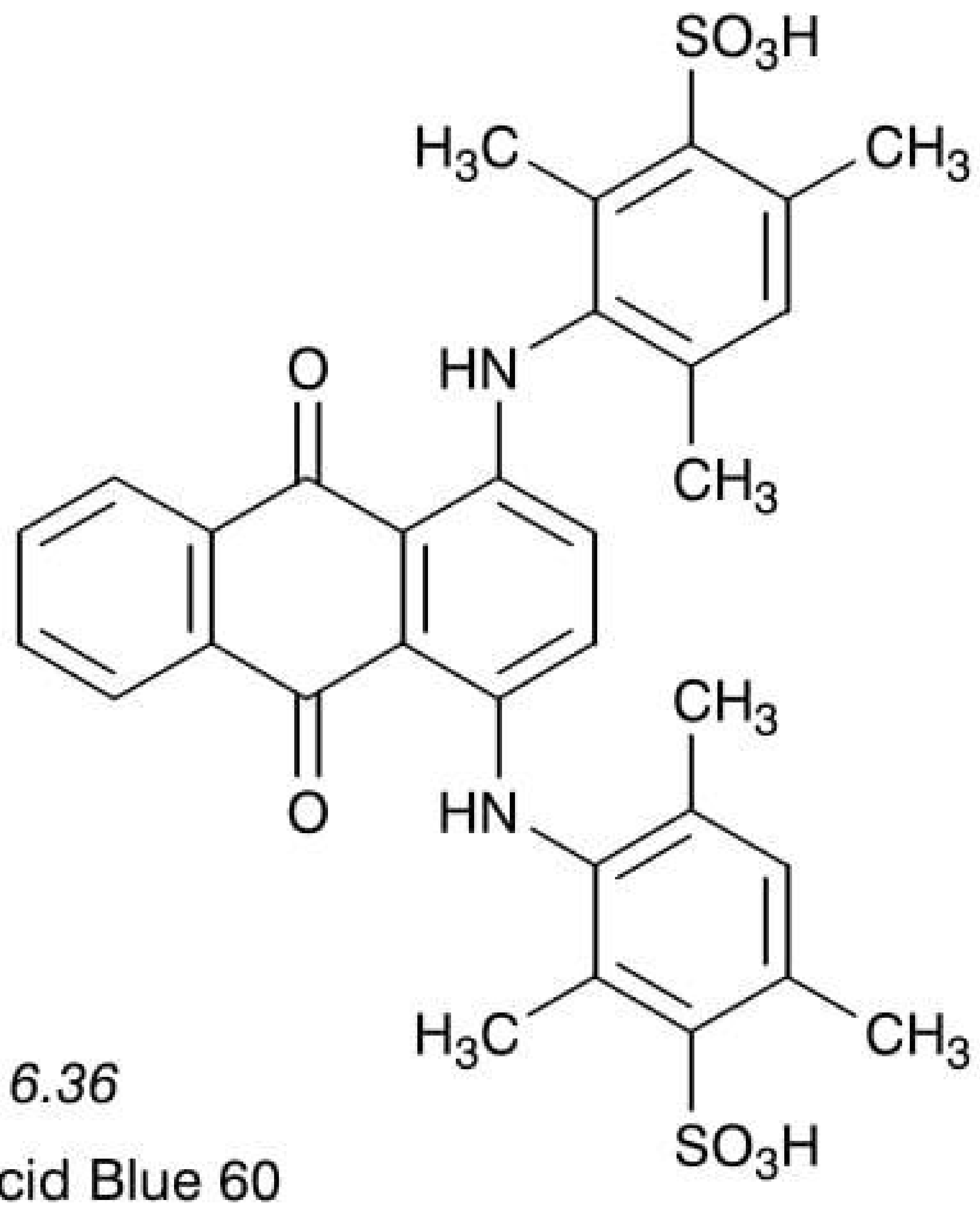
Milling dyes with very good wet fastness are obtained by the reaction of one mole of a diamine with two moles of bromamine acid, as in the case of CI Acid Blue 127 (6.35). This dye is suitable for dyeing wool bright blue from a neutral or weakly acid bath.



6.35

CI Acid Blue 127

Condensation of one mole of leucoquinizarin (6.22) with two moles of an arylamine in the presence of boric acid, followed by oxidation and sulphonation, is the route to some symmetrically substituted acid dyes; these are blue to green according to the structure of the amine. The classical, but still important, dye CI Acid Green 25 (6.27) has already been mentioned. A related dye of commercial significance is CI Acid Blue 80 (6.36), which can be obtained either from leucoquinizarin or from 1,4-dichloroanthraquinone. Unsymmetrically substituted 1,4-diaminoanthraquinone derivatives bearing only one sulphonic acid group are better for the level dyeing of nylon than are their disulphonated analogues.



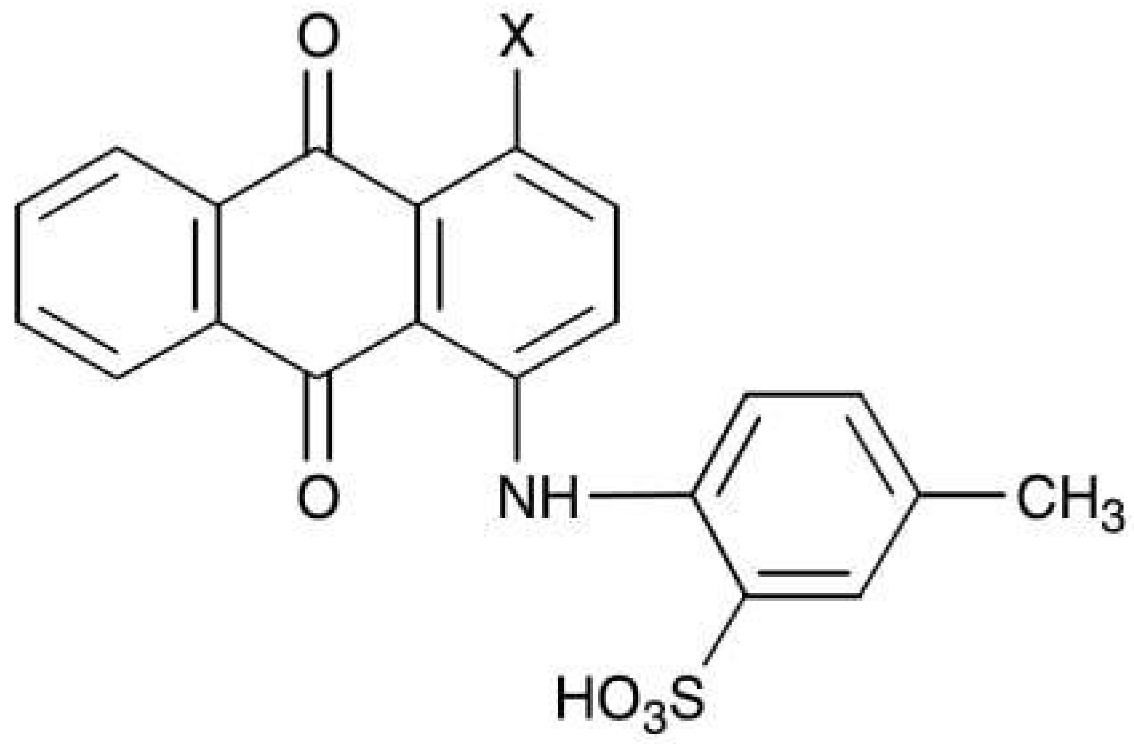
6.36

CI Acid Blue 60

A suitable example is CI Acid Blue 27 (6.37; X = $NHCH_3$), which is made from 4-bromo-1-methylaminoanthraquinone by nucleophilic displacement followed by sulphonation. Some commercial acid dyes based on 1,4-diaminoanthraquinone contain substituents in both the 2- and the 3-positions. Thus, for example, CI Acid Violet 41 (6.38) is produced by the condensation of 1,4-diamino-2,3-dichloroanthraquinone with phenol in the presence of sodium sulphite and manganese dioxide.

Aminohydroxyanthraquinone derivatives are available from leucoquinizarin by heating with an appropriate arylamine and boric acid in aqueous ethanol, followed by oxidation. The use of *p*-toluidine and subsequent sulphonation gives CI Acid Violet 43 (6.37; X = OH).

The photodegradation of CI Acid Green 25 (6.27) on nylon proceeds by hydrogen atom abstraction to produce the leuco compound [13].



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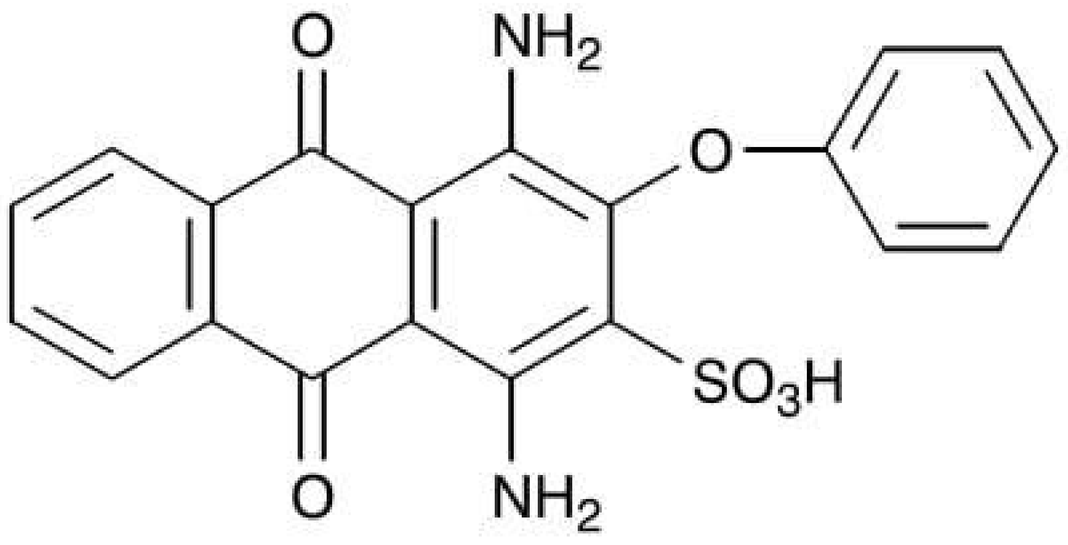


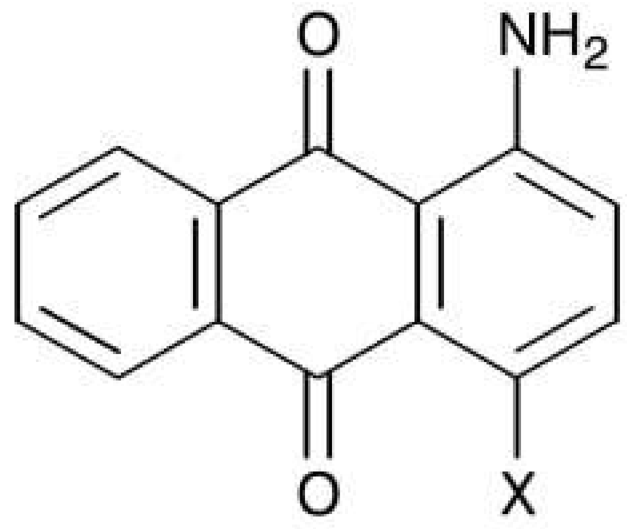
6.38

CI Acid Violet 41

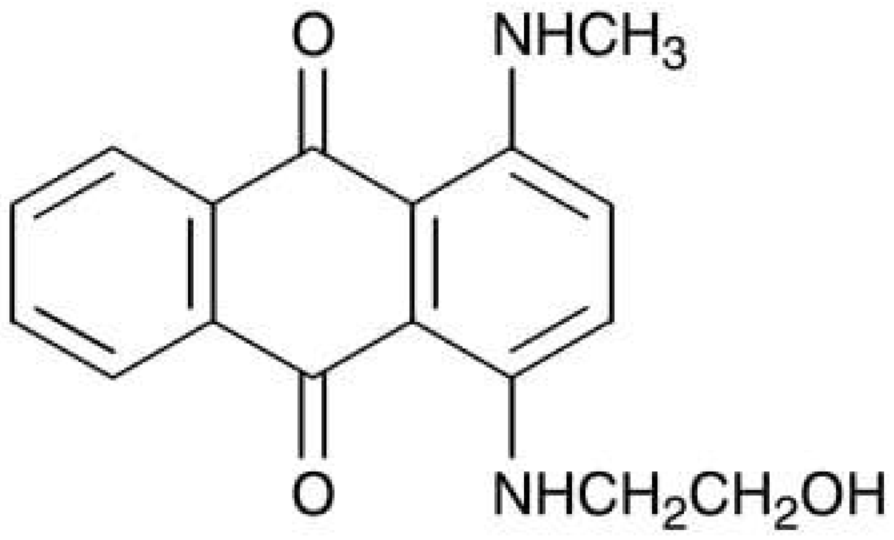
Disperse dyes

Anthraquinone dyes are second only to azo dyes in importance as disperse dyes and are predominant in the red, violet, blue and blue-green sectors [14]. Because anthraquinone disperse dyes are relatively expensive to manufacture, successful attempts were made to replace some of them with technically equivalent and more economical products [15]. The replacement process has been most successful in the red region using, for example, heterocyclic azo dyes and novel chromogens. The brilliance of the anthraquinones with their narrow spectral absorption bands is difficult to attain with other structures, however, as is their high light fastness and chemical stability. The development of anthraquinone disperse dyes is included in a review by Dawson [16].

Dyes for cellulose acetate are relatively simple molecules, typified by CI Disperse Red 15 (6.39; X = OH), CI Disperse Violet 4 (6.39; X = $NHCH_3$) and CI Disperse Blue 3 (6.40), the last-named being manufactured from leucoquinizarin and the appropriate amines. The unsymmetrically substituted product inevitably contains significant amounts of the related symmetrical compounds. The widely used CI Disperse Blue 3 is known to cause skin sensitisation when on nylon [17] and can also provoke an allergic reaction [18]. Bright red 2-alkoxy-1-amino-4-hydroxyanthraquinones, such as CI Disperse Red 4 (6.41), can be obtained from 1-amino-2,4-dibromoanthraquinone by hydrolysis to give 1-amino-2-bromo-4-hydroxyanthraquinone (CI Disperse Violet 17), which is then condensed with the appropriate alcohol.

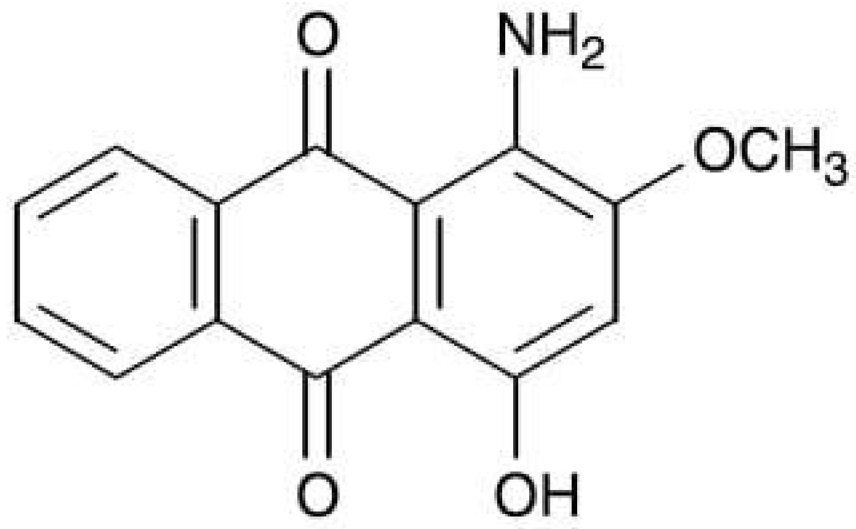


6.39



6.40

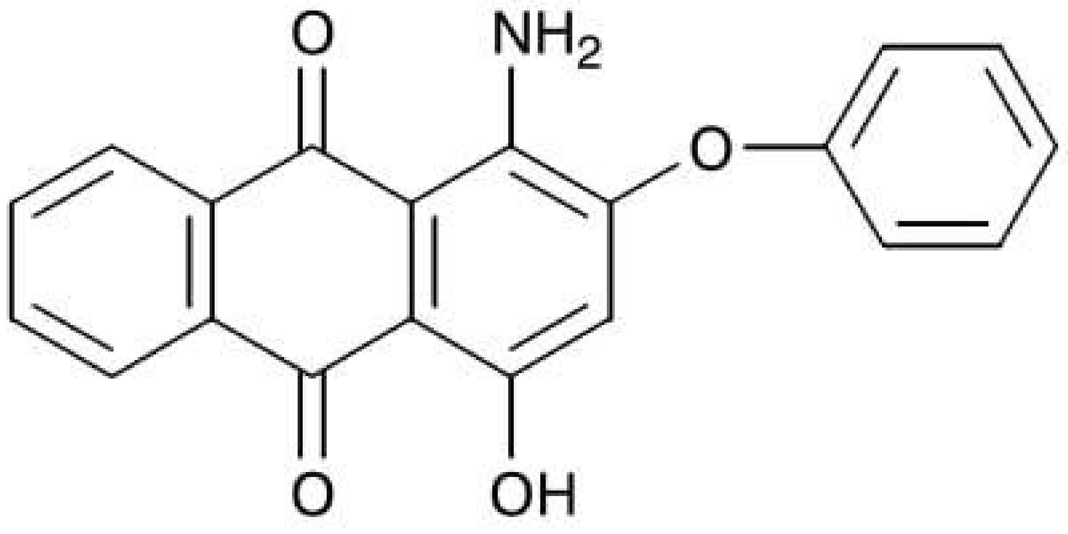
CI Disperse Blue 3



6.41

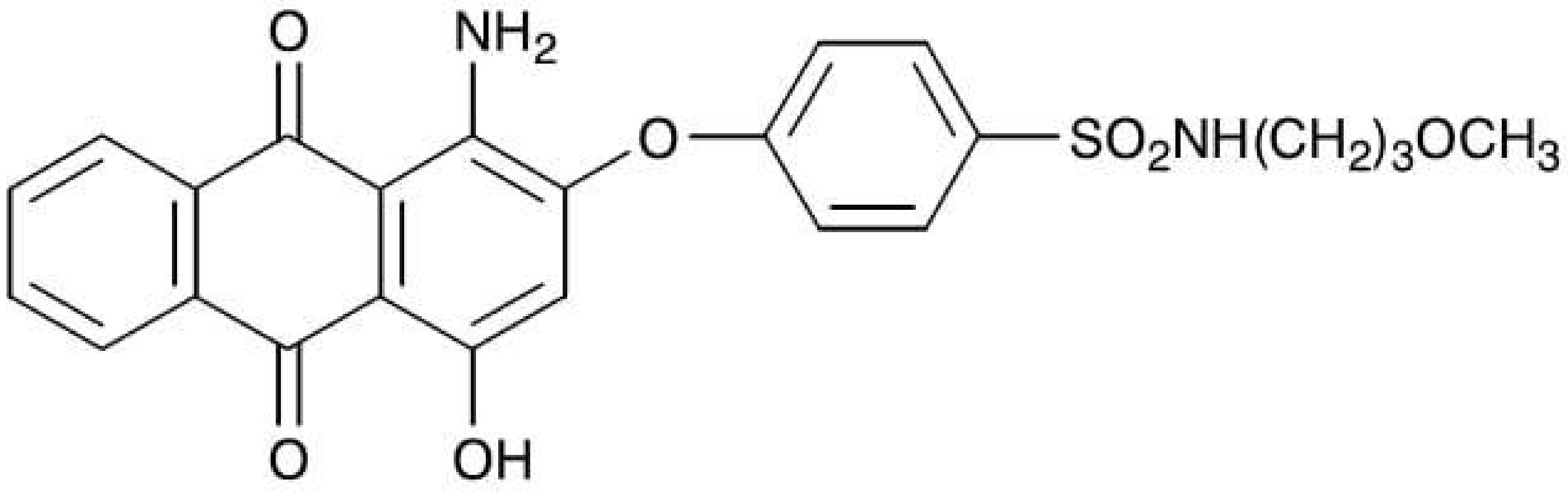
CI Disperse Red 4

Suitable disperse dyes for polyester require good sublimation fastness and generally contain additional or more hydrophobic substituents compared with acetate dyes. Thus, for example, CI Disperse Red 60 (6.42) is important for the dyeing of polyester fabrics but has only moderate sublimation fastness. It is, however, the most important red dye for transfer printing. Improved sublimation fastness can be achieved if substituents are introduced into the phenoxy ring. Exceptional fastness is achieved by chlorosulphonation of CI Disperse Red 60 followed by condensation with 3-methoxypropylamine to give the brilliant red dye 6.43 [16].



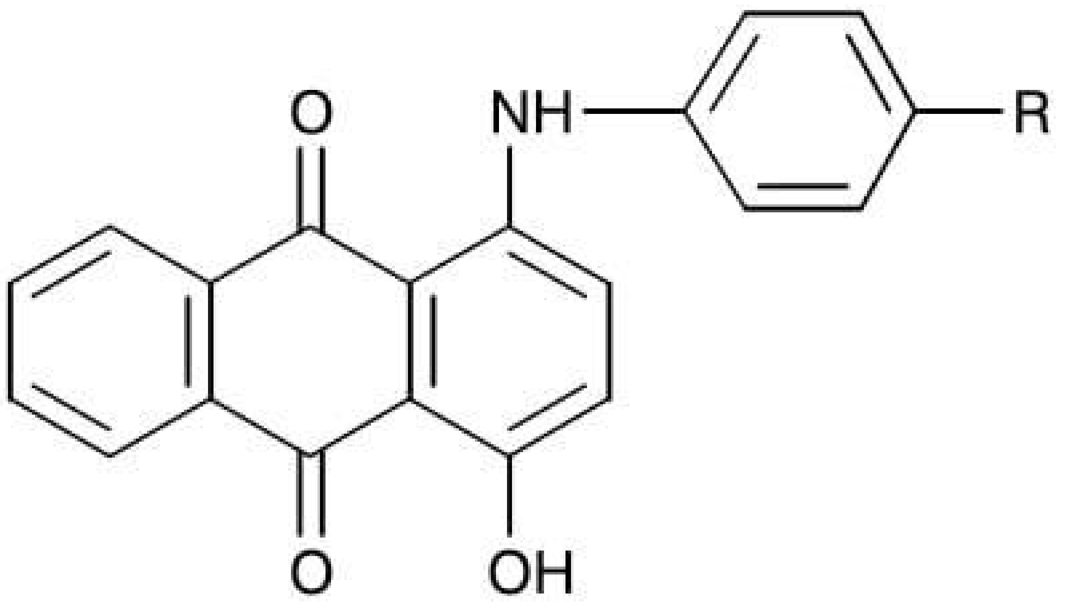
6.42

CI Disperse Red 60

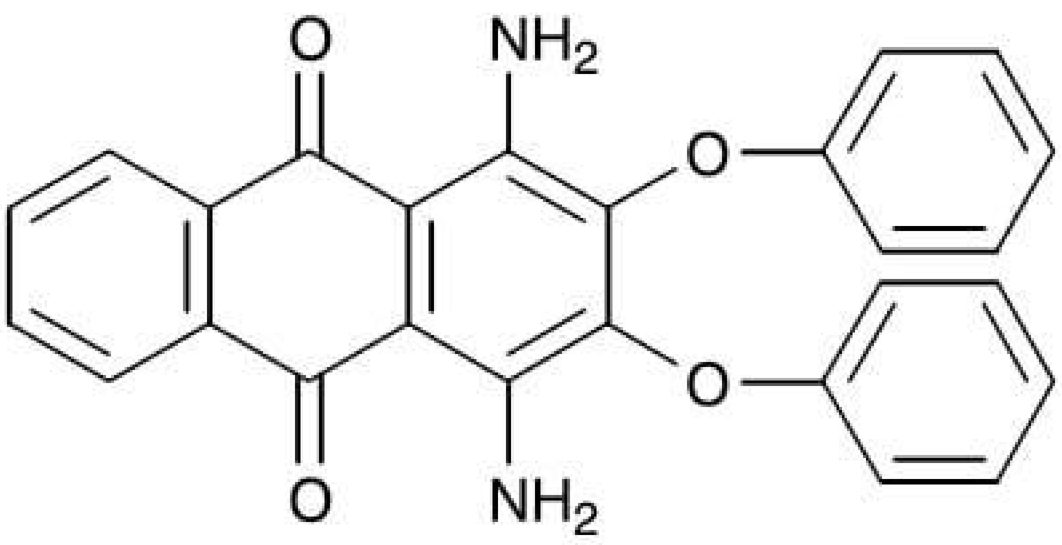


6.43

Monoarylation of 1-amino-4-hydroxyanthraquinone (6.39; X = OH) results in violet dyes such as CI Disperse Violet 27 (6.44; R = H) and the bluish violet CI Disperse Blue 72 (6.44; R = CH_3); the latter dye is also important as CI Solvent Violet 13. Chlorination of 1,4-diaminoanthraquinone with sulphuryl chloride gives the 2,3-dichloro derivative (CI Disperse Violet 28), which on condensation with phenol yields CI Disperse Violet 26 (6.45). Monoaryl or dialkyl derivatives of 1,4-diaminoanthraquinone (6.19; CI Disperse Violet 1) are blue. Typical examples include CI Disperse Blue 19 (6.46) and CI Disperse Blue 23 (6.47).

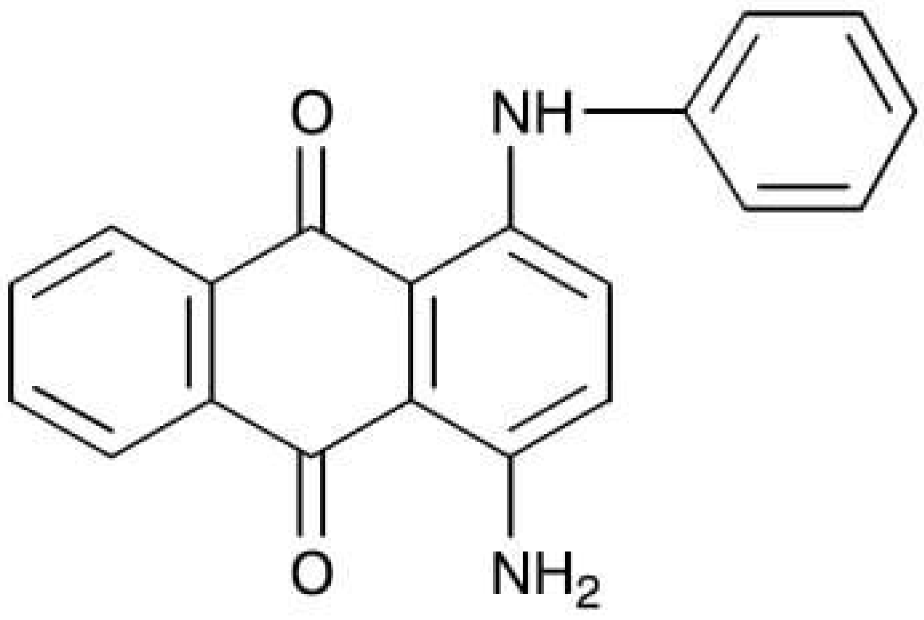


6.44



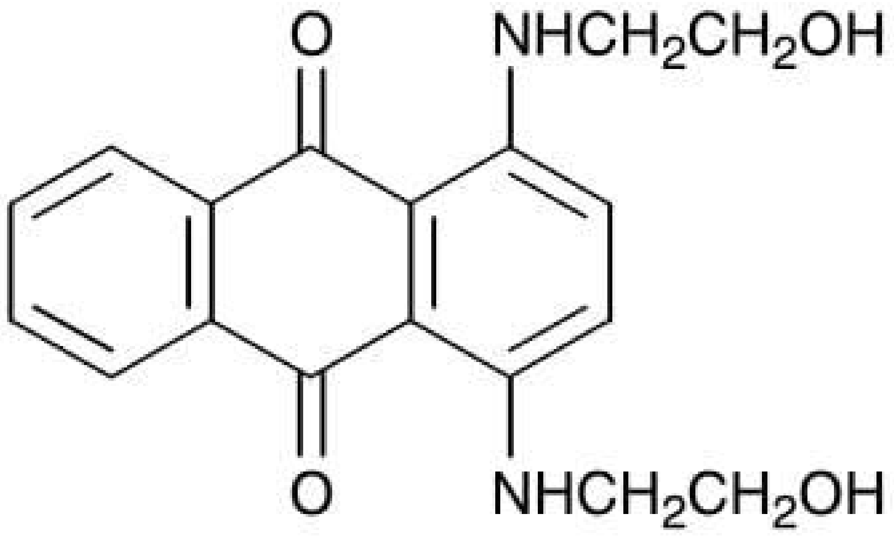
6.45

CI Disperse Violet 26



6.46

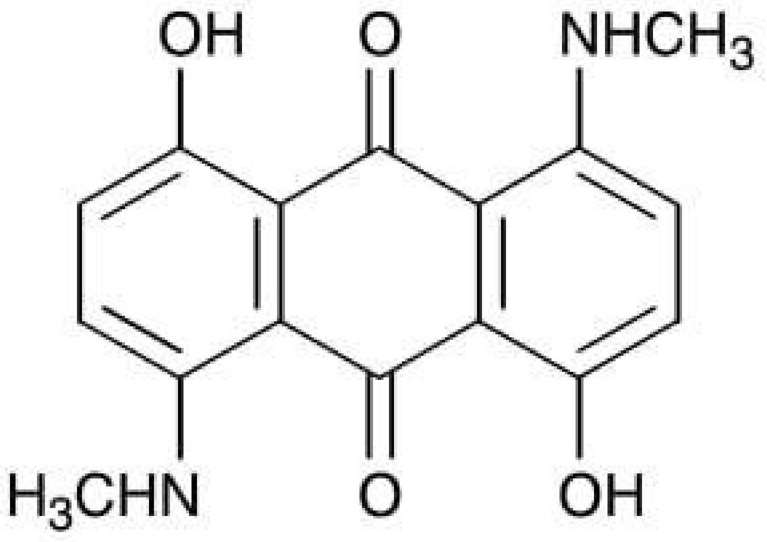
CI Disperse Blue 19



6.47

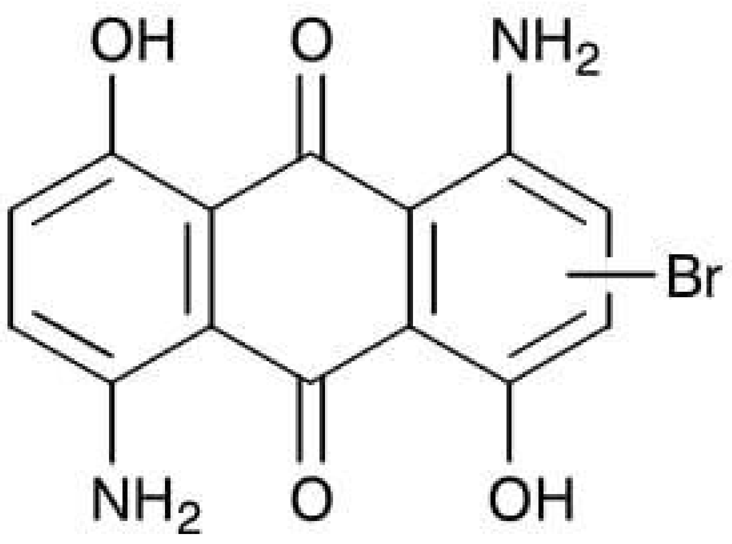
CI Disperse Blue 23

Many commercially important blue dyes are derived from tetra-α-substituted anthraquinones, especially the diamino derivatives of anthrarufin (6.13) and chrysazin (6.14). Examples include CI Disperse Blue 26 (6.48) and CI Disperse Blue 56 (6.49). Progressive methylation of 1,8-diamino-4,5-dihydroxy- and 1,5-diamino-4,8-dihydroxy-anthraquinone leads to a series of reddish-blue to greenish-blue dyes [19]. The presence of *N,N*-dimethylamino substituents results in marked hypsochromic shifts in the visible absorption maxima due to steric hindrance (compare 6.26). The presence of amino groups is often associated with inferior fastness to burnt gas fumes. This drawback can be overcome by the use of dyes such as CI Disperse Blue 27 (6.50), which, although relatively expensive, has very good all-round fastness properties on both cellulose acetate and polyester. This dye can be obtained from chrysazin (6.14) by nitration and subsequent condensation with *p*-(2-hydroxyethyl)aniline. Bright blue dyes for polyester can be manufactured from the well-known acid dye CI Acid Blue 45 (6.29) by the C-arylation of its boric ester with, for example, a mixture of phenol and anisole, followed by removal of the sulphonic acid groups. This procedure gives CI Disperse Blue 73 (6.51; R = H or CH_3). 1,4,5,8-Tetra-aminoanthraquinone (CI Disperse Blue 1) is a cellulose acetate dye of long standing, as is the product of partial methylation, CI Disperse Blue 31. The parent dye is now known to be carcinogenic [20].



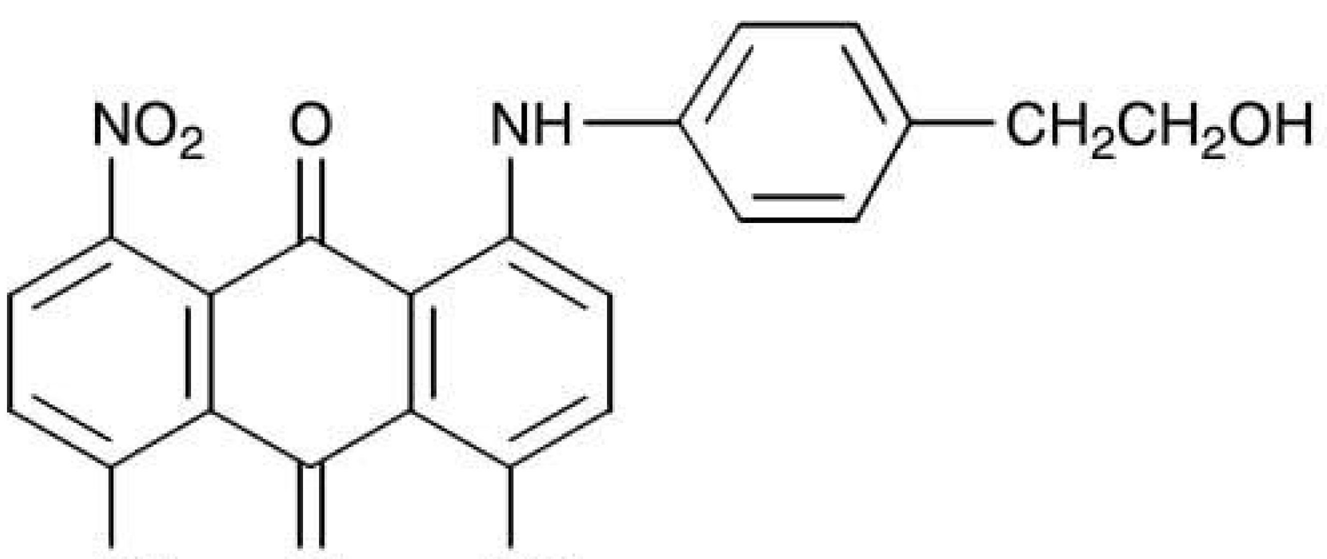
6.48

CI Disperse Blue 26



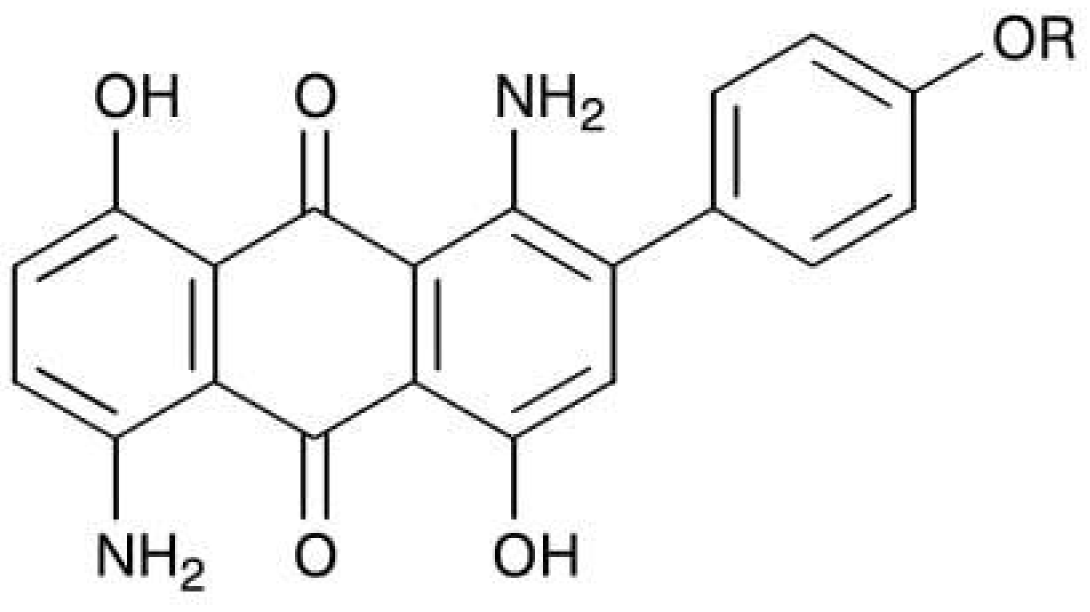
6.49

CI Disperse Blue 56



6.50

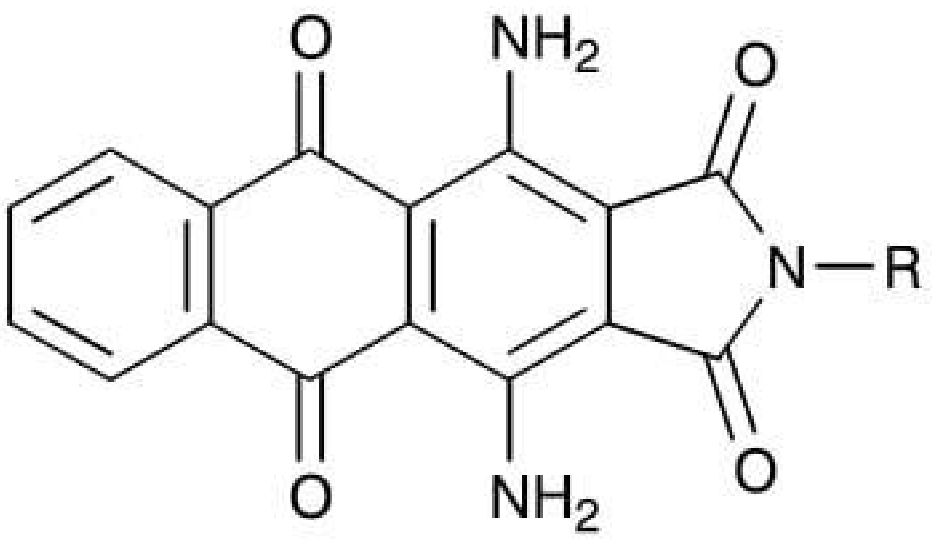
CI Disperse Blue 27



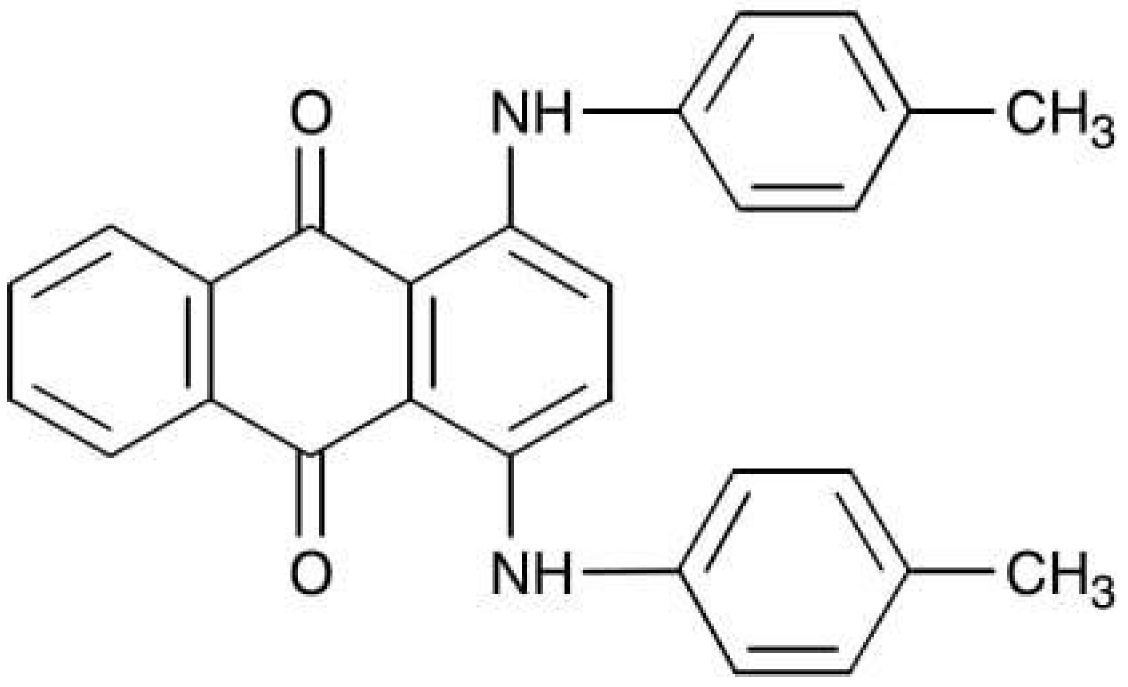
6.51

Few heterocyclic anthraquinone analogues are of established importance as disperse dyes. An interesting exception is the system 6.52, which provides bright turquoise blue dyes of very good light fastness on polyester [21]. A route to CI Disperse Blue 60 (6.52; R = $CH_2CH_2CH_2OCH_3$) involves hydrolysis of 1,4-diamino-2,3-dicyanoanthraquinone followed by alkylation of the resulting imide; several closely related products can be obtained by varying the alkyl group.

Not many green anthraquinone disperse dyes are available commercially. One example is CI Disperse Green 6:1 (6.53), which has wider use as CI Solvent Green 3 and is the precursor of CI Acid Green 25 (6.27).



6.52

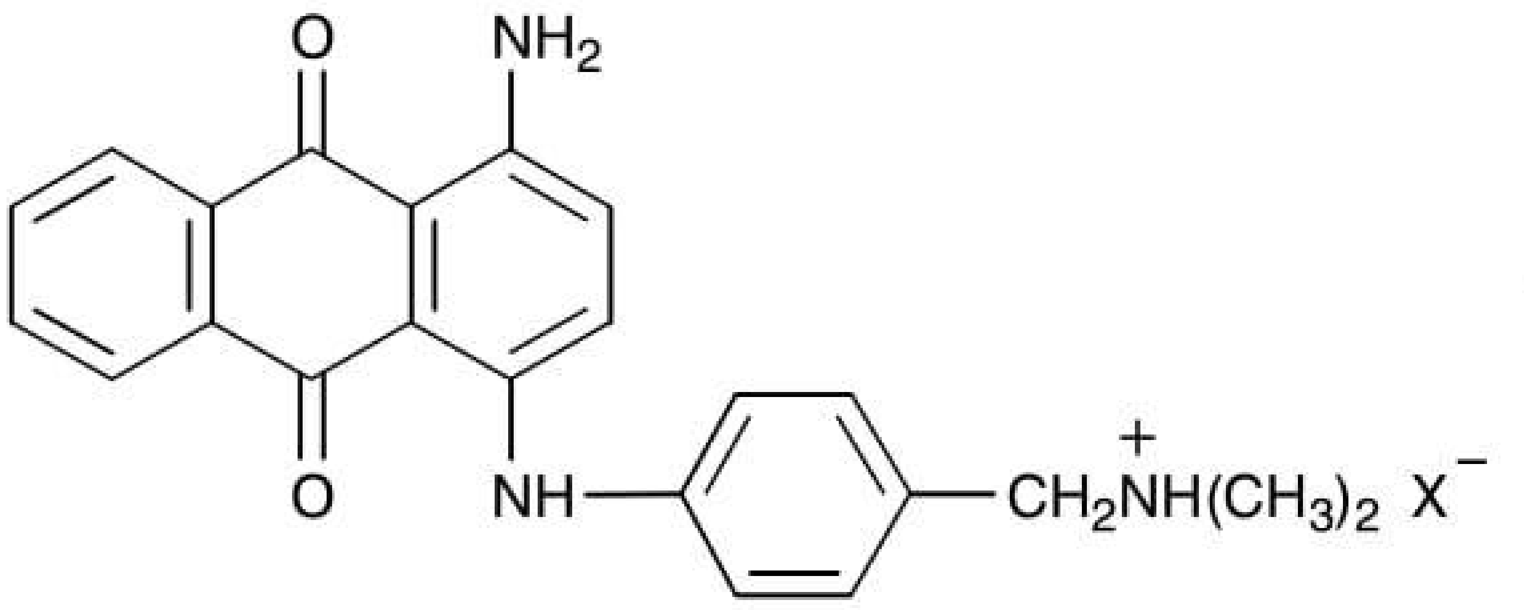


6.53

CI Disperse Green 6:1

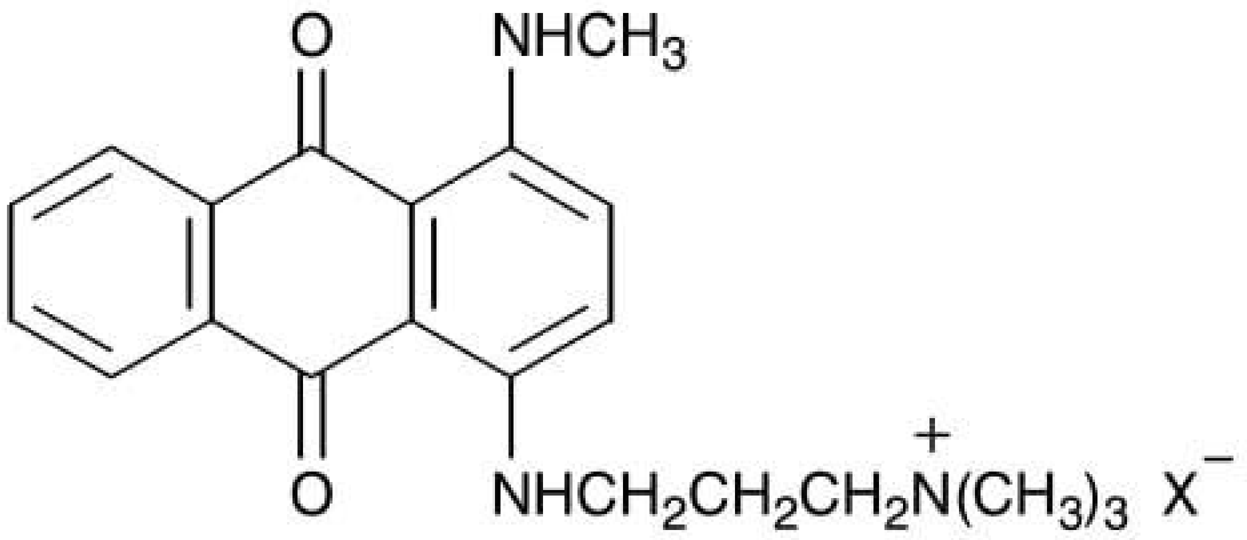
Basic dyes

Some anthraquinone dyes with pendant cationic groups are used commercially on acrylic and modacrylic fibres [22]. Only two disclosed structures are included in the latest revision of the *Colour Index*, the dyes being the reddish blue CI Basic Blue 47 (6.54) and the greenish blue CI Basic Blue 22 (6.55).



6.54

CI Basic Blue 47



6.55

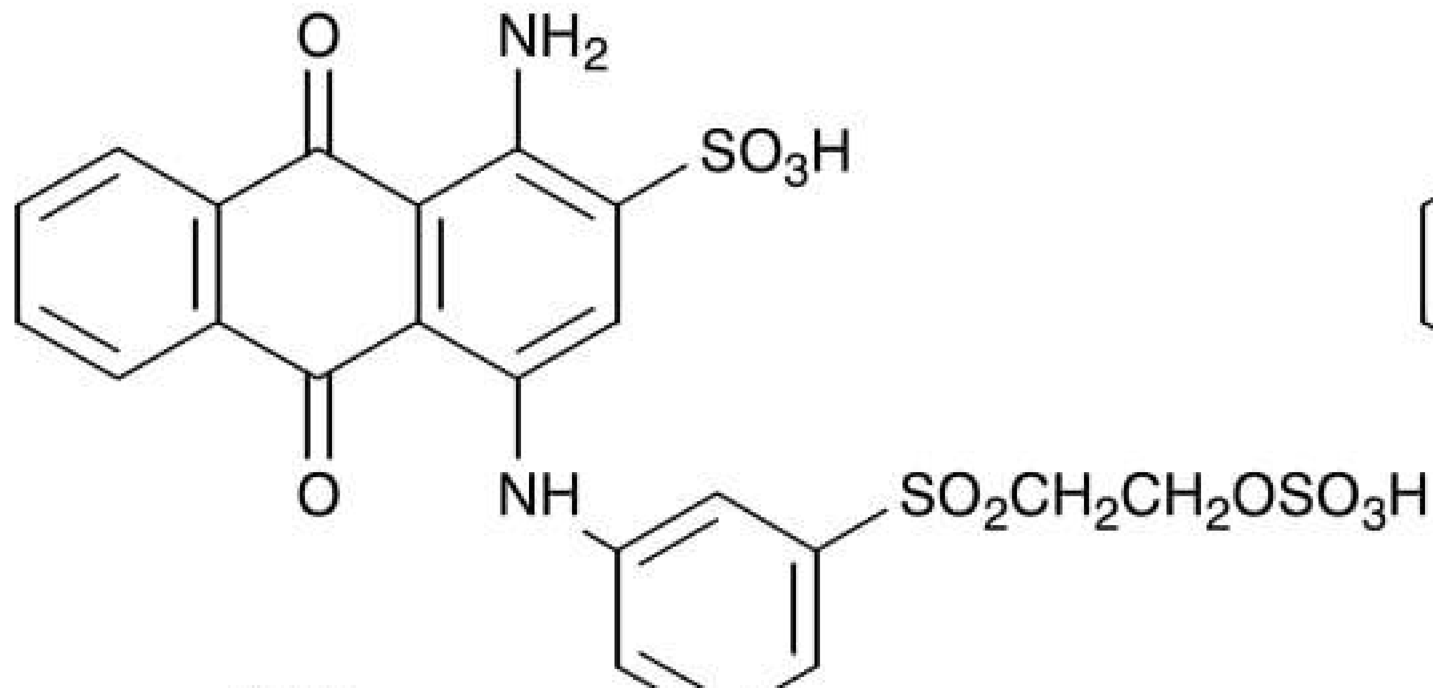
CI Basic Blue 22

Reactive dyes

The chemistry of reactive dyes is discussed in detail in Chapter 7. However, it is appropriate to point out in this section that the anthraquinone system provides several commercially valuable bright blue reactive dyes. Bromamine acid (6.10) is the key intermediate for the synthesis of the vinylsulphone dye CI Reactive Blue 19 (6.56), which finds application in dyeing and printing. The dichlorotriazinyl dye CI Reactive Blue 4 (6.57) is derived from the same intermediate and is used in protein purification [23]. CI Reactive Blue 6 (6.58), obtained from the reaction of 1,4-diaminoanthraquinone with epichlorohydrin, was the only blue dye in the Procinyl (ICI) range for nylon. Anthraquinone blues have been replaced to some extent by derivatives of the intrinsically bright triphenodioxazine chromogen [24].

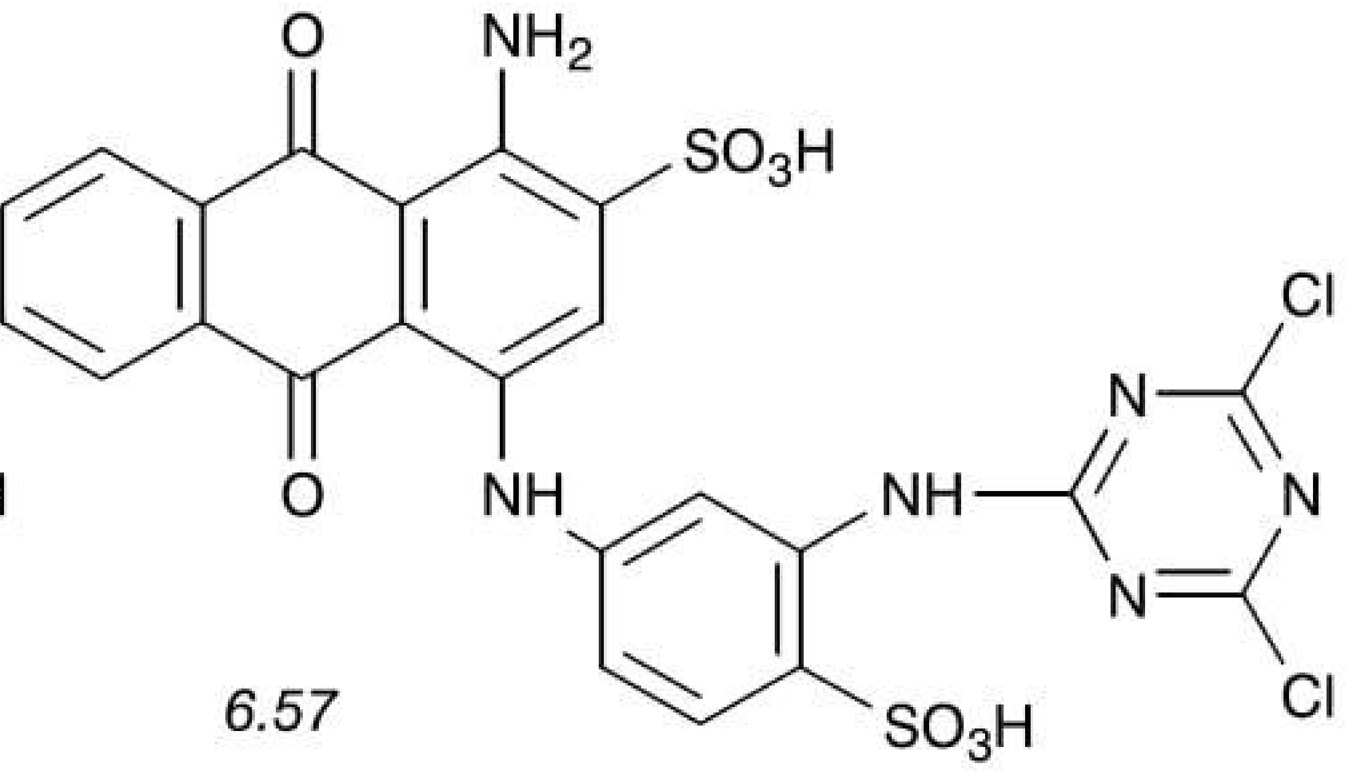
6.2 POLYCYCLIC VAT DYES

Vat dyes are insoluble in water and are applied to cellulosic fibres, usually with sodium dithionite under alkaline conditions, by a vatting process involving reduction to produce a



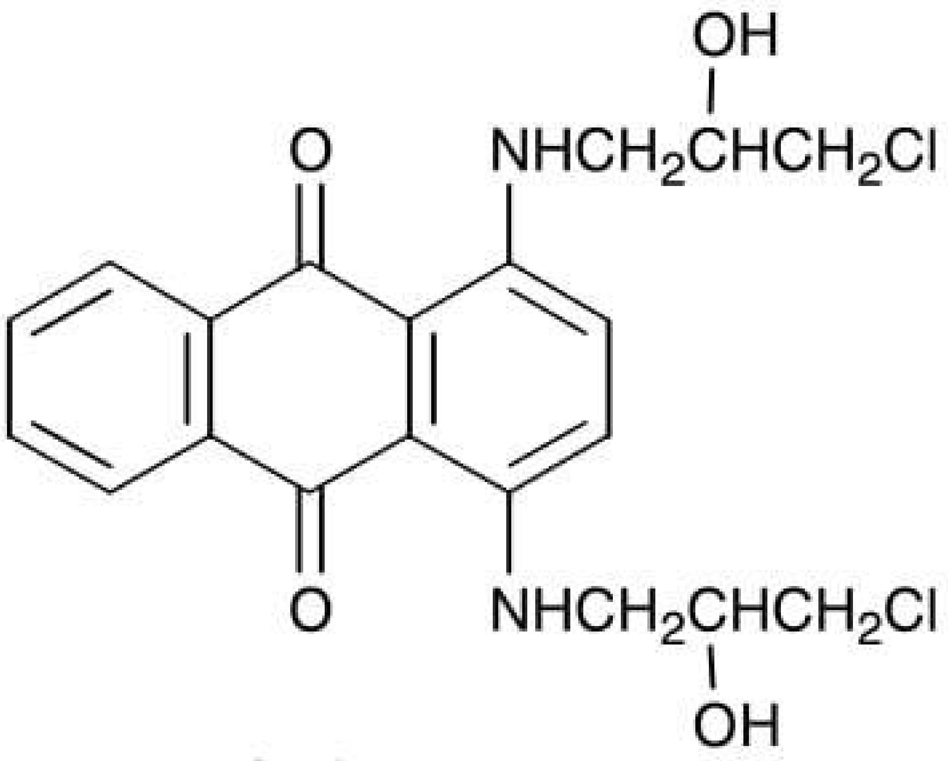
6.56

CI Reactive Blue 19



6.57

CI Reactive Blue 4

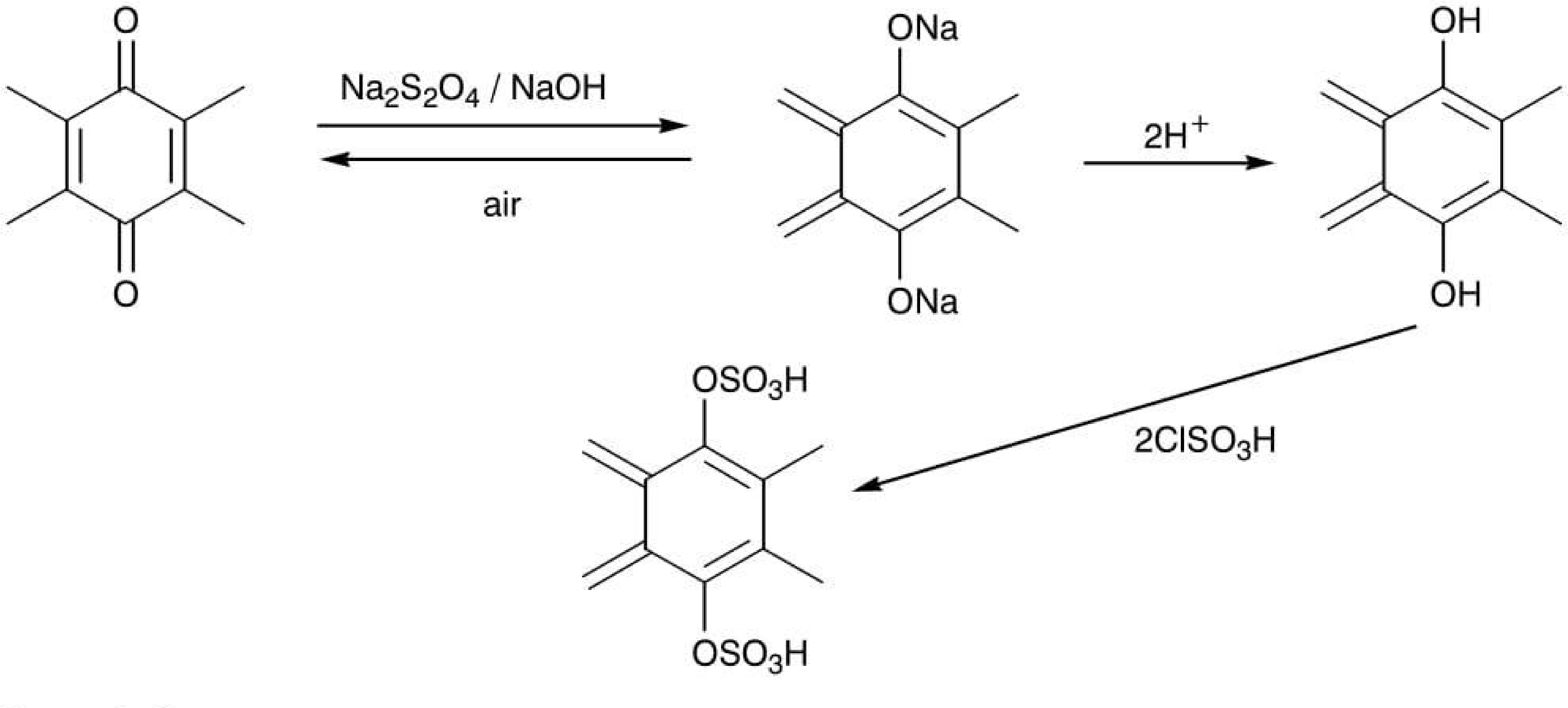


6.58

CI Reactive Blue 6

water-soluble leuco form which possesses affinity for the substrate. Air or chemical oxidation then results in regeneration of the insoluble form of the colorant trapped within the fibre structure.

Vat dyes based on anthraquinone and related polycyclic systems generally exhibit outstanding fastness properties. Most vat dyes contain two carbonyl groups linked by a conjugated (quinonoid) system (Scheme 6.10). They can be applied as the water-soluble disulphuric esters of the leuco forms; these have low affinity for cellulose and can be obtained by esterifying the leuco compound with chlorosulphonic acid. Reduction and esterification may be carried out without isolating the leuco compound using pyridine and iron together with chlorosulphonic acid [25].



Scheme 6.10

Anthraquinonoid systems are the most important vat dyes, providing hues covering the whole of the visible spectrum. Nevertheless, the main commercial products are found within the blue, green, brown and black sectors. Some of the relatively simple yellow and orange dyes cause phototendering of the dyed substrate, bringing about adverse structural changes on exposure to light.

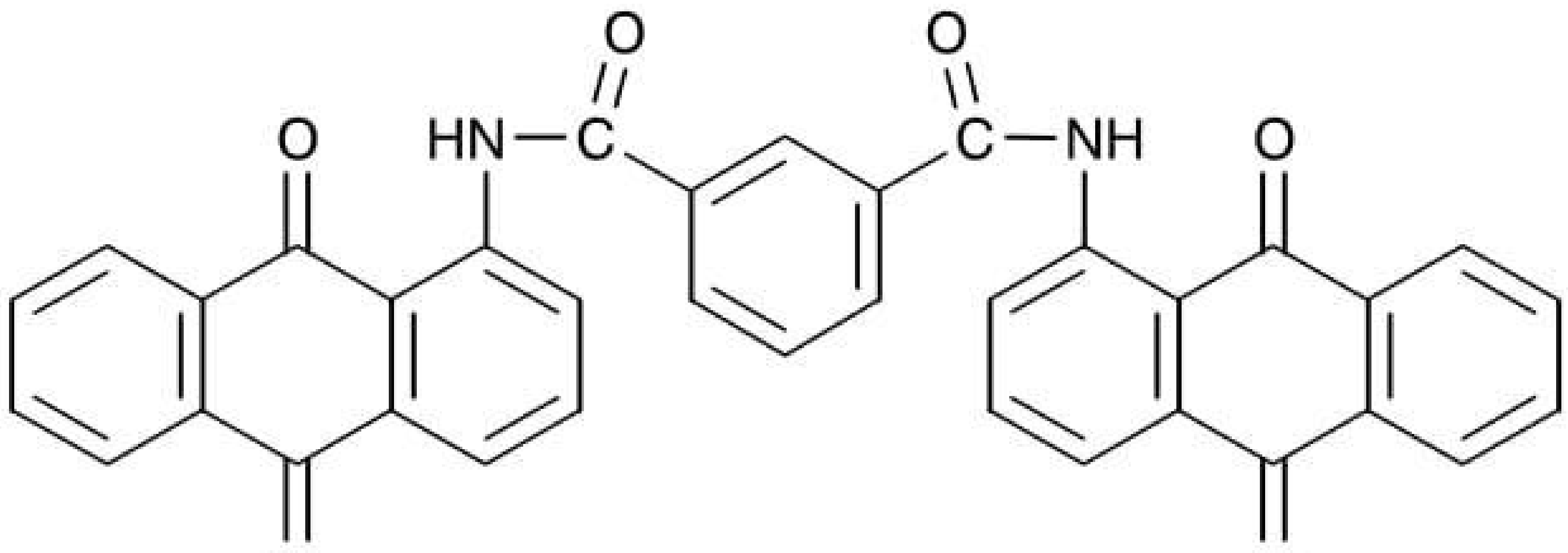
Most of the currently available vat dyes have been known for many years and very few new dyes have been marketed during the last thirty years [26]. Recent research efforts have concentrated on improved methods of manufacture and more economical finishing of traditional vat dyes.

The general stability of the polycyclic vat dyes permits many of them to be used as pigments [27]. Several types of polycyclic vat colorants provide structures suitable for use on cellulosic fibres for infrared camouflage [28].

6.2.1 Anthraquinones

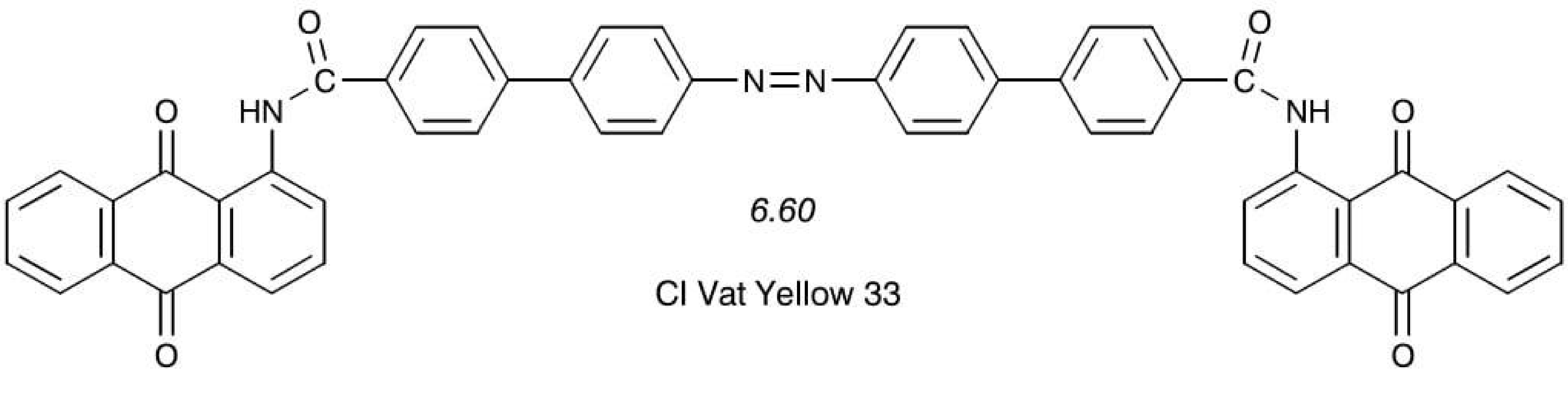
In 1909 Deinet observed that the product of *N*-benzoylation of 1-aminoanthraquinone could be applied as a vat dye. Although the leuco form of 1-aminoanthraquinone has no affinity for cotton, the corresponding benzoyl derivative does have a moderate affinity.

Acylaminoanthraquinones are structurally the simplest of the vat dyes, and are used for yellow, orange, red and violet hues. Numerous acylaminoanthraquinones have been examined for use as vat dyes but only a few have survived competition from more cost-effective types. One example is CI Vat Yellow 26 (6.59), which is made from 1-aminoanthraquinone and isophthaloyl chloride. Another yellow dye of commercial importance is CI Vat Yellow 33 (6.60), which is made by reducing 4′-nitrobiphenyl-4-carboxylic acid with glucose and sodium carbonate. The resulting azo compound is acylated with thionyl chloride before condensing with 1-aminoanthraquinone. It is of significance that the azo bridge remains intact during the vatting process; in this dye the azo group is unable to tautomerise into a hydrazone and consequently resists reduction [29].



6.59

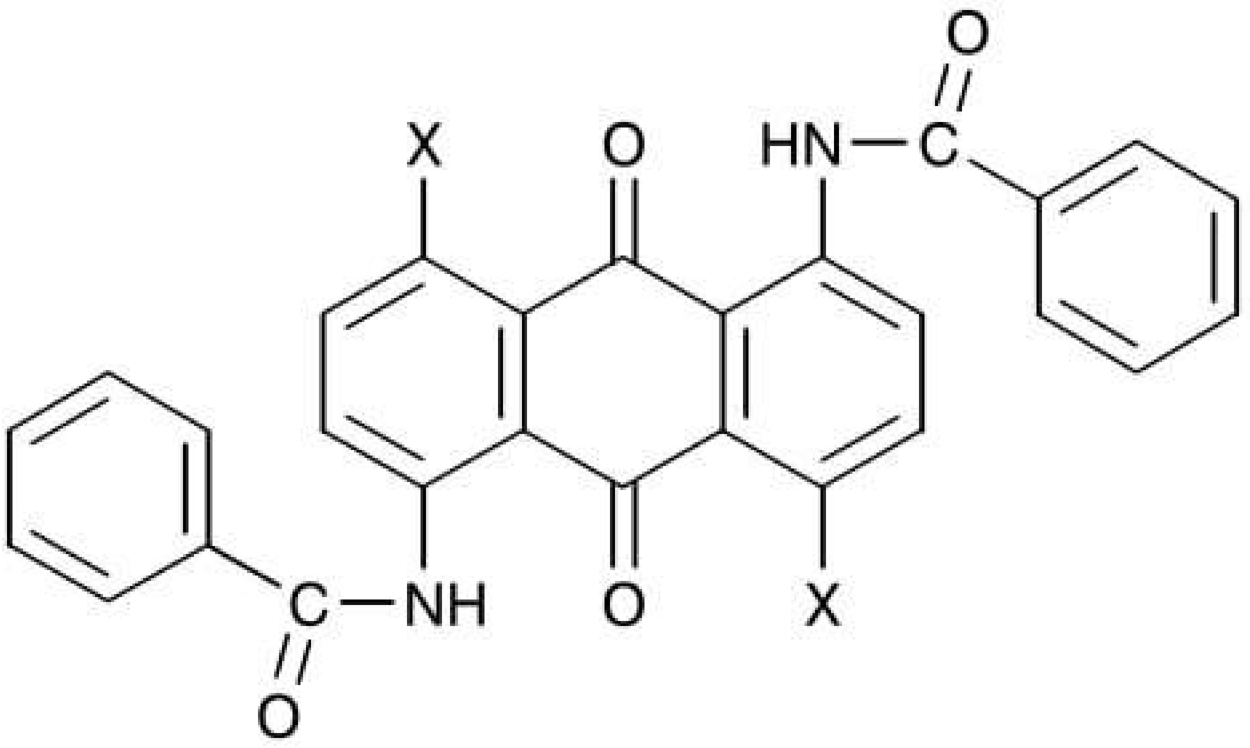
CI Vat Yellow 26



6.60

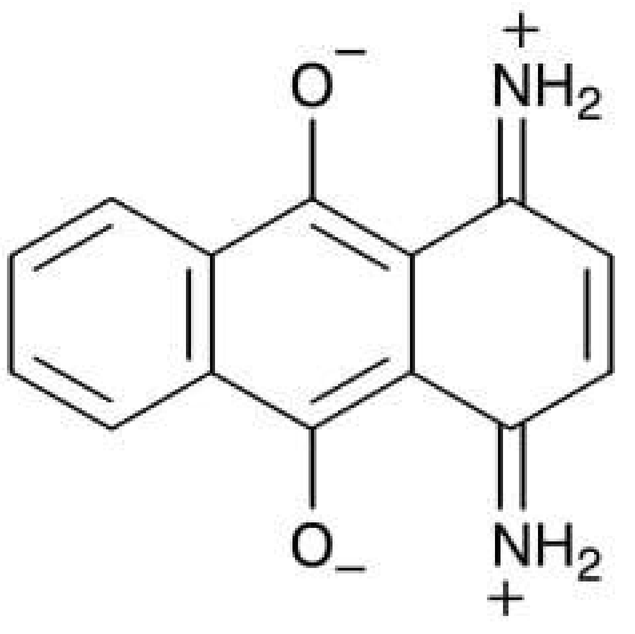
CI Vat Yellow 33

Derivatives of 1,4- and 1,5-diaminoanthraquinone provide some important examples in this class. Relatively simple dyes include CI Vat Yellow 3 (6.61; X = H) and CI Vat Violet 15 (6.61; X = OH).

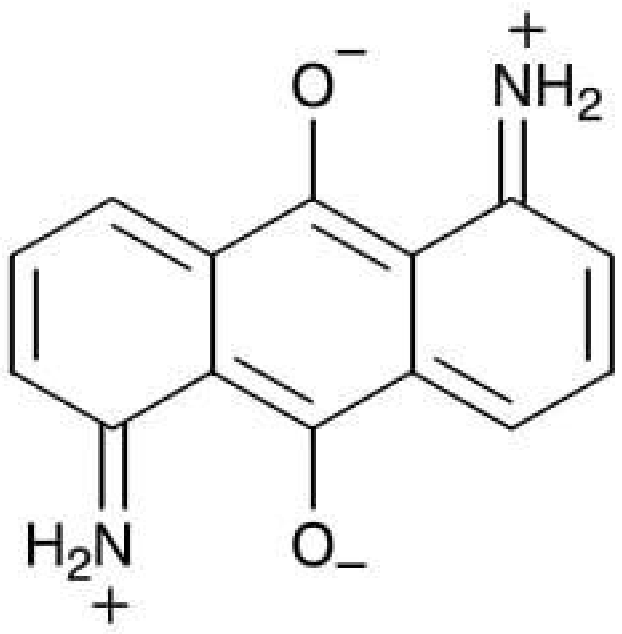


6.61

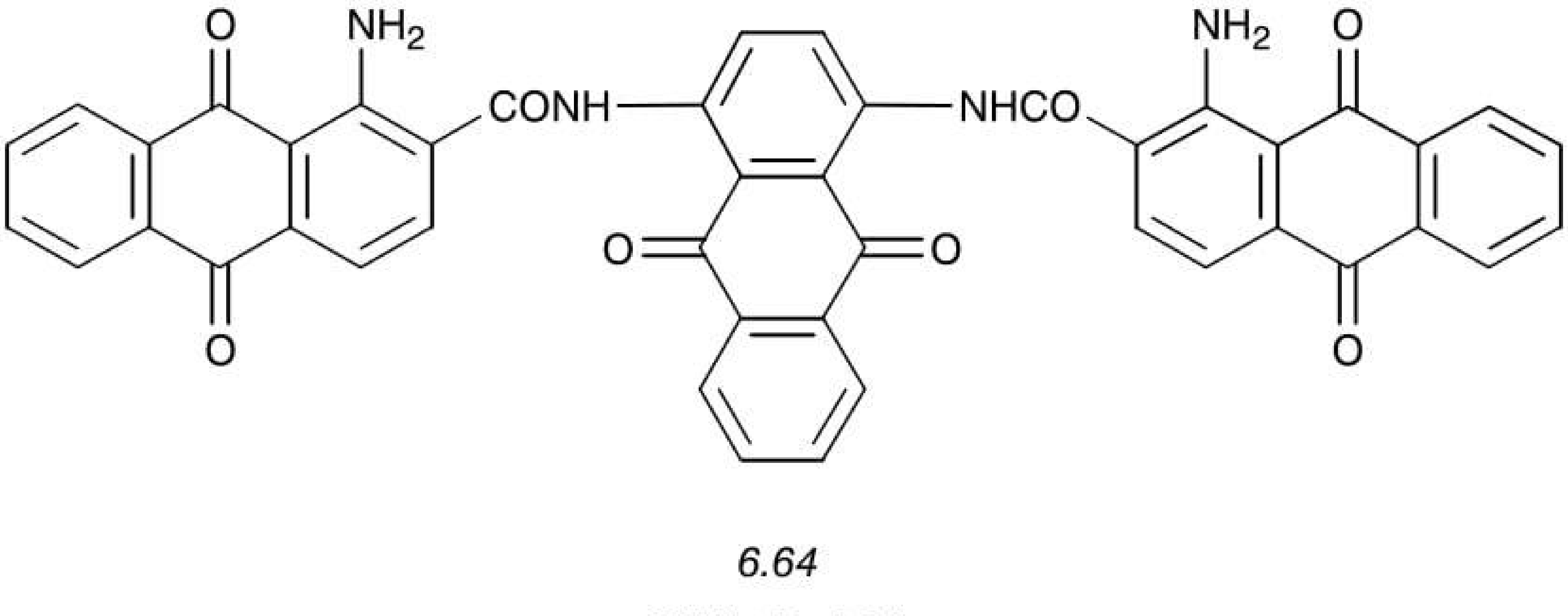
It is generally found that dyes based on the 1,4-diaminoanthraquinone system are more bathochromic than isomers derived from 1,5-diamino-anthraquinone. This difference can be related to the relative stabilities of the dipolar excited states of the dyes. Qualitatively, the 1,4-disubstituted derivatives are aromatic (6.62) and therefore at a lower energy, whereas the 1,5-disubstituted isomers (6.63) are not. Consequently, the energy difference between the ground state of the molecule and its first excited state is smaller for 1,4-diaminoanthraquinones than for the 1,5-isomers. For example, the 1,4-isomer of CI Vat Yellow 3 (6.61; X = H) is CI Vat Red 42, although this dye is no longer in commercial use. A more complex example is CI Vat Red 21 (6.64), which contains amino groups in the acyl ring systems.



6.62



6.63

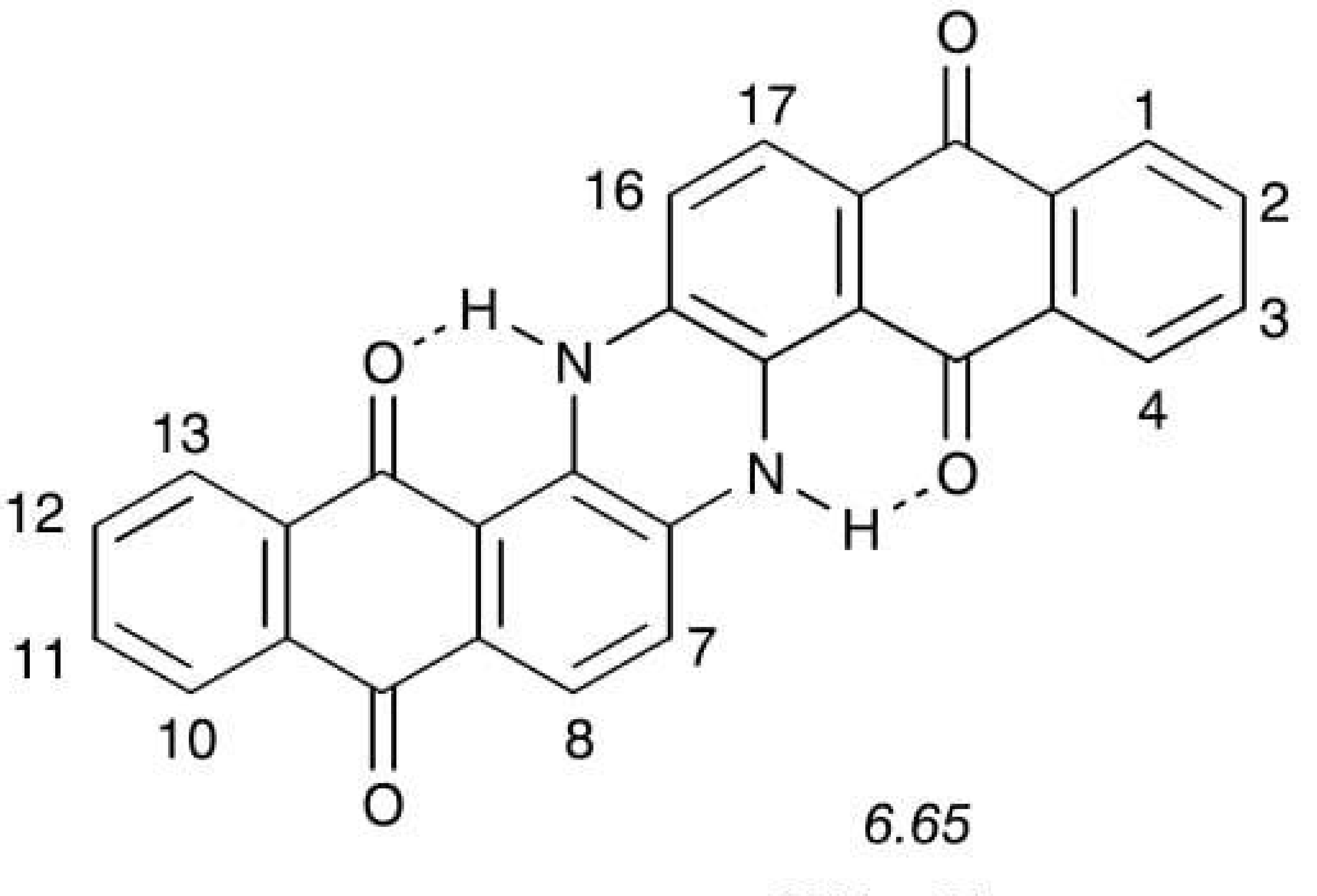


6.64

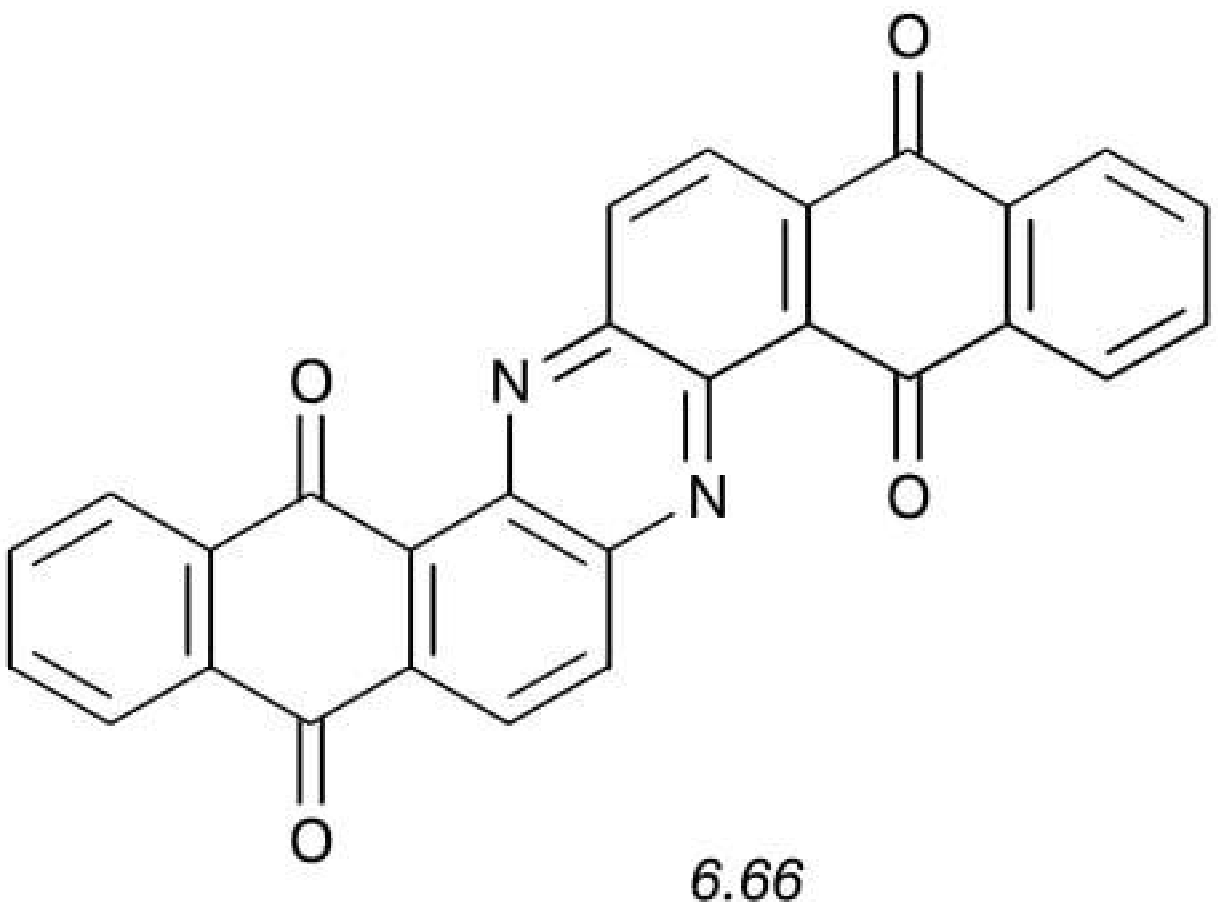
CI Vat Red 21

6.2.2 Indanthrones

In 1901 Bohn discovered the first vat dyes based on anthraquinone, a landmark in the history of synthetic dyes. In an attempt to prepare an anthracene analogue of indigo (6.113), Bohn applied the Heumann synthesis to 2-aminoanthraquinone by fusing the condensation product of this amine and chloroacetic acid with potassium hydroxide. The brilliant blue product was named indanthrene, a name coined from those of indigo and anthracene. Bohn showed that the same product resulted from the alkali fusion of 2-aminoanthraquinone, so the dye could not be an analogue of indigo. The new vat dye was marketed by BASF as Indanthren Blue R (CI Vat Blue 4) and was subsequently given the chemical name indanthrone (6.65). The structure was proposed on the basis of elemental analysis ($C_{28}H_{14}O_4N_2$), suggesting the loss of four atoms of hydrogen from two molecules of 2-aminoanthraquinone), the absence of azo and of primary amino groups and the exceptional stability. This was confirmed by synthesis: for example, Bohn obtained indanthrone by heating 1-amino-2-bromoanthraquinone in nitrobenzene solution under Ullmann conditions.



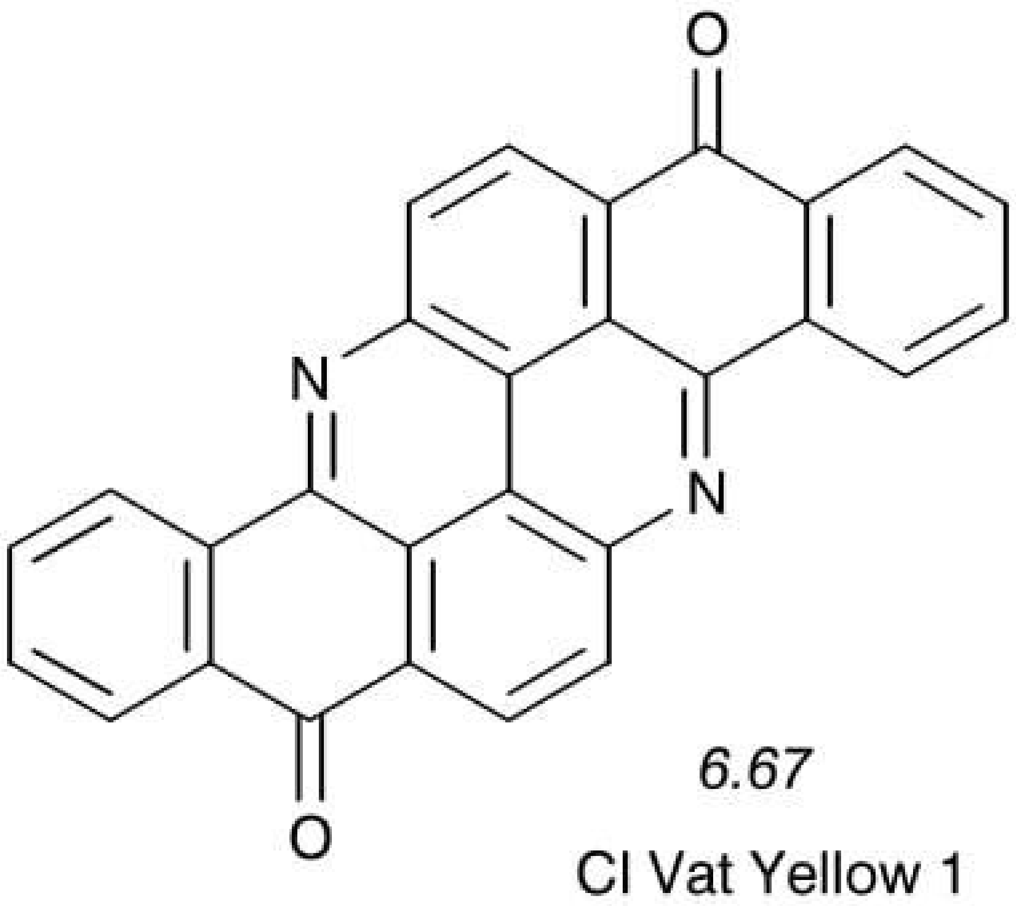
6.65
CI Vat Blue 4



6.66

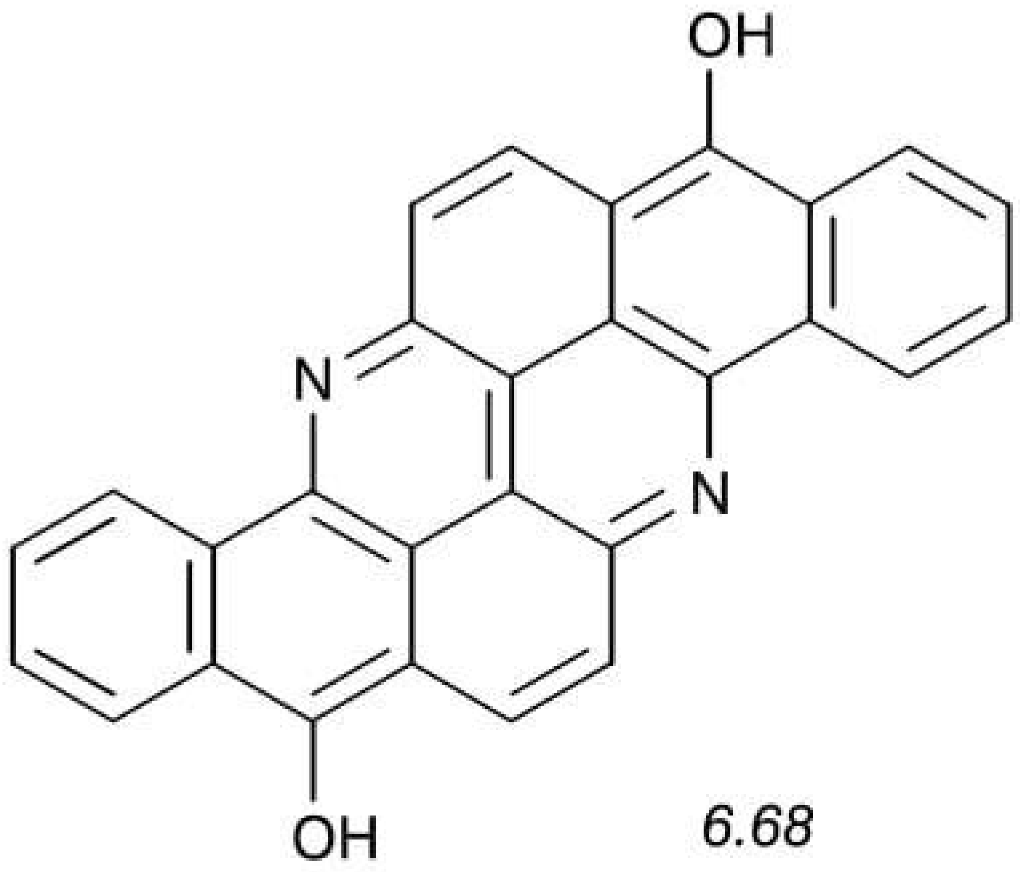
Indanthrone has low fastness to bleaching because the corresponding yellowish green azine (6.66) is formed. Its importance at the time of its discovery lay in the dearth of fast dyes for cotton. Indanthrone is also used as a pigment (CI Pigment Blue 60).

Very careful control of the fusion conditions is necessary in order to minimise the formation of by-products. Alkali fusion at approximately 220 °C gives mainly the blue alkali salt of leuco indanthrone; air oxidation is then required to produce the dye. Fusion at lower temperatures results in the formation of alizarin (6.2), whereas reaction at a higher temperature (above 300 °C) affords significant amounts of a yellow dye as well as the blue indanthrone. The yellow dye was first marketed by BASF as Flavanthren (CI Vat Yellow 1) and was subsequently given the chemical name flavanthrone (6.67). Today flavanthrone is used mainly as a pigment (CI Pigment Yellow 24). Flavanthrone is readily reduced to a blue leuco form; hydrogen abstraction to generate the leuco form can also take place on cellulose, leading to fibre damage. The leuco compound is believed, on the basis of spectroscopic evidence, to have the structure 6.68 [30]. The yellow to blue colour change is made use of in testing for the presence of a reducing agent under alkaline conditions. The structure of flavanthrone was confirmed by an Ullmann synthesis using the Schiff base (6.69) obtained from 2-amino-1-chloroanthraquinone, which gave a bianthraquinonyl precursor (6.70), as in Scheme 6.11. Hydrolysis of compound 6.70 gives the corresponding diamine, which subsequently undergoes cyclodehydration to flavanthrone. In a related industrial synthesis, the diphthalimide of 2-amino-1-chloroanthraquinone is converted into the corresponding bianthraquinonyl, which undergoes hydrolysis and ring closure in dilute sodium hydroxide.

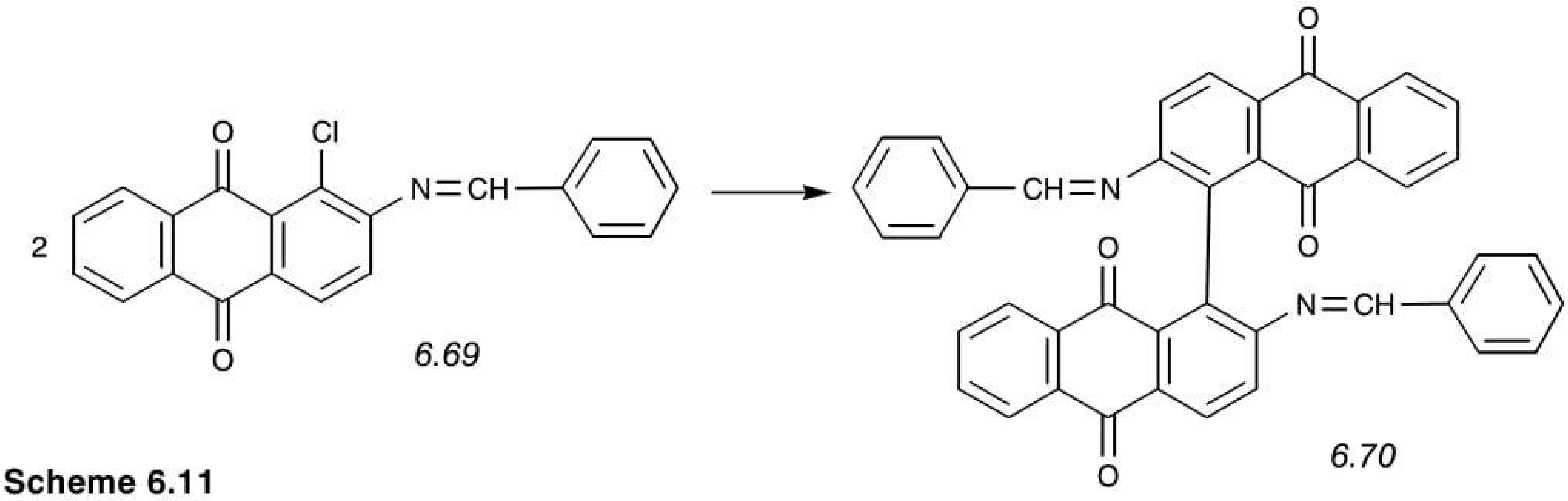


6.67

CI Vat Yellow 1



6.68

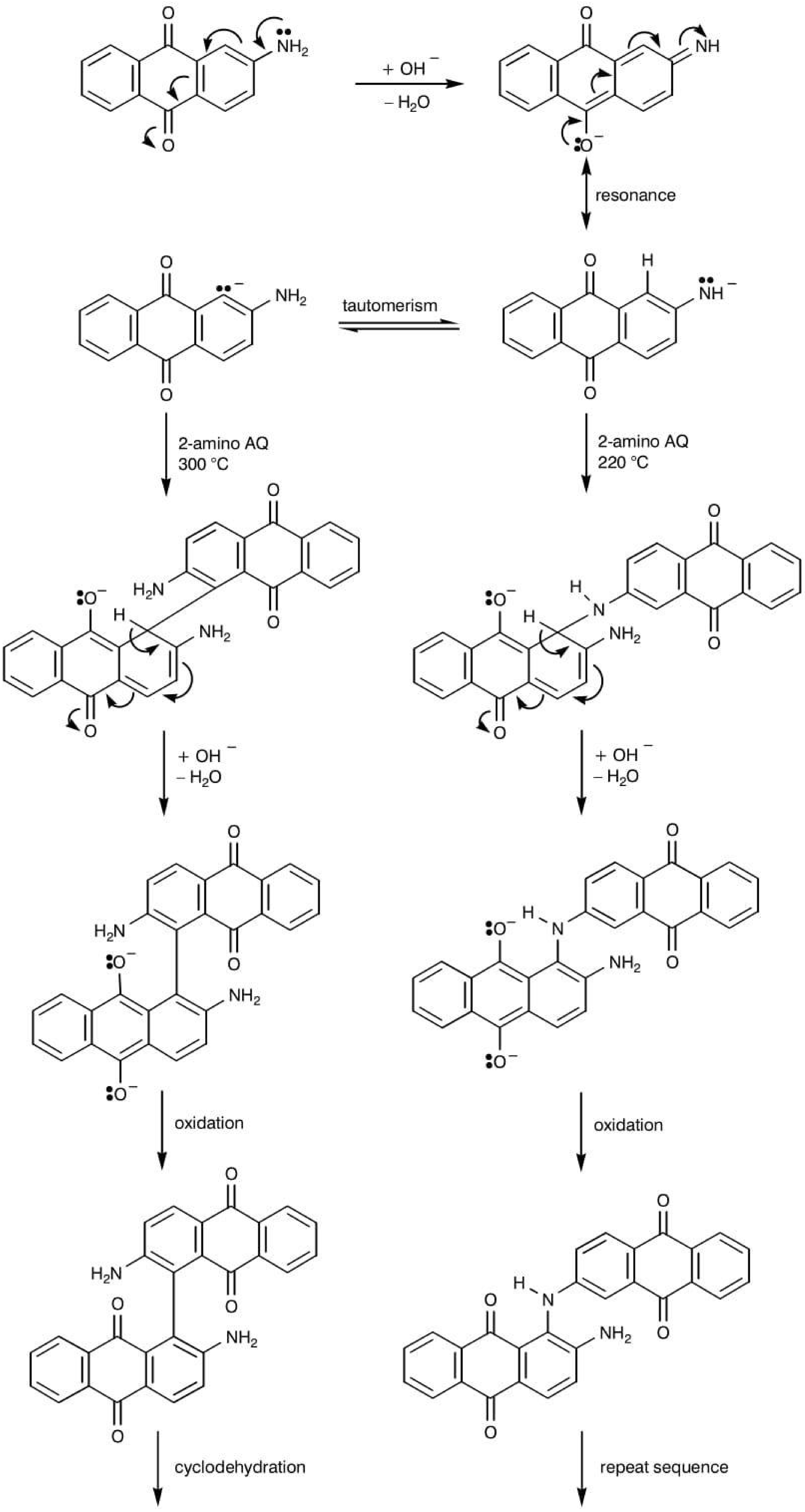


Scheme 6.11

The formation of indanthrone and flavanthrone, as well as alizarin, during the alkali fusion of 2-aminoanthraquinone can be explained mechanistically on the basis of the initial loss of a proton. The resulting anionic species can be represented as a resonance hybrid and is also tautomeric (Scheme 6.12). Primary 1-hydroxylation of 2-aminoanthraquinone is probably the first step in the formation of the alizarin by-product (compare Scheme 6.8). Such an attack may initiate the formation of flavanthrone [31]. It is also possible to envisage the formation of all three species by a radical mechanism [32].

The normal blue vat dye obtained from indanthrone corresponds to a dihydroanthraquinone (compare flavanthrone) and yields a sparingly soluble disodium salt. It seems likely that strong hydrogen bonding between the inner hydroxy groups and the azine nitrogen atoms accounts for the ready formation of the planar molecule 6.71. The infrared spectrum of the disodium salt indicates the absence of carbonyl groups. Treatment of the salt with dimethyl sulphate produces the corresponding dimethyl diether.

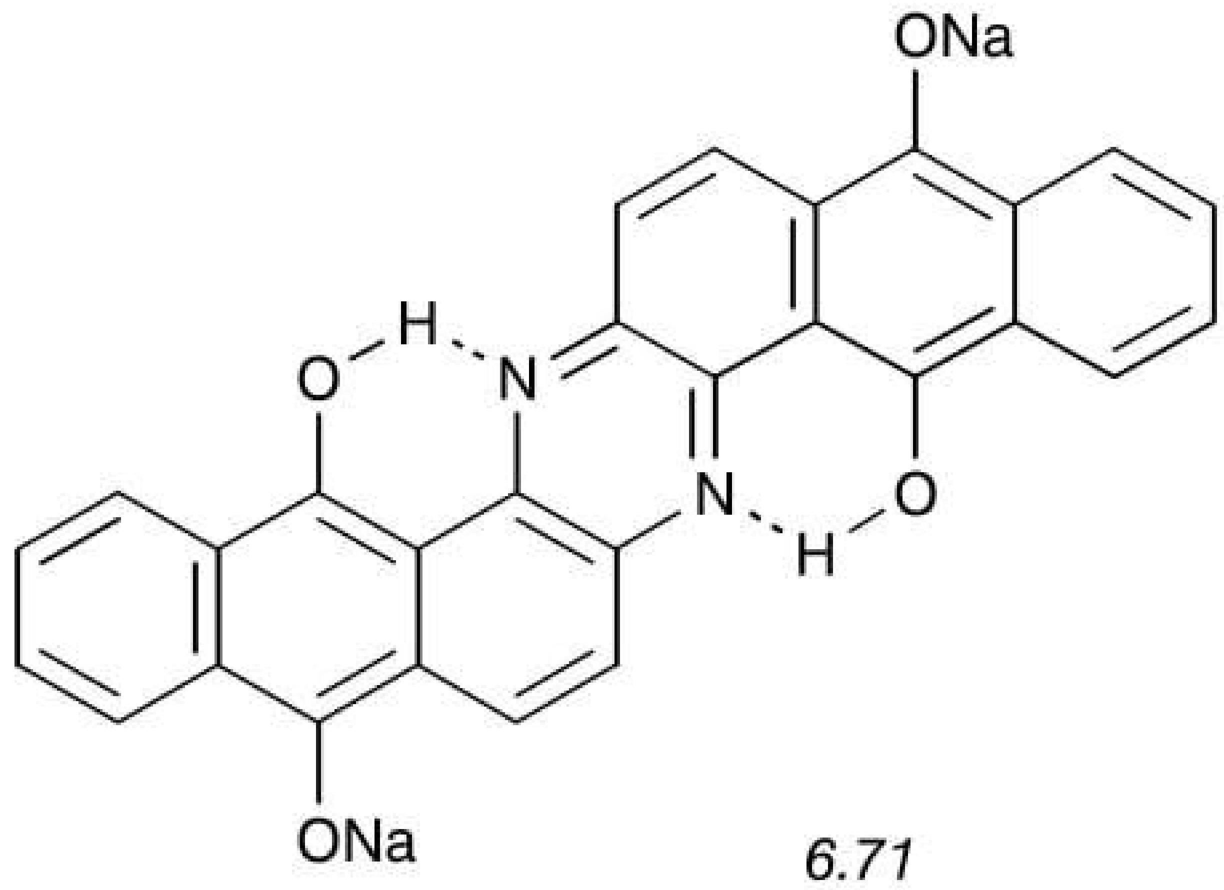
Halogenated indanthrones provide improved resistance to hypochlorite treatments and many derivatives have been examined. Direct halogenation of indanthrone leads to substitution at the 7-, 8-, 16- and 17-positions. The commercially important 7,16-dichloroindanthrone (6.72; CI Vat Blue 6) can be synthesised by a rather lengthy route from phthalic anhydride and chlorobenzene (Scheme 6.13). Polycyclic vat dyes of this type also find use as electrophotographic photoreceptors.



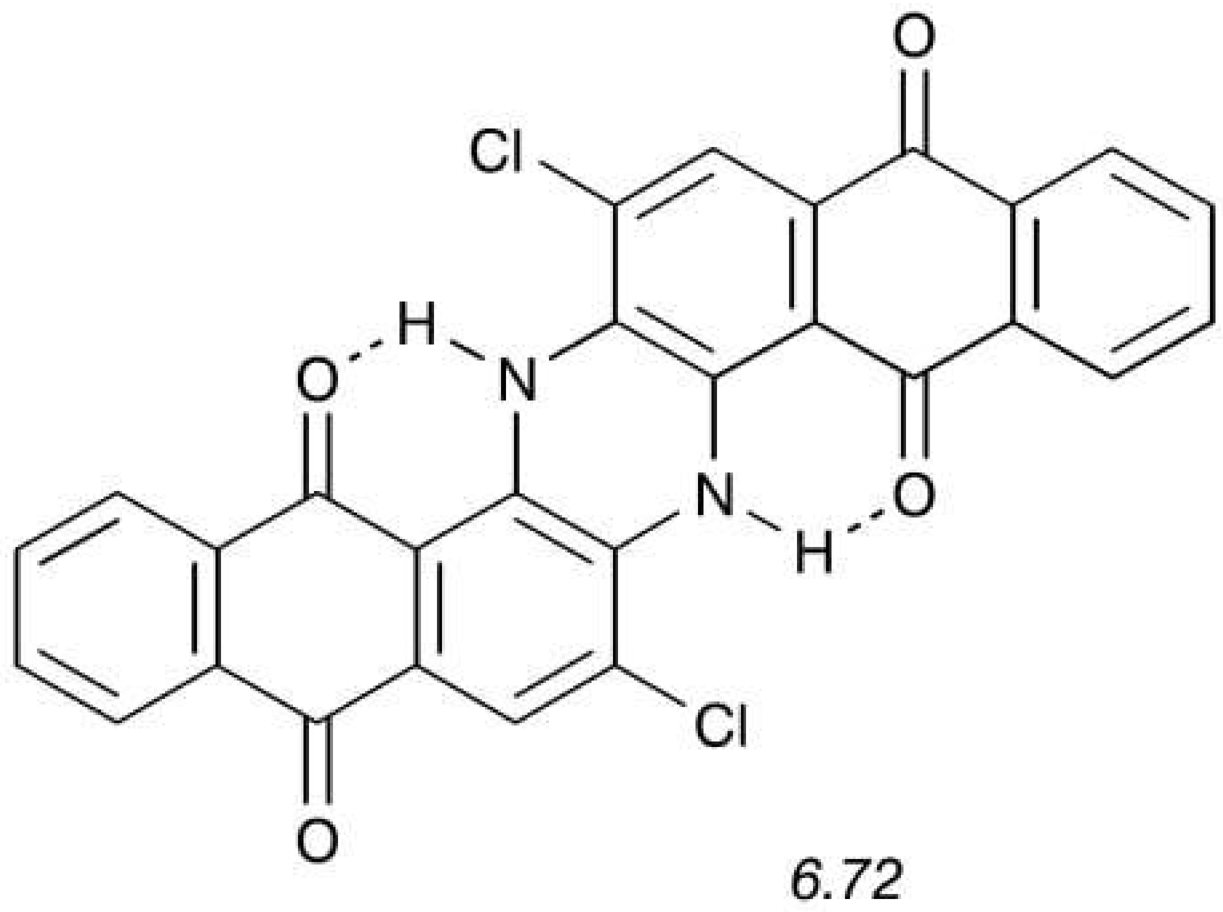
6.67
Flavanthrone

6.65
Indanthrone

Scheme 6.12

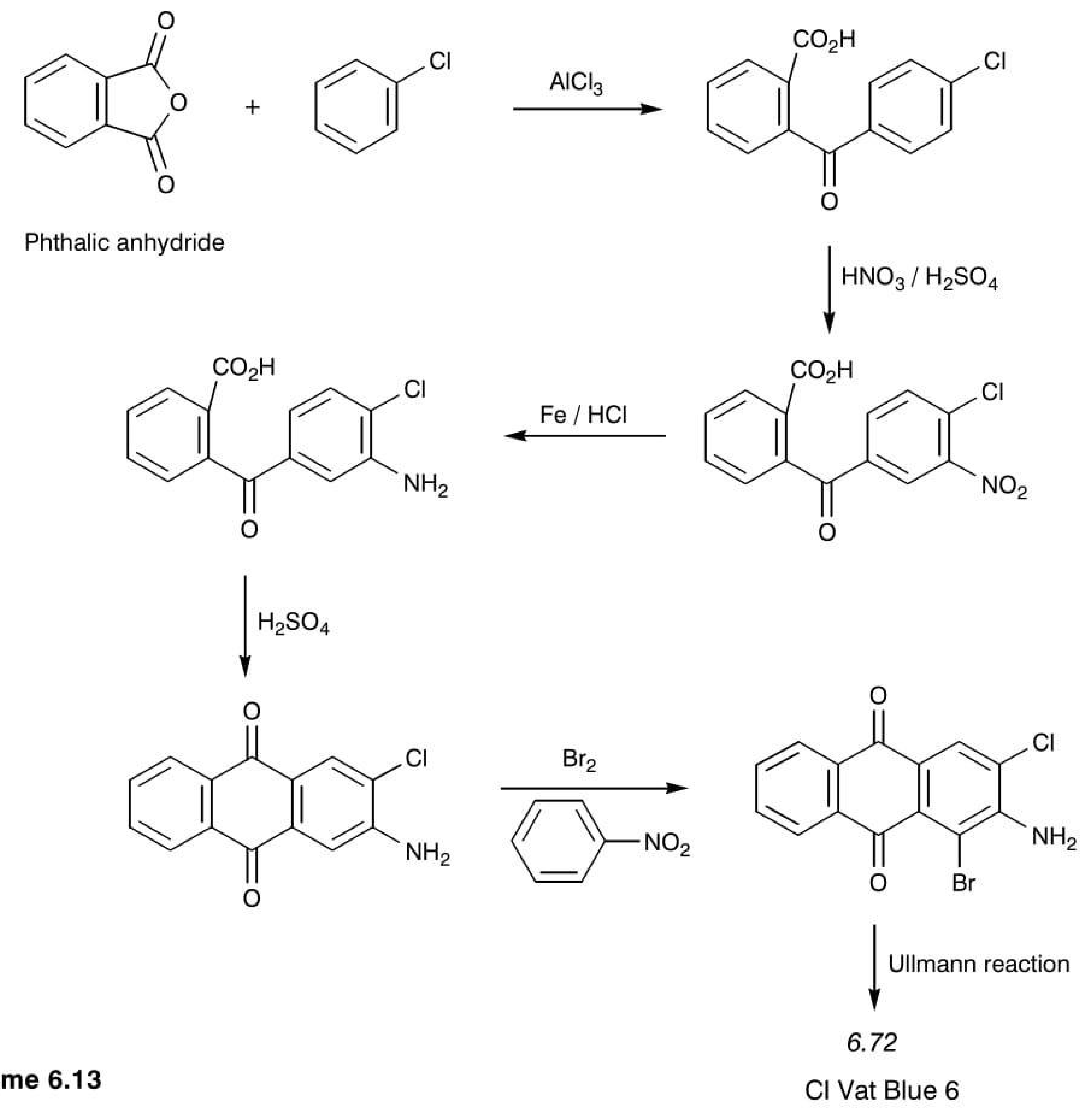


6.71



6.72

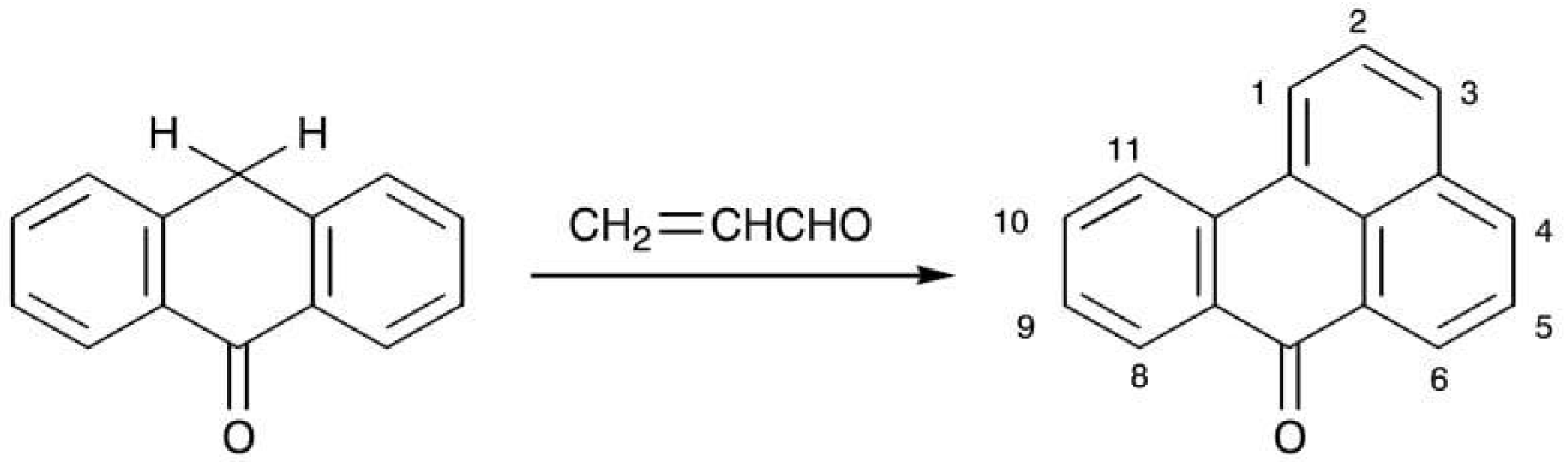
CI Vat Blue 6



Scheme 6.13

6.2.3 Benzanthrone derivatives

Benzanthrone (6.73) is the source of various commercially important violet, blue and green vat dyes. This tetracyclic system can be prepared from a mixture of anthraquinone and propane-1,2,3-triol (glycerol) by heating with iron powder in concentrated sulphuric acid. The reaction involves reduction of anthraquinone to anthrone (6.74) followed by condensation (Scheme 6.14) with propenal (acrolein), the latter compound being generated



6.74

Anthrone

6.73

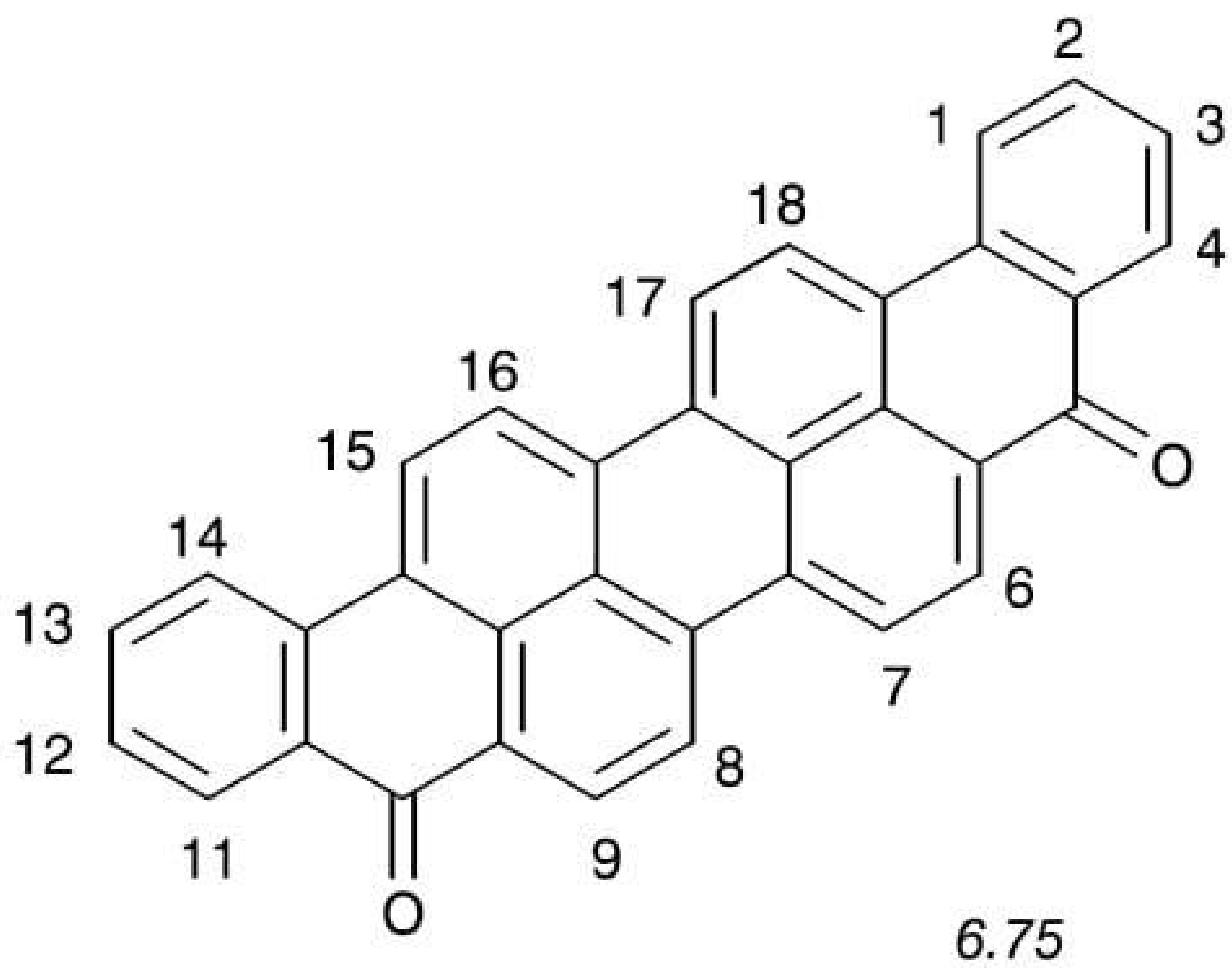
Benzanthrone

Scheme 6.14

from glycerol by dehydration. The structure of benzanthrone was confirmed by Scholl who prepared it by cyclising 1-benzoylnaphthalene with aluminium chloride.

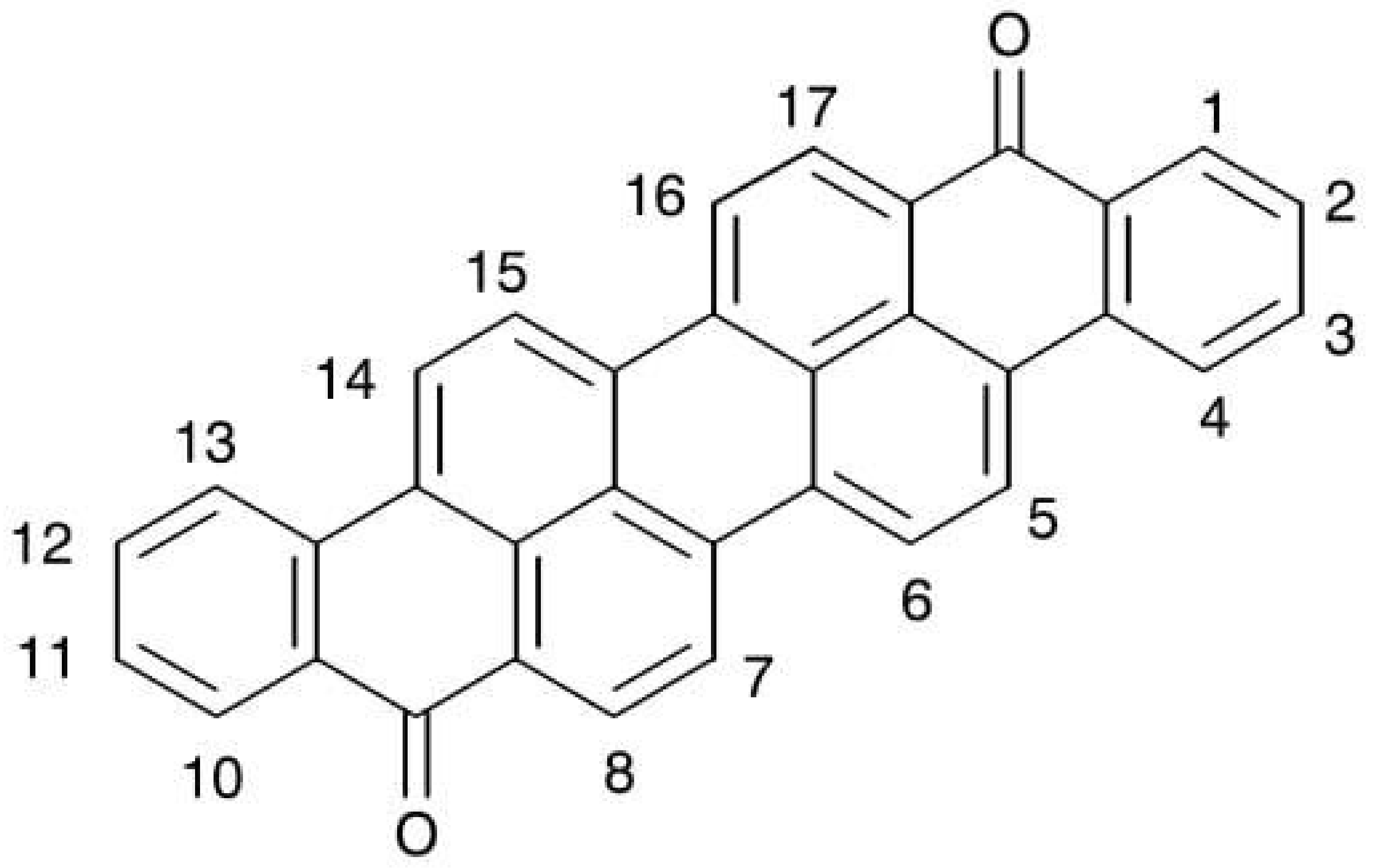
The benzanthrone system is susceptible to both electrophilic and nucleophilic attack. The most reactive sites towards electrophiles are the 3- and 9-positions, which can be compared with the 4,4′-positions in biphenyl. The 9-position is somewhat deactivated by the carbonyl group, however. Thus, for example, monobromination takes place at the 3-position and further substitution gives 3,9-dibromobenzanthrone. Nitration and benzoylation similarly give rise to the 3-substituted product. The 3-position is in fact *peri*-hindered (compare naphthalene) so that sulphonation yields the 9-sulphonic acid. Electron withdrawal by the carbonyl group activates the 4- and 6-positions towards nucleophilic attack: for example, hydroxylation occurs at these sites.

In 1904 Bally obtained a bluish violet solid by alkali fusion of benzanthrone at approximately 220 °C. Two isomeric compounds were isolated by vatting the reaction mixture and filtering off a sparingly soluble sodium salt. Oxidation of the filtrate gave a blue vat dye, violanthrone (6.75; CI Vat Blue 20), as the main component. The less soluble residue similarly afforded a violet product, isoviolanthrone (6.76; CI Vat Violet 10). The formation of isoviolanthrone can be suppressed by carrying out the fusion in a solvent such as naphthalene or a polyethylene glycol in the presence of sodium acetate and sodium nitrite. Dyes of this type are often referred to as dibenzanthrones.



6.75

CI Vat Blue 20



6.76

CI Vat Violet 10

It was established in 1929 by Lüttringhaus and Neresheimer that 4,4′-bibenzanthronyl (6.77) is an intermediate in the formation of violanthrone. Thus, compound 6.77 results when an Ullmann reaction is carried out on 4-chlorobenzanthrone; the same product is obtained when benzanthrone reacts under relatively mild conditions (approximately 110 °C) with a mixture of potassium hydroxide and potassium acetate in 2-methylpropan-1-ol (isobutanol). Alkali fusion at a higher temperature then converts 4,4′-bibenzanthronyl into violanthrone. Use of aluminium chloride also leads to ring closure (Scholl reaction).

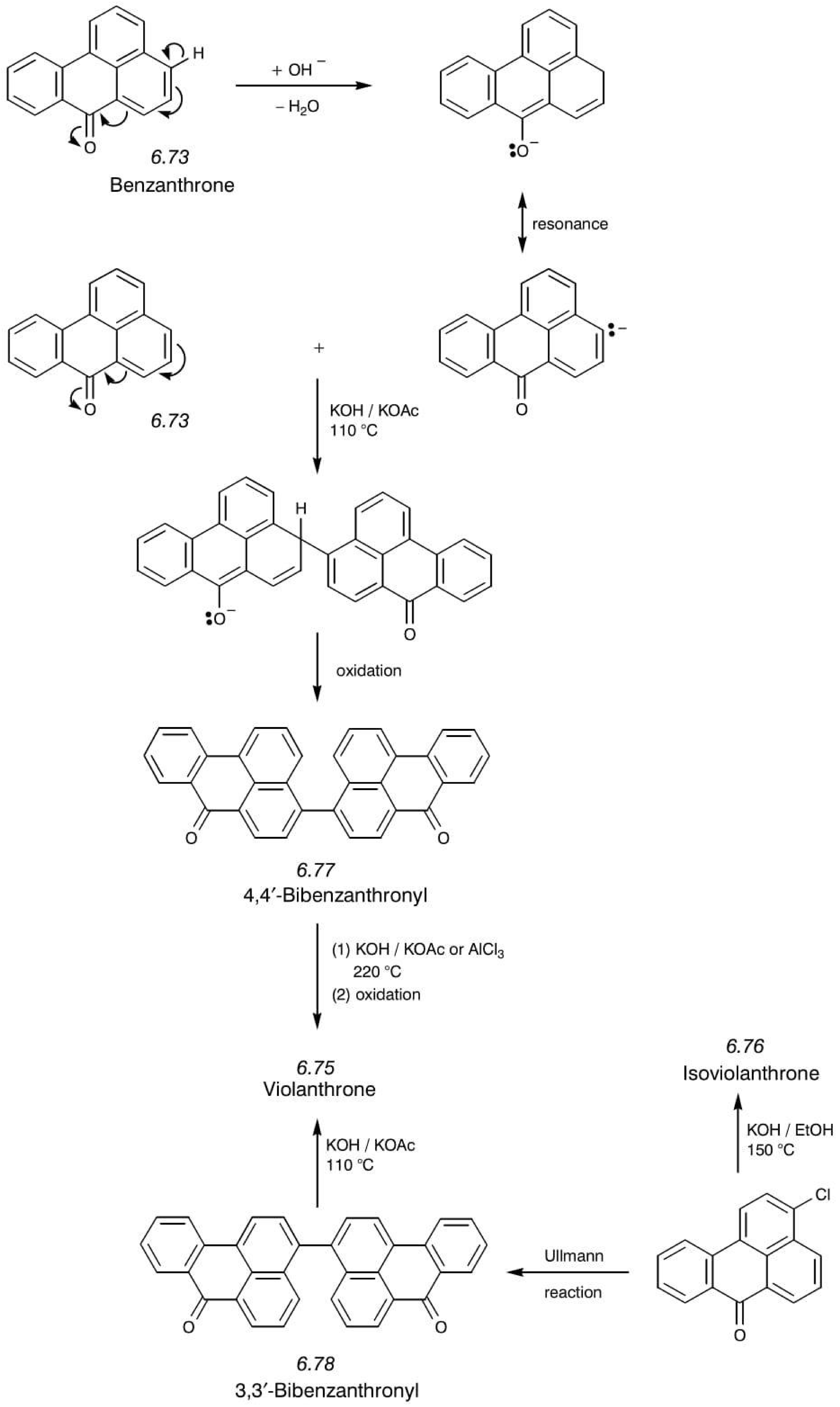
Mechanistically it is likely that the resonance-stabilised anion resulting from deprotonation at the 4-position of benzanthrone couples with non-ionised benzanthrone. Linkage across the 3- and 3′-positions under more strongly alkaline conditions may also involve loss of a proton, coupling and oxidation (Scheme 6.15). Chlorination of benzanthrone followed by an Ullmann reaction produces 3,3′-bibenzanthronyl (6.78), which readily undergoes 4,4′-coupling under mild conditions. 3,3′-Bibenzanthronyl is available from benzanthrone directly by treatment with manganese dioxide in sulphuric acid.

Isoviolanthrone (6.76) was first made by heating 3-chlorobenzanthrone with ethanolic potassium hydroxide at 150 °C (Scheme 6.15). The reaction probably involves deprotonation at the 4-position to form a carbanion which then displaces the chloro substituent in another molecule of 3-chlorobenzanthrone. Repeating the sequence in the intermediate 3,4′-bibenzanthronyl derivative then gives isoviolanthrone. In an improved, but mechanistically obscure, method of synthesis 3-chlorobenzanthrone is treated with sodium sulphide to produce 3,3′-bibenzanthronyl sulphide; this compound is converted into isoviolanthrone on refluxing with potassium hydroxide in isobutanol. Isoviolanthrone itself is no longer used as a vat dye but some halogenated derivatives are commercially available. For example, dichlorination of isoviolanthrone in nitrobenzene gives CI Vat Violet 1, which is also useful as a pigment (CI Pigment Violet 31). The greenish blue 6,15-dimethoxy derivative (CI Vat Blue 26) is also of some importance.

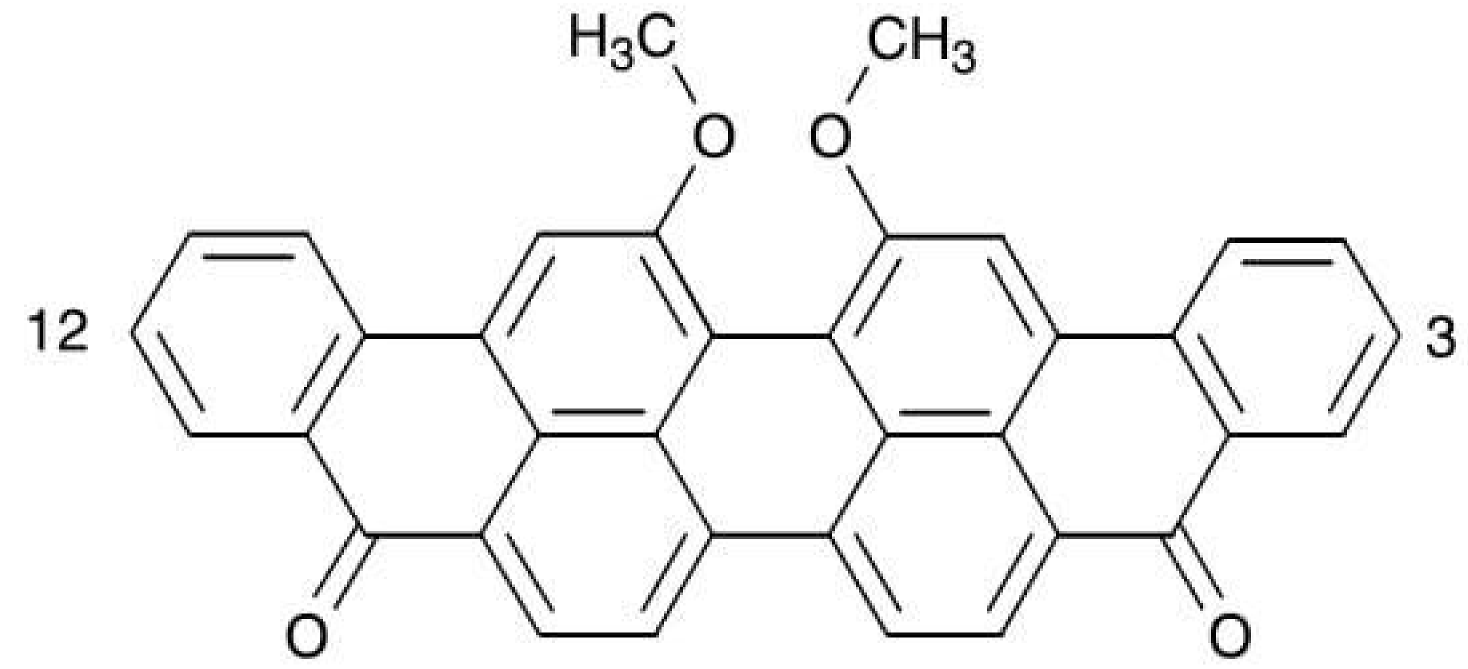
Nitration of violanthrone gives CI Vat Green 9, the main component of which is the 16-nitro derivative. Vatting gives the corresponding amino compound, which gives a bluish black hue when oxidised on the fibre. Several halogenated derivatives, such as the trichloro derivative CI Vat Blue 18, are of industrial significance.

Of special importance is the outstanding bright green vat dye originally marketed by Scottish Dyes as Caledon Jade Green (6.79; CI Vat Green 1), discovered in 1920 by Davies, Fraser-Thomson and Thomas. Oxidation of violanthrone with manganese dioxide and sulphuric acid gives 16,17-dihydroxyviolanthrone. Methylation of this diol yields the dimethoxy derivative (6.79). This dye has excellent fastness to light, alkali and chlorine. Its constitution was confirmed by a lengthy synthesis from 2-methoxybenzanthrone. An alternative method of manufacture involves the oxidation of 4,4′-bibenzanthronyl (6.77) with manganese dioxide and sulphuric acid to give violanthrone-16,17-dione (6.80), which on reduction with sodium bisulphite gives an excellent yield of the 16,17-diol. Treatment of CI Vat Green 1 with bromine in oleum gives the 3,12-dibromo derivative (CI Vat Green 2). The substitution pattern was confirmed by the n.m.r. spectrum of the dimethyl diether of the leuco compound. Many other alkyl derivatives of 16,17-dihydroxyviolanthrone have been examined but few remain of commercial significance. Of some interest is the navy blue vat dye CI Vat Blue 16, in which the 16- and 17-positions are connected by an ethylenedioxy bridge (6.81).

Violanthrone and isoviolanthrone are effectively *cis* and *trans* isomers. The important *cis* compound absorbs more intensely and at a longer wavelength than the *trans* isomer (Table

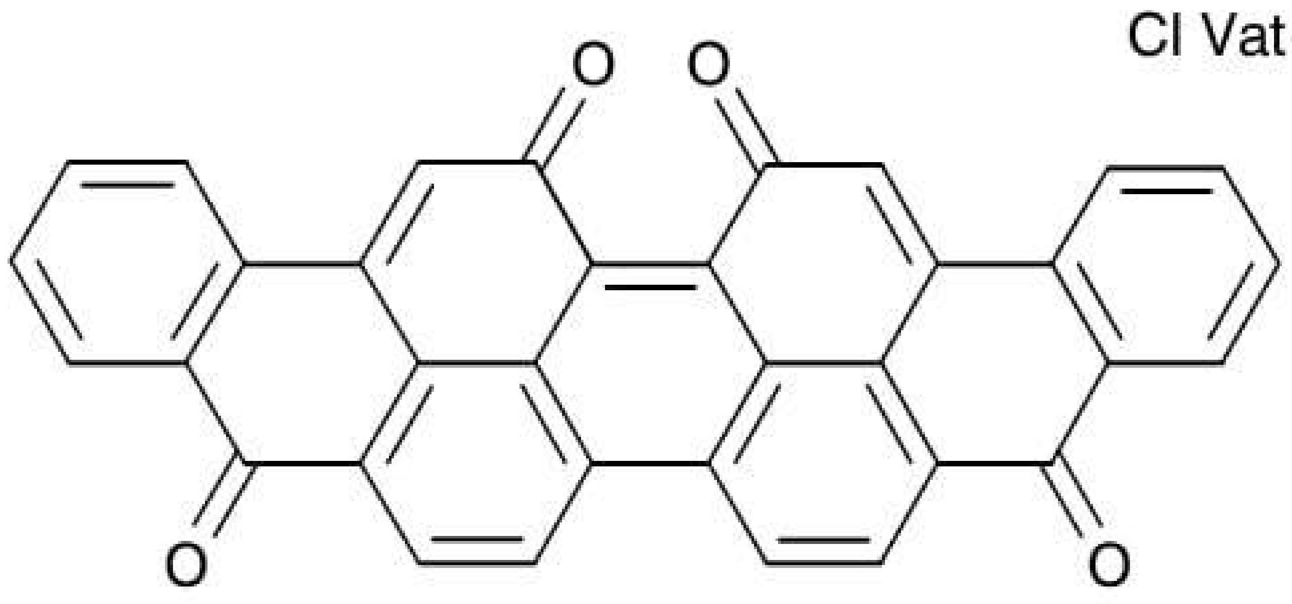

H
+ OH −
− H2O
O
6.73
Benzanthrone
O−
resonance
+
KOH / KOAc
110 °C
O
6.73
O
H
O−
O
oxidation
O
O
6.77
4,4′-Bibenzanthronyl
(1) KOH / KOAc or AlCl3
220 °C
(2) oxidation
6.75
Violanthrone
6.76
Isoviolanthrone
KOH / EtOH
150 °C
KOH / KOAc
110 °C
Cl
Ullmann
reaction
O
O
O
6.78
3,3′-Bibenzanthronyl

Scheme 6.15



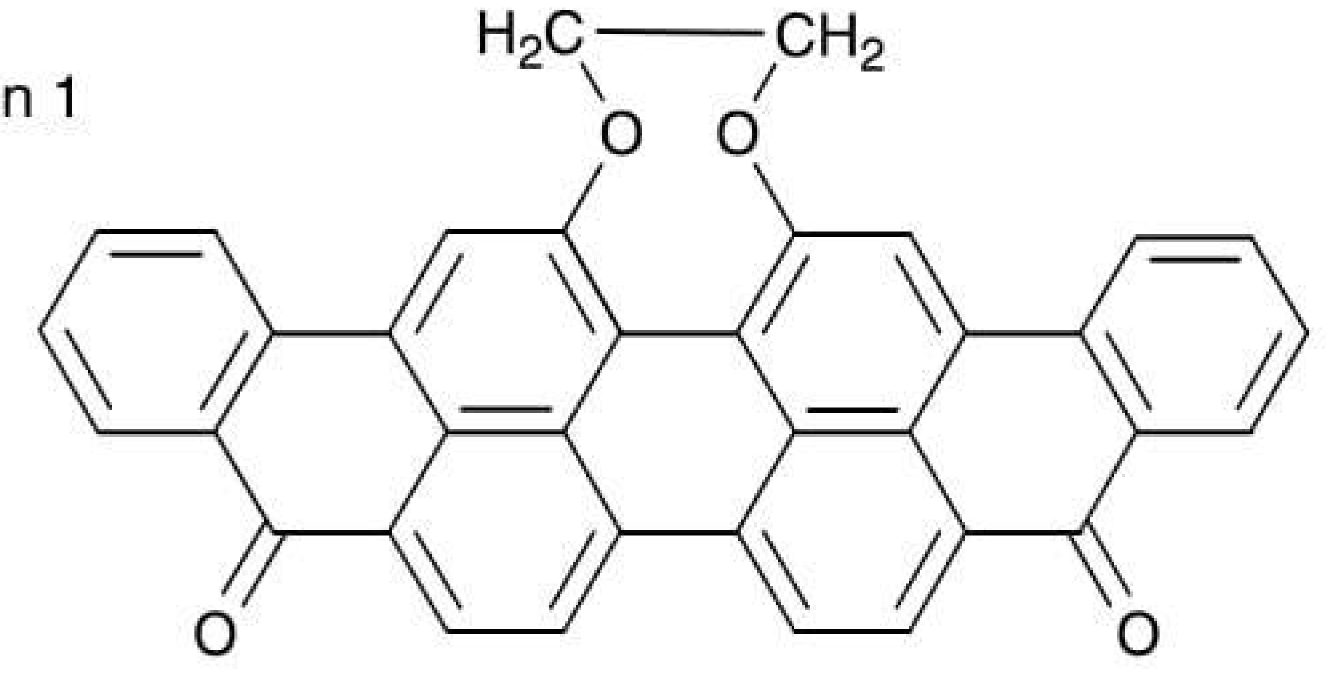
6.79

CI Vat Green 1



6.80

Violanthrone-16,17-dione



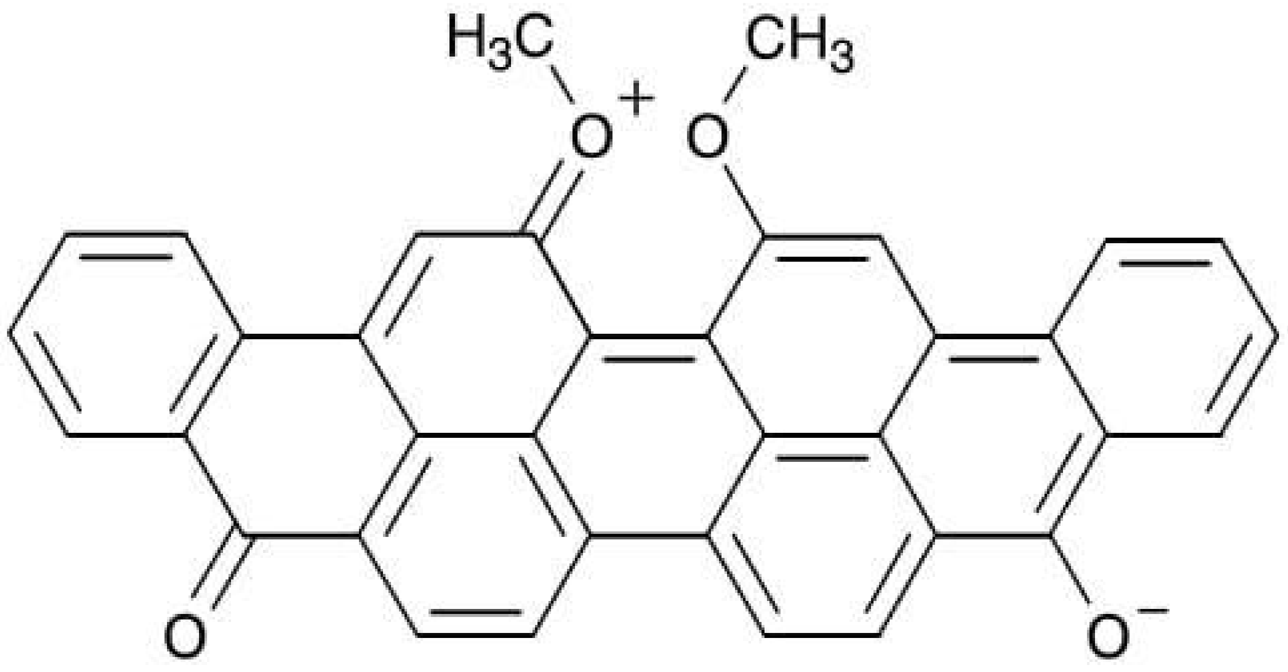
6.81

CI Vat Blue 16

6.3). These differences are found to be general for this type of vat dye and can be accounted for theoretically by the PPP-MO approach [33]. It is of interest to compare the absorption maxima of violanthrone and some of its derivatives in Table 6.3. Steric crowding at an essential single bond [34] normally results in a hypsochromic shift of the absorption band as shown by the 16,17-dimethyl derivative and, to a lesser extent, by the 16-methoxy compound. In contrast, however, the blue 16,17-bridged violanthrone (6.81) exhibits a bathochromic effect that is somewhat greater in the green dimethoxy analogue. Since the steric requirements of the two methoxy groups are not significantly less than those of the equivalent methyl groups, it must be concluded that this bathochromic shift is electronic in origin. A possible explanation is the formation of a stabilised excited state (6.82) in the case of the dimethoxy dye in which some attraction exists between the adjacent oxygen atoms; any steric clash can be minimised by rotation of the methoxy groups away from the plane of the ring system. A pronounced bathochromic effect is also exhibited by the 7,8-dimethoxy isomer, in which the substituents are similarly situated, but not by the 3,12-dimethoxy compound [32]. It is likely that the constraint imposed by the puckered eight-membered ring in the 16,17-bridged dye reduces the interaction between the oxygen lone-pair orbitals and the π-orbitals of the polycyclic system.

Table 6.3 Spectral data for some dibenzanthrones in dimethylformamide

CI Vat	Compound	λ_{max} (nm)	ε_{max}
Violet 10	Isoviolanthrone (6.76)	588	41 700
Blue 20	Violanthrone (6.75)	600	60 260
	16-Methoxyviolanthrone	598	38 900
Green 1	16,17-Dimethoxyviolanthrone	636	41 700
Blue 16	16,17-Bridged violanthrone	618	
	16,17-Dimethylviolanthrone	575	

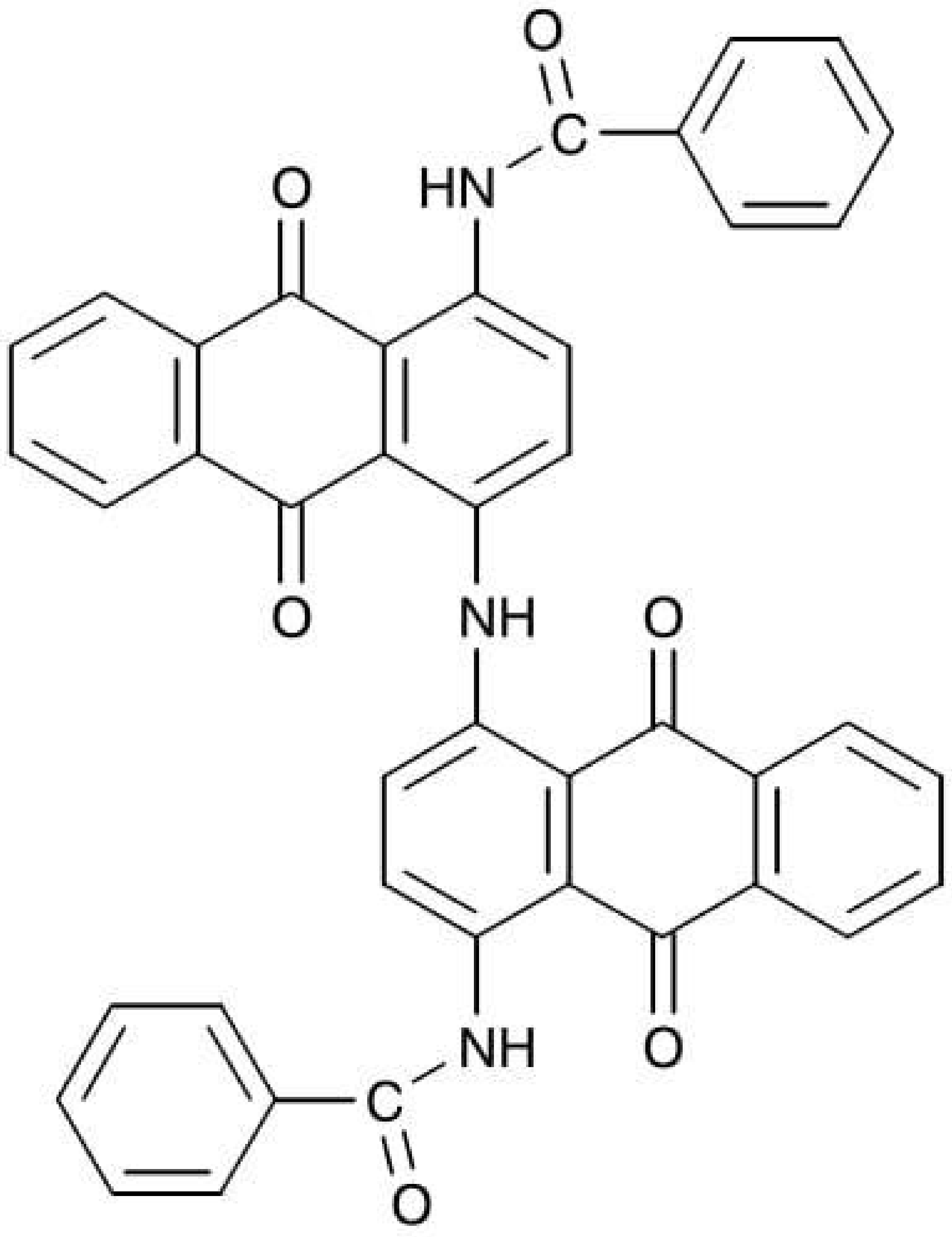


6.82

6.2.4 Carbazole derivatives

Diphthaloylcarbazole derivatives constitute an important group of vat dyes, possessing good all-round fastness properties and providing hues ranging from yellow to black.

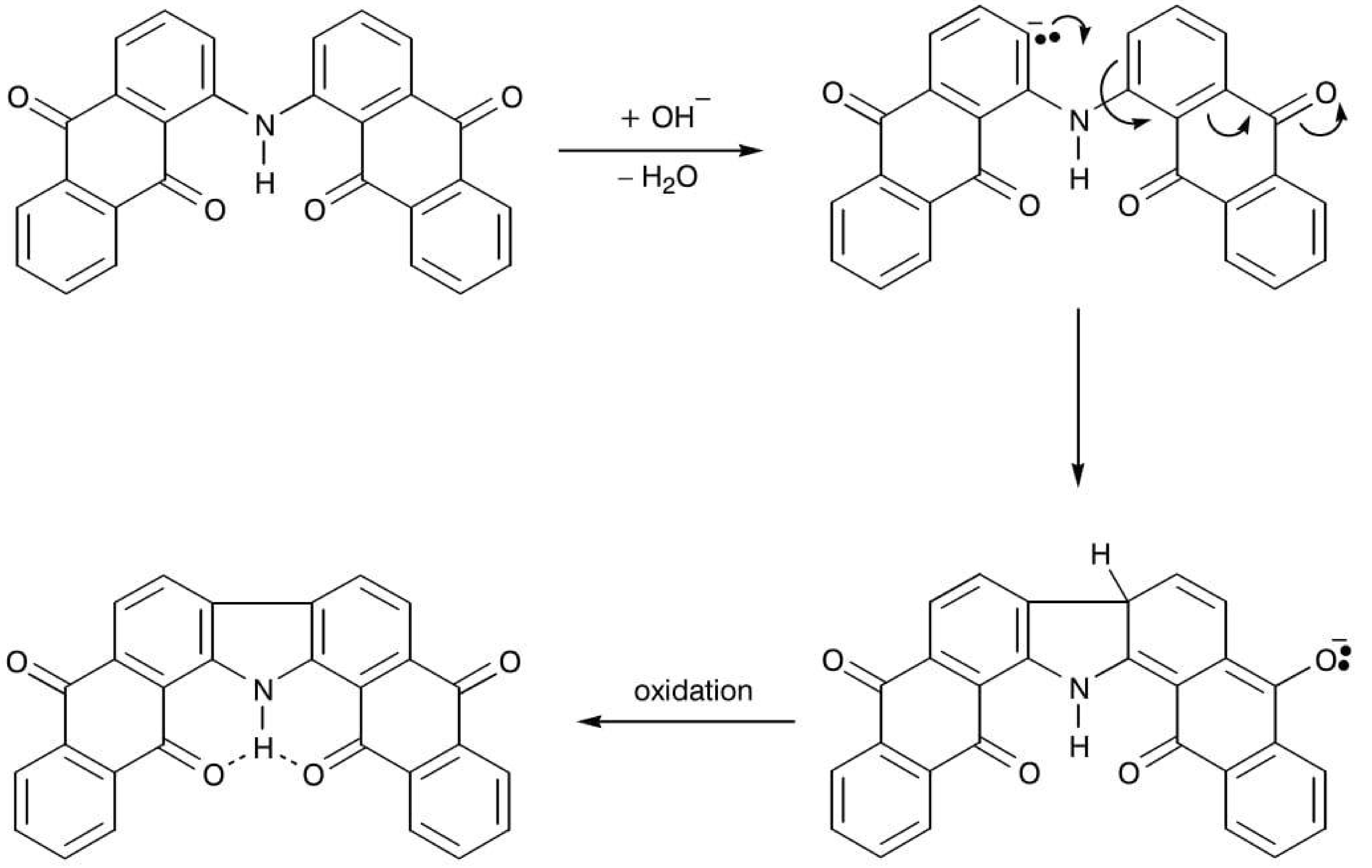
The precursors of the carbazoles are the anthrimides, in particular the 1,1′-dianthraquinonylamines (1,1′-dianthrimides). These intermediates were originally used as vat dyes themselves, but very few give bright colours and the vatting process also brings about reduction to 1-aminoanthraquinone. Only one dianthrimide is currently active in the *Colour Index* [11]; this grey vat dye is CI Vat Black 28 (6.83). 1,1′-Dianthrimides are easily prepared by heating a 1-aminoanthraquinone with a 1-chloroanthraquinone in nitrobenzene or another solvent in the presence of sodium carbonate and a copper catalyst.



6.83

CI Vat Black 28

In 1910 Mieg found that 1,1′-dianthrimides undergo carbazolisation (ring closure) when heated with potassium hydroxide at approximately 220 °C or with aluminium chloride at a somewhat lower temperature (Scholl reaction). The simplest dye of this type (6.84; CI Vat Yellow 28) is no longer manufactured. Cyclisation under strongly basic conditions is probably initiated by deprotonation (Scheme 6.16); an oxidation step is necessary after ring closure. The characteristic structure of this type of vat dye, which is stabilised by intramolecular hydrogen bonding (6.84), was established by an alternative synthesis based on the Graebe



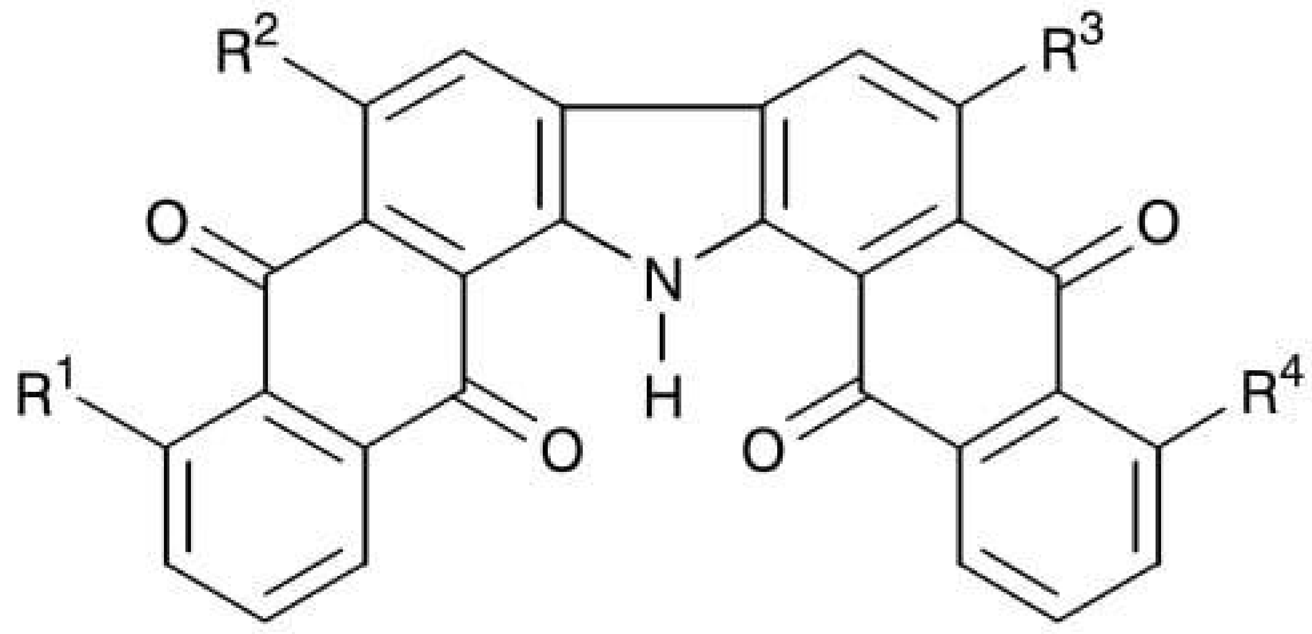
6.84

CI Vat Yellow 28

Scheme 6.16

route to carbazole and involving an Ullmann reaction with 2-chloro-1-nitroanthraquinone, followed by reduction and cyclisation.

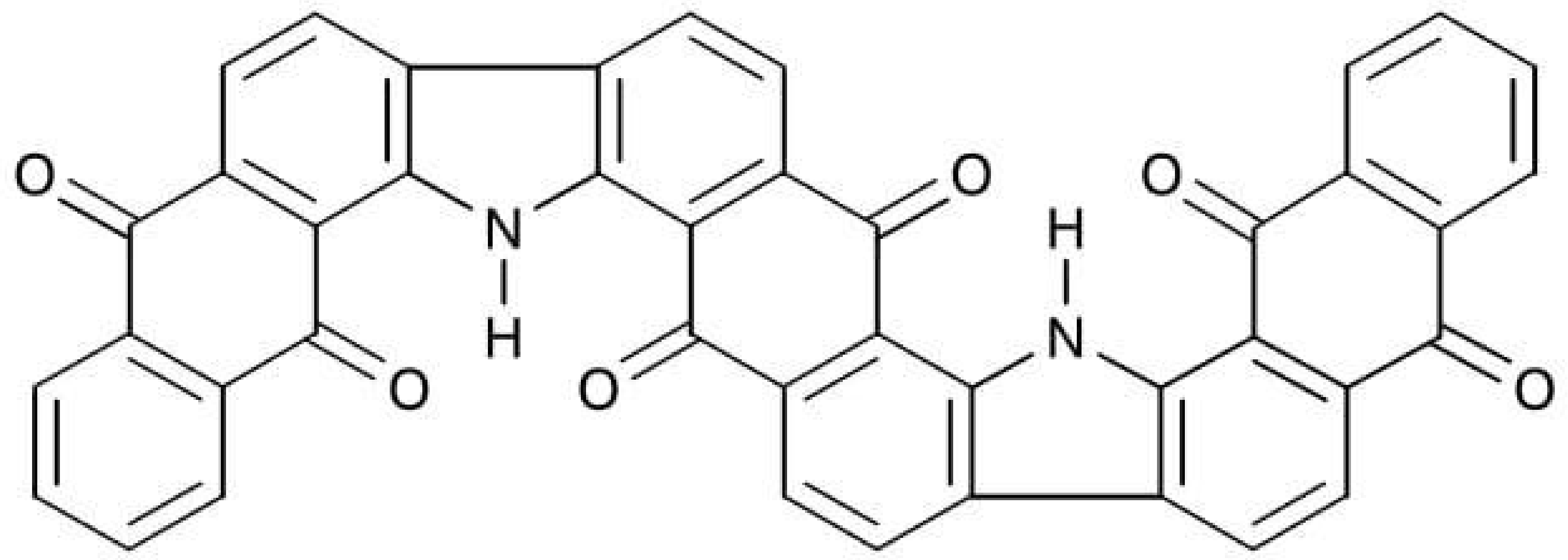
The parent dye (6.84), which has a phototendering action on cellulose, is now obsolete but several relatively simple benzoylamino derivatives are of commercial importance. Thus CI Vat Orange 15 (6.85; $R^1 = R^4 =$ NHCOPh, $R^2 = R^3 =$ H) is a 1,5-diaminoanthraquinone type whereas the more bathochromic olive vat dye CI Vat Black 27 (6.85; $R^1 = R^4 =$ H, $R^2 = R^3 =$ NHCOPh) is a 1,4-diaminoanthraquinone derivative. The unsymmetrically substituted isomer (6.85; $R^1 = R^3 =$ H, $R^2 = R^4 =$ NHCOPh) is a useful brown vat dye (CI Vat Brown 3).



6.85

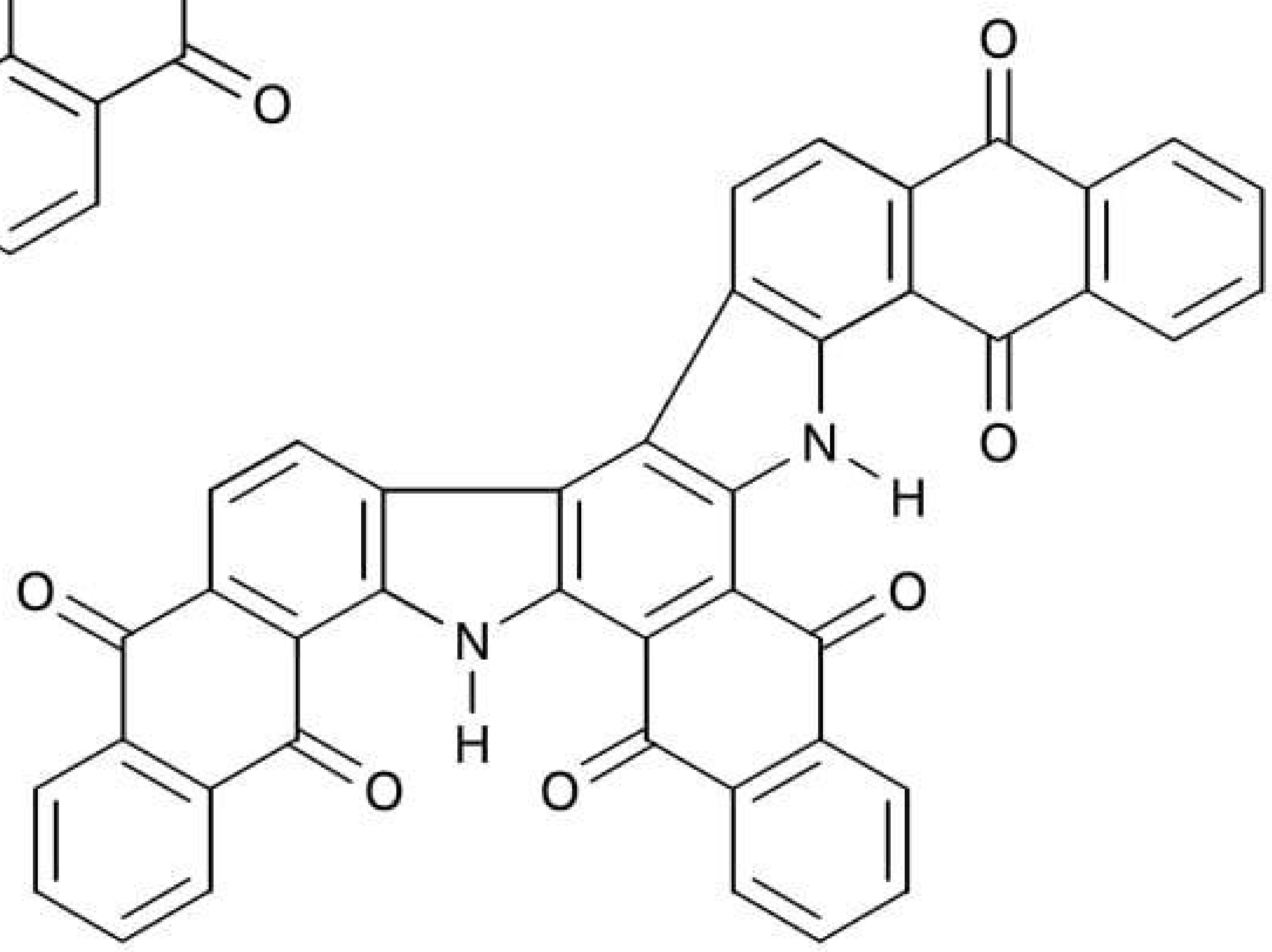
The presence of two benzoylamino groups in the dianthrimide system permits carbazole ring closure to take place relatively easily in concentrated sulphuric acid at approximately 30 °C. It is likely that the benzoylamino groups assist protonation at the adjacent carbonyl group and thereby aid the subsequent cyclisation process. The final oxidation step can take place with sulphuric acid alone. It is possible that the cyclisation occurs by a radical mechanism [32].

Various more complex dyes of industrial significance contain more than one carbazole system. For example, CI Vat Orange 11 (6.86) contains two carbazole components and a central unit derived from 1,5-diaminoanthraquinone. This dye is prepared by carbazolisation of the trianthrimide produced when two moles of 1-chloroanthraquinone react with one mole of 1,5-diaminoanthraquinone. The equivalent isomeric dye obtained from 1,4-diaminoanthraquinone is reddish brown (6.87; CI Vat Brown 1). The interesting, symmetrically-substituted tetracarbazole dye CI Vat Green 8 (6.88) was first synthesised in 1911 by Hepp from 1,4,5,8-tetrachloroanthraquinone. Not surprisingly, the product ($C_{70}H_{28}N_4O_{10}$; relative molecular mass 1084) is of very low solubility. The structure was confirmed in 1957 by Jayaraman, who found no evidence of uncyclised anthrimides in the UV spectrum of the dye solution in concentrated sulphuric acid [32].



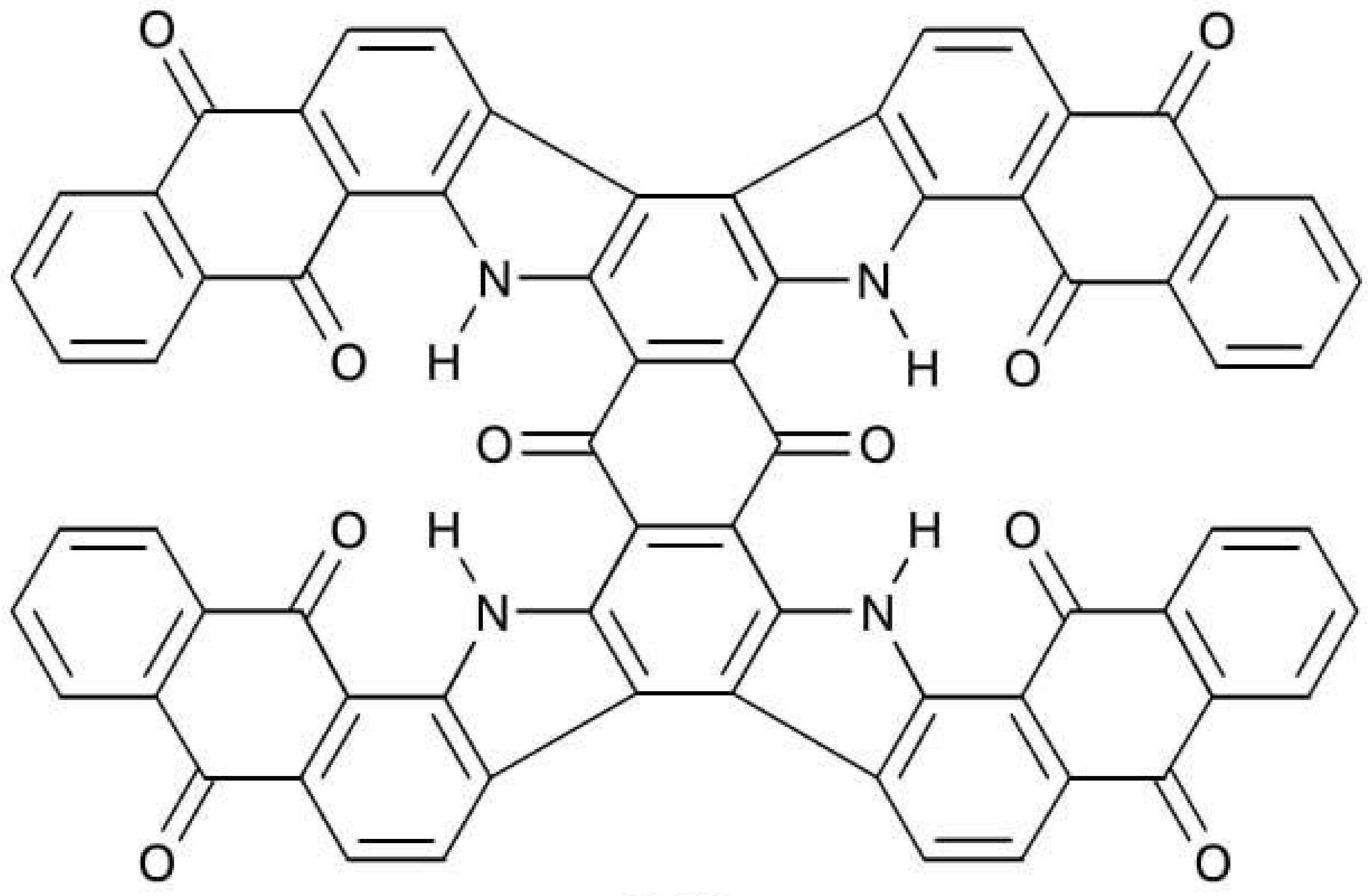
6.86

CI Vat Orange 11



6.87

CI Vat Brown 1

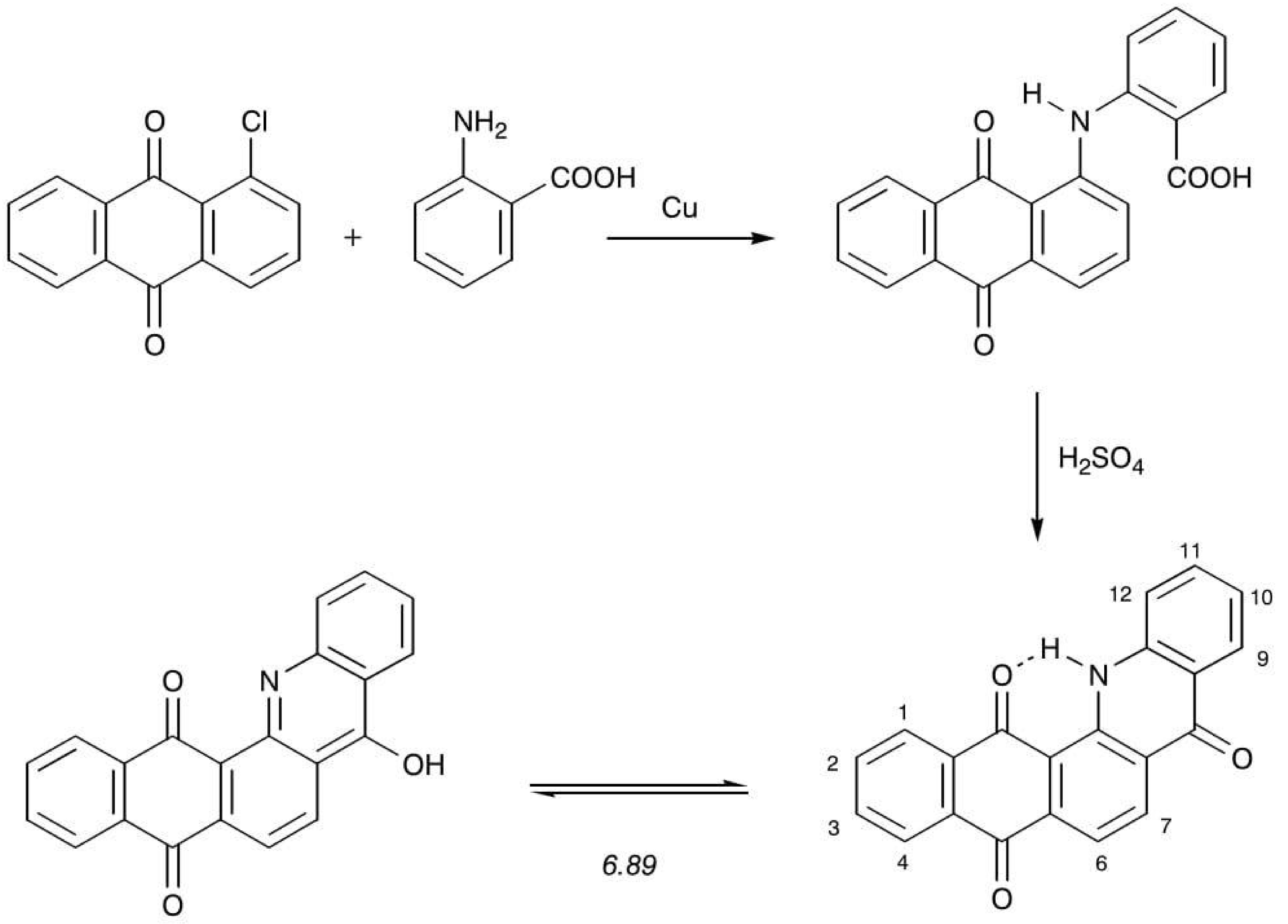


6.88

CI Vat Green 8

6.2.5 Acridone derivatives

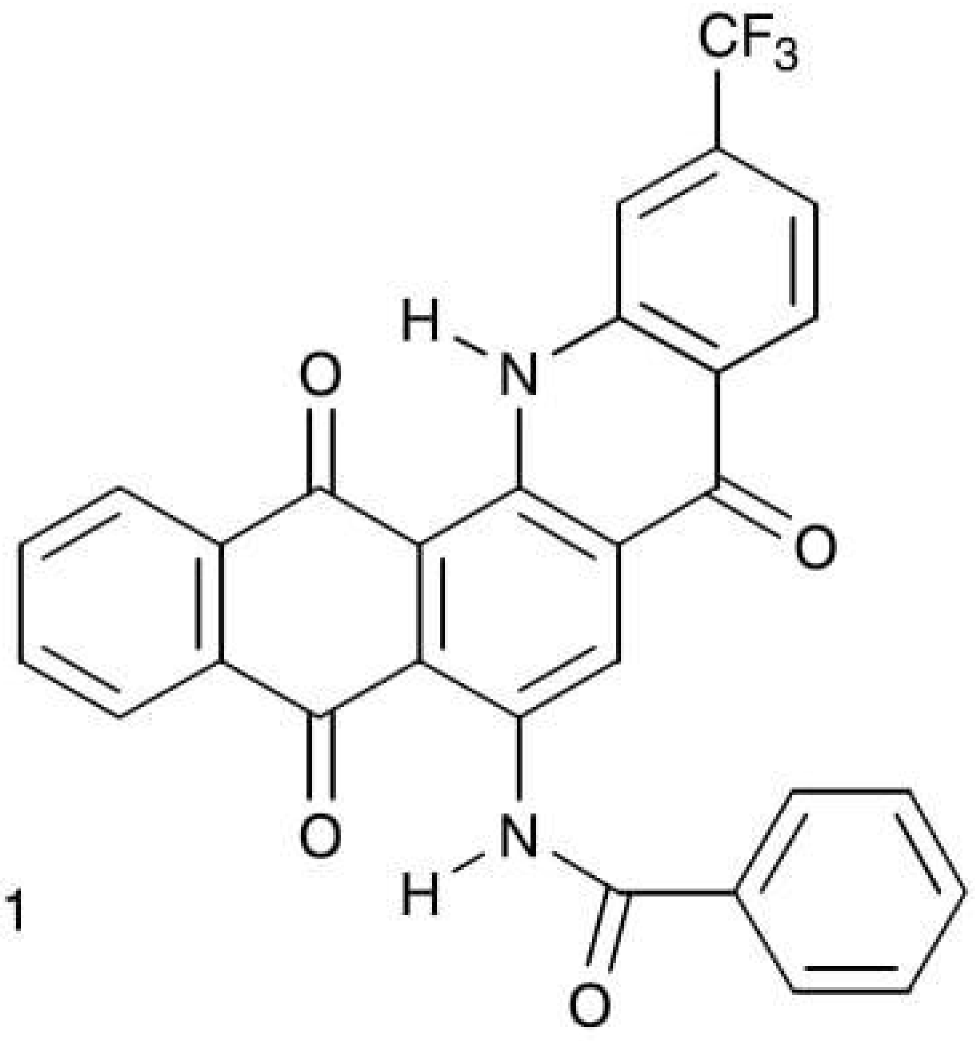
The first anthraquinone vat dye containing an acridone ring system was synthesised in 1909 by Ullmann. The parent compound (6.89) can be made by condensation of 1-chloroanthraquinone with anthranilic acid in the presence of copper, followed by cyclodehydration in concentrated sulphuric acid (Scheme 6.17).



Scheme 6.17

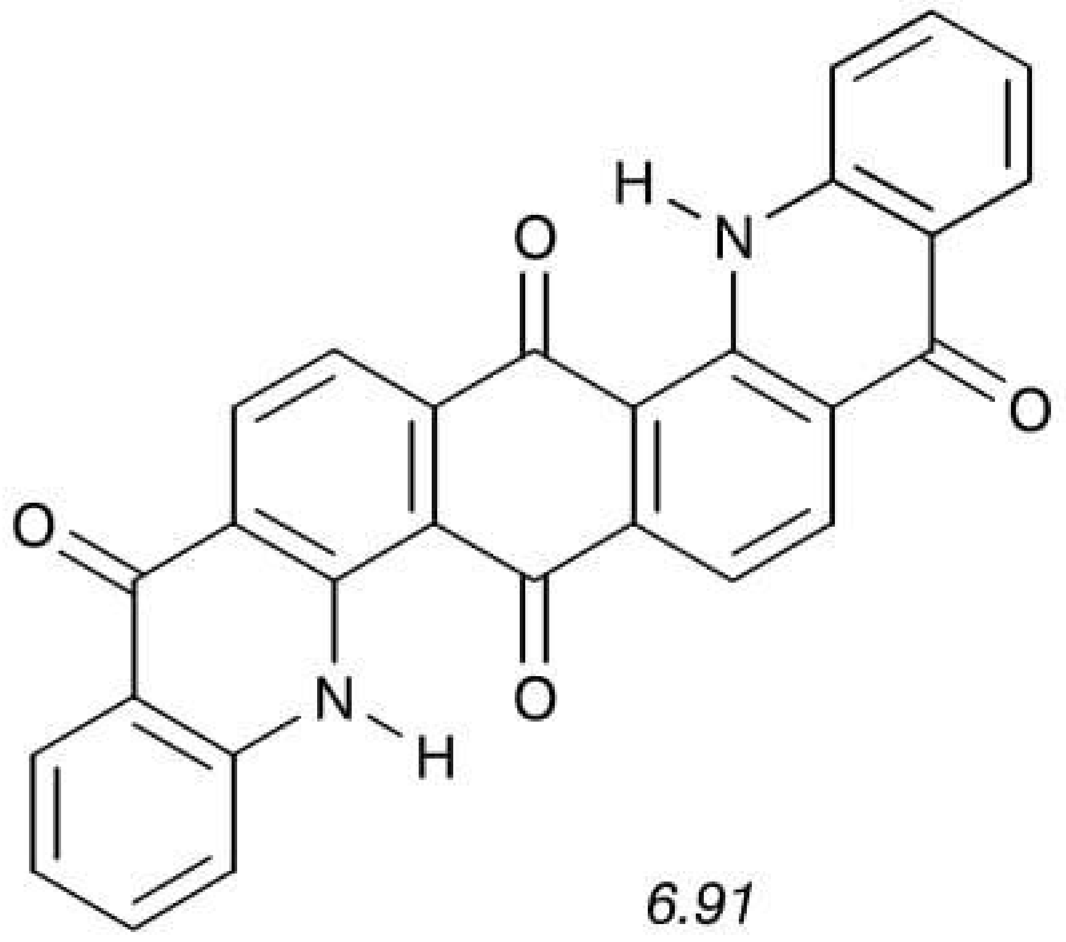
Alternatively, the synthesis may begin by condensing aniline with the 1-chloro-2-carboxy intermediate. Acridone vat dyes of this type have excellent light fastness but only moderate resistance to alkali due to the keto-enol equilibrium. It is interesting that this pentacyclic dye is approximately 30 nm more bathochromic than the closely related tetracyclic 1-amino-2-benzoylanthraquinone.

The parent acridone is not useful as a vat dye, although some halogenated derivatives are commercially important. Chlorination of dye 6.89 with sulphuryl chloride gives the reddish violet CI Vat Violet 14, which consists mainly of the 6,10,12-trichloro compound. The colour of acridone derivatives is very sensitive to the number and position of substituents; for example, the 6-chloro derivative is violet, whereas the 9,12-dichloro compound is red and its 9,11-isomer is orange. The presence of a substituted amino group at the 6-position leads to blue dyes such as CI Vat Blue 21 (6.90). This dye is obtained from bromamine acid (6.10) and 4-trifluoromethylanthranilic acid, followed by ring closure, during which desulphonation takes place, and finally benzoylation. The relatively simple bisacridone CI Vat Violet 13 (6.91) is the original dye made in 1909 by Ullmann from 1,5-dichloroanthraquinone; this product is still of industrial importance.



6.90

CI Vat Blue 21

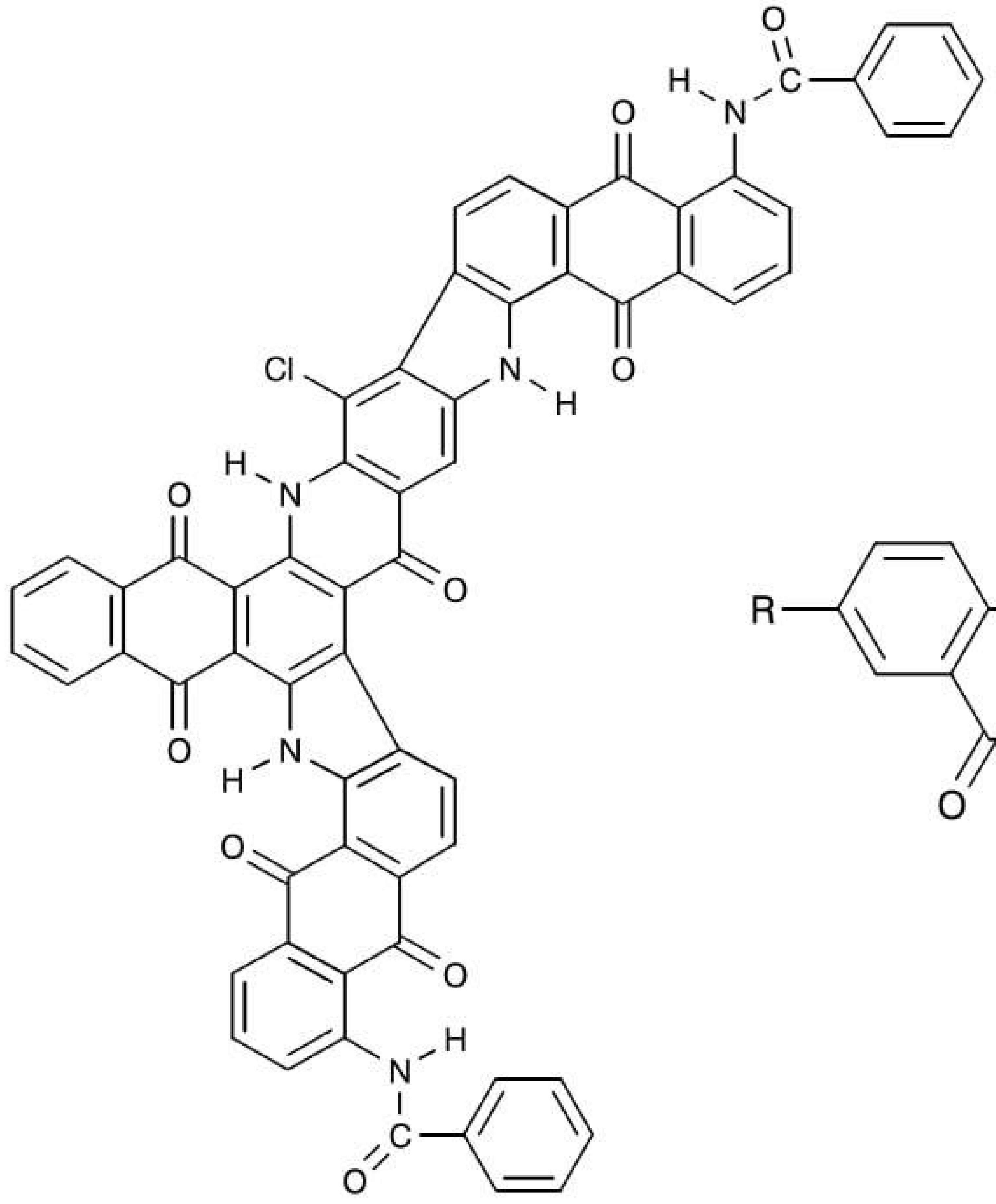


6.91

CI Vat Violet 13

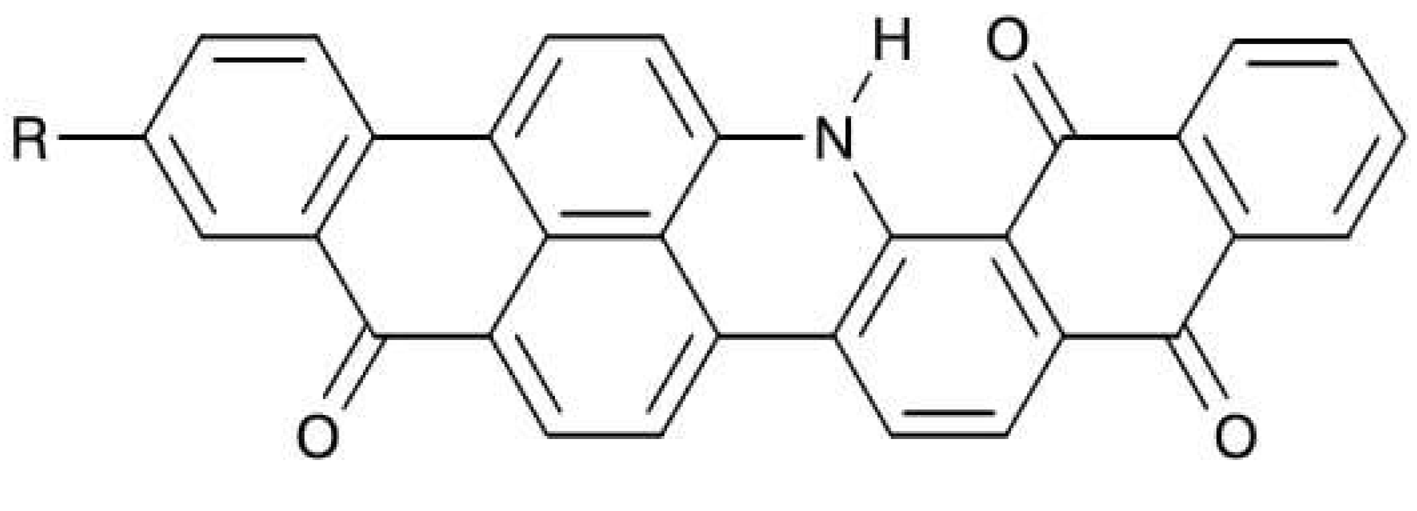
Various complex carbazole-acridone dyes have been exploited to obtain brown, khaki, grey and olive hues. The fused carbazole-acridone CI Vat Brown 55 (6.92), which possesses excellent all-round fastness properties, is currently available. This compound can be obtained from the 6,10,12-trichloro derivative (CI Vat Violet 14) by condensation with two equivalents of 1-amino-5-benzoylaminoanthraquinone, followed by carbazolisation.

The important olive green dye CI Vat Green 3 (6.93; R = H), which has outstanding light fastness, can be regarded as an acridone analogue. This dye is readily available by condensing 3-bromobenzanthrone with 1-aminoanthraquinone under Ullmann conditions followed by ring closure with potassium hydroxide. A useful derivative (6.93; R = 1-anthraquinonylamino), prepared in a similar manner from 3,9-dibromobenzanthrone, is a brownish grey dye (CI Vat Black 25).



6.92

CI Vat Brown 55

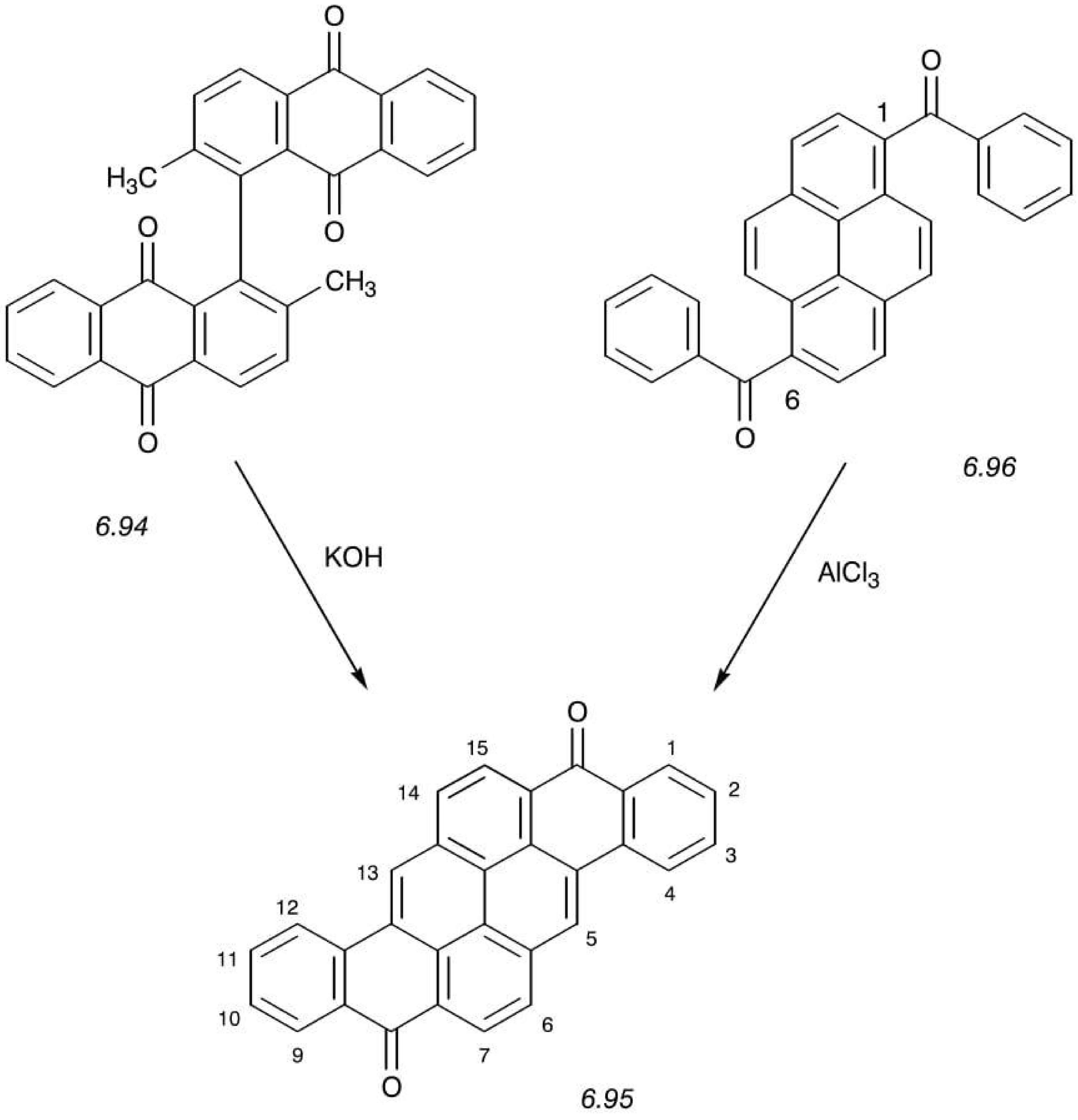


6.93

6.2.6 Miscellaneous polycyclic quinones

The carbocyclic analogue of flavanthrone was first prepared in 1905 by Scholl. Chlorination of 2-methylanthraquinone with sulphuryl chloride yields the 1-chloro derivative, which under Ullmann conditions gives 2,2′-dimethyl-1,1′-bianthraquinonyl (6.94). Treatment of the latter compound with ethanolic potassium hydroxide produces pyranthrone (6.95; CI Vat Orange 9). This cyclisation reaction (Scheme 6.18) was the first example of its kind and probably proceeds via carbanion formation. As well as being an anthrone derivative, pyranthrone is a fused benzanthrone and also contains a central pyrene ring system. Pyranthrone, a powerful phototenderer, gives rise to brilliant orange hues of good fastness properties. Bromination of pyranthrone in chlorosulphonic acid gives mainly the reddish orange 4,12-dibromo derivative, CI Vat Orange 2.

An alternative route to pyranthrone, involving baking 1,6-dibenzoylpyrene (6.96) with aluminium chloride, was also devised by Scholl (Scheme 6.18). The Scholl reaction is a key step in the synthesis of several polycyclic quinones; the cyclisation of 1-benzoylnaphthalene to give benzanthrone (6.73) has already been mentioned. The mechanism of this cyclodehydrogenation reaction may involve an initial protonation step, if traces of water are present, or complexation with aluminium chloride. Electrophilic substitution is thereby



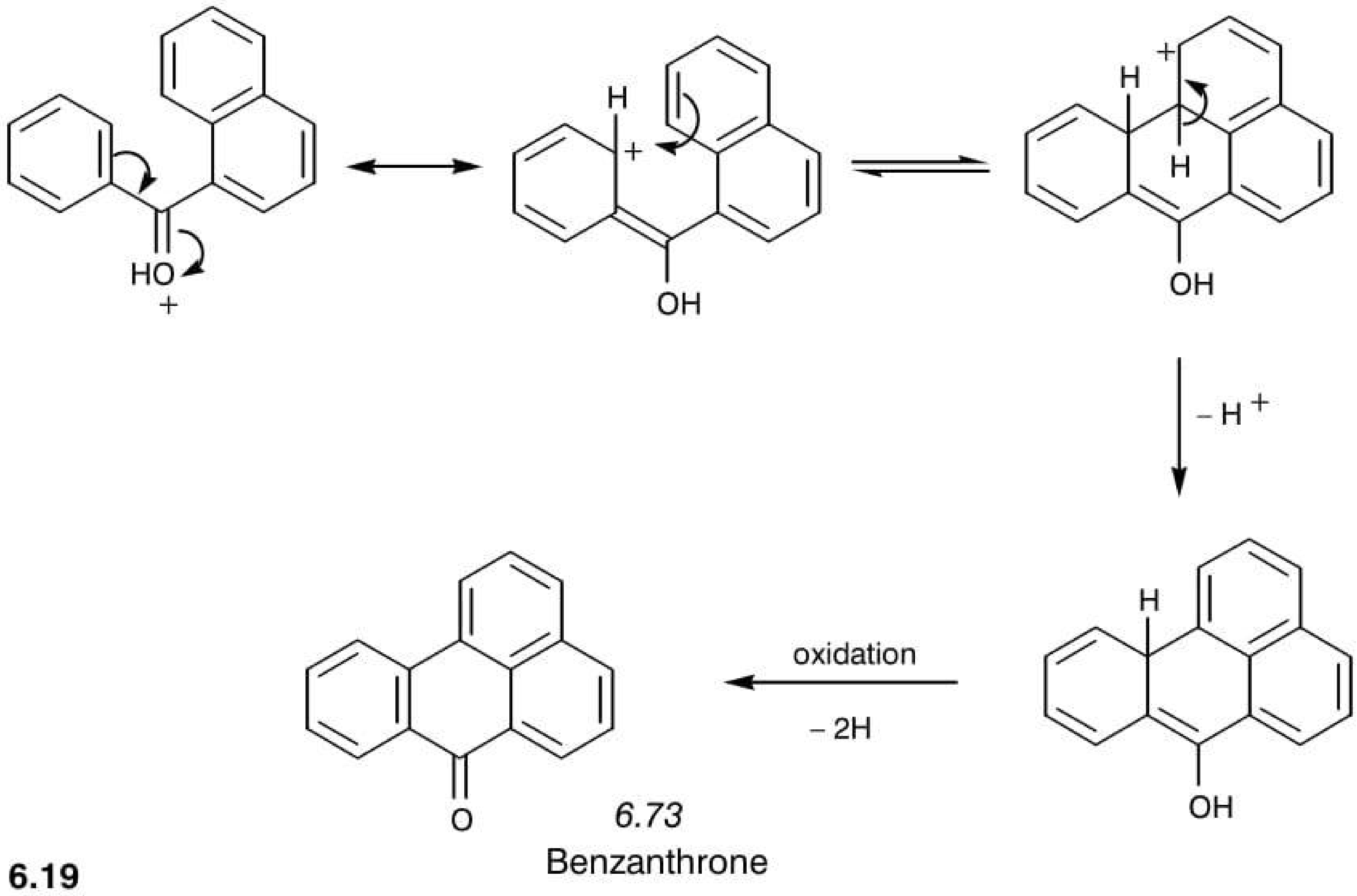
6.94

6.96

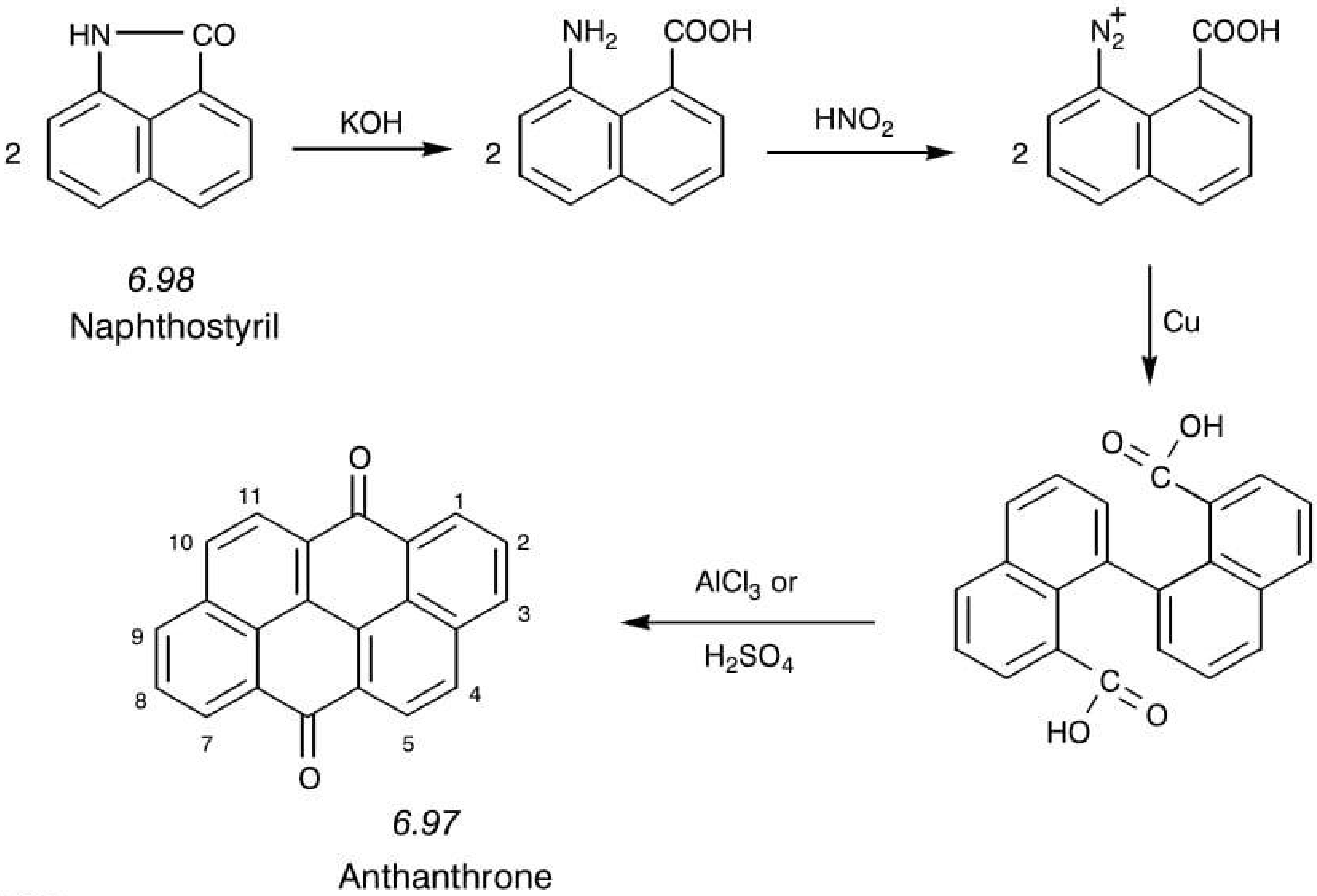
6.95

CI Vat Orange 9

Scheme 6.18



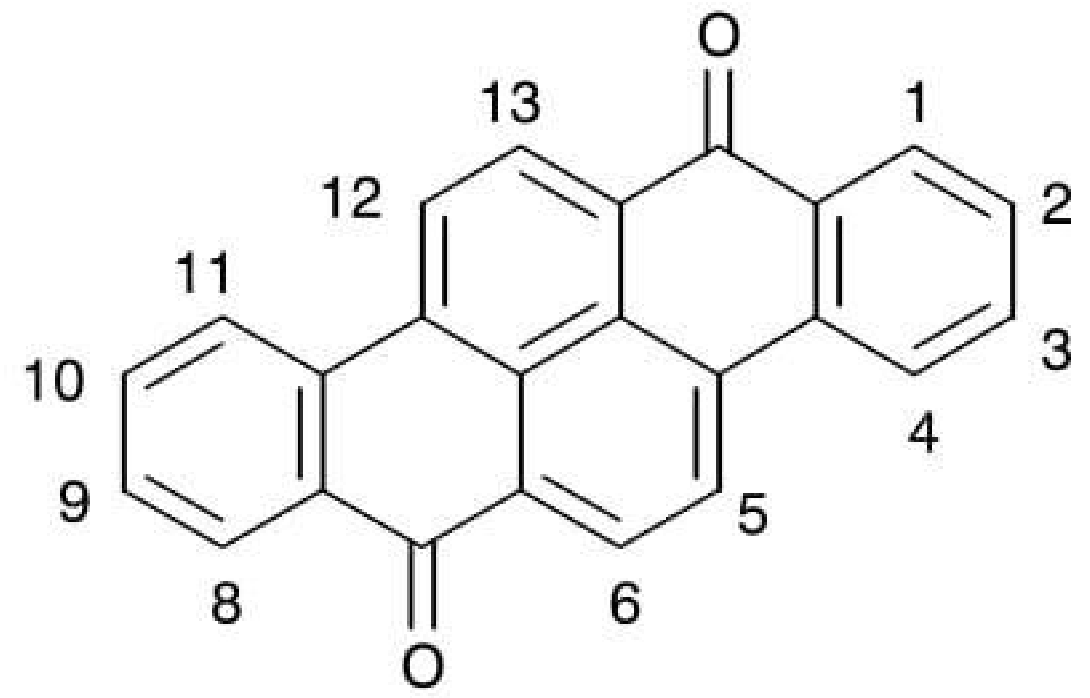
Scheme 6.19



Scheme 6.20

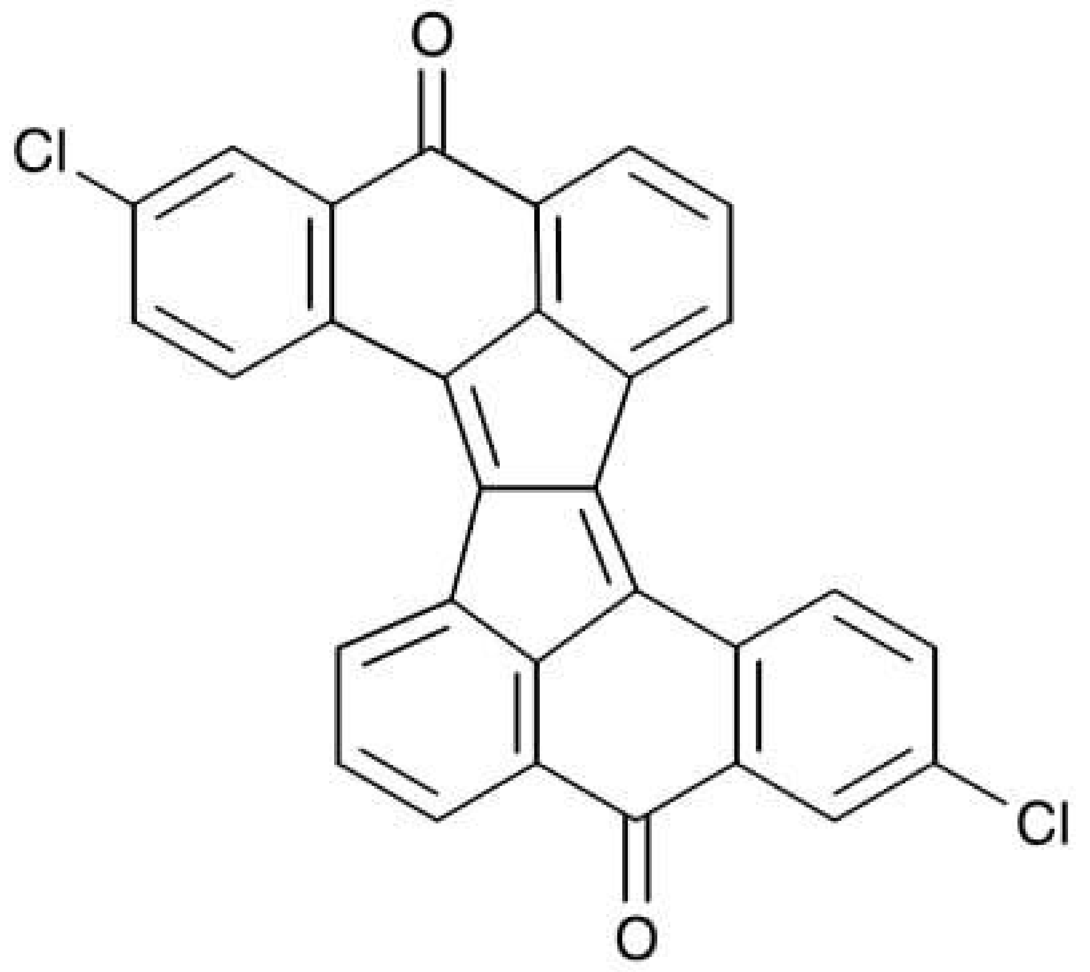
promoted and is then followed by an oxidation step (Scheme 6.19). It has been suggested that radical cations are formed as intermediates [35].

The anthanthrone system (6.97) was discovered in 1912 by Kalb. In the latter stages the synthesis of anthanthrone involves hydrolysis of naphthostyril (6.98), diazotisation and biaryl formation under Gattermann conditions to give 1,1′-binaphthyl-8,8′-dicarboxylic acid before cyclodehydration (Scheme 6.20). The leuco derivative of anthanthrone itself has little affinity for cellulose and the oxidation product has low tinctorial power. However, bromination of anthanthrone or of the intermediate dicarboxylic acid leads to the bright reddish orange 4,10-dibromo derivative CI Vat Orange 3, which possesses good general fastness properties and finds use as a pigment, CI Pigment Red 168. This derivative is used as a charge generation material in commercial photocopiers and laser printers [36]. Treatment of one mole of 4,10-dibromoanthanthrone with two moles of 1-amino-4-benzoylaminoanthraquinone gives the bluish grey dye CI Vat Black 29.



6.99

CI Vat Yellow 4



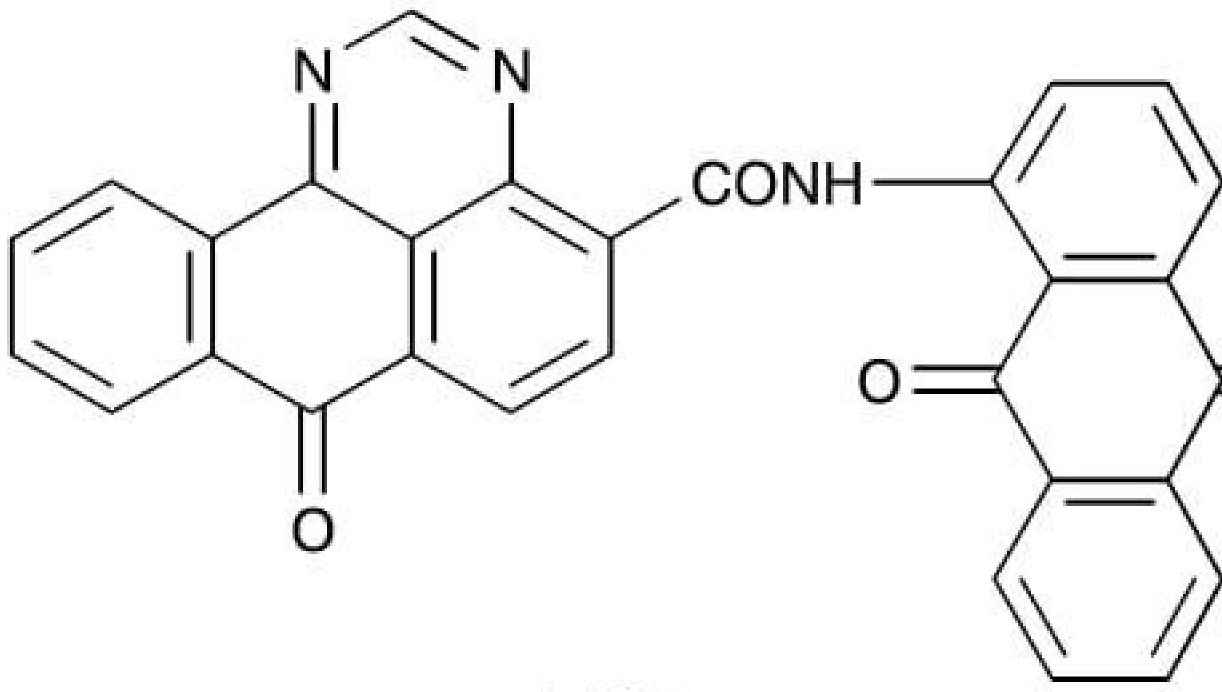
6.100

CI Vat Brown 45

There are several isomeric dibenzopyrenequinones, of which only CI Vat Yellow 4 (6.99) is of commercial importance. This compound is synthesised from 1,5-dibenzoylnaphthalene using the Scholl cyclisation procedure; the same product can be obtained in a similar manner from 3-benzoylbenzanthrone. Its dibromo derivative CI Vat Orange 1, prepared by direct bromination, possesses improved fastness to light, washing and bleaching. The parent dye is now known to be carcinogenic [20].

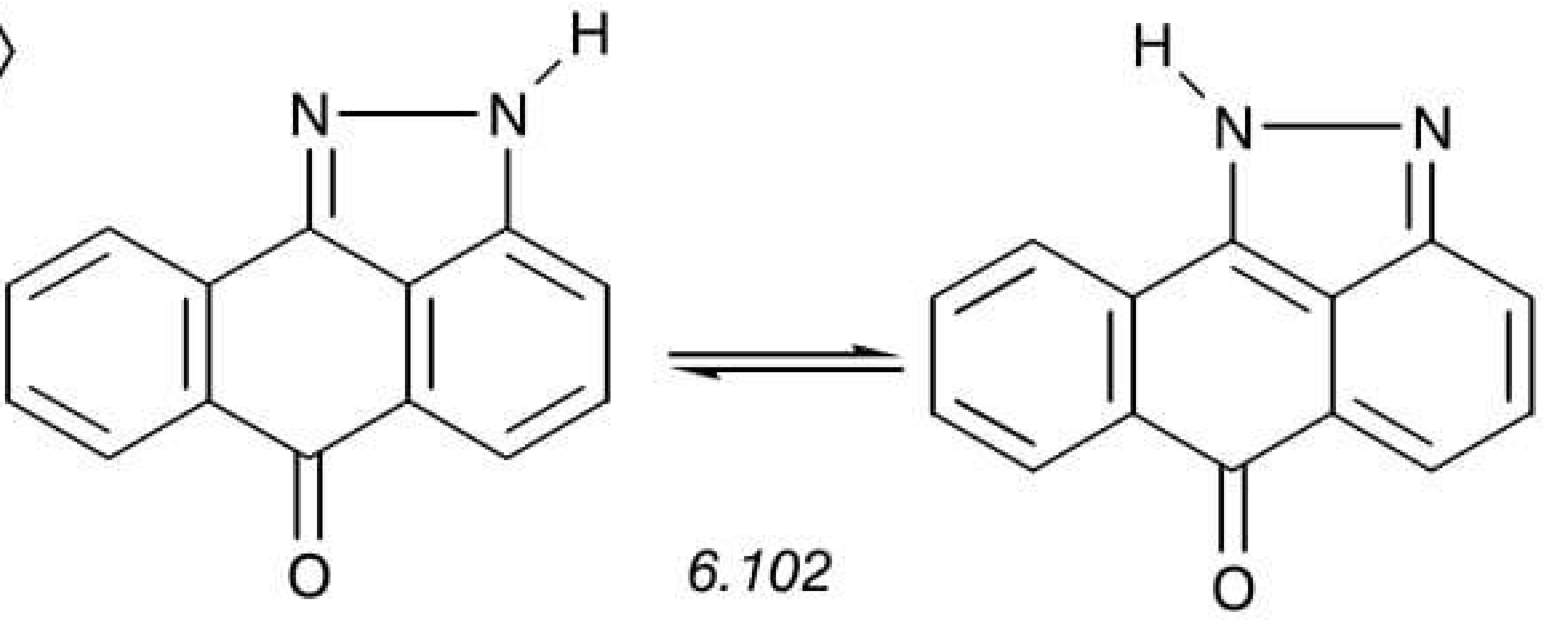
The reddish brown dye CI Vat Brown 45 (6.100) is a dichloro derivative of the unusual acedianthrone system. This dye is prepared by condensing two moles of 2-chloroanthrone with one mole of glyoxal followed by oxidative cyclisation, which probably takes place in a stepwise manner [31].

The 1,9-heterocyclic derivative flavanthrone (6.67) has already been described. Several related heterocyclic compounds are of importance as vat dyes. The 1,9-pyrimidanthrone derivative 6.101 is of commercial significance both as a vat dye (CI Vat Yellow 20) and also as a pigment (CI Pigment Yellow 108). The pyrimidine ring system, which prevents phototendering on cellulose, can be obtained from the appropriately substituted 1-aminoanthraquinone with dimethylformamide and either thionyl chloride ($SOCl_2$) or phosgene ($COCl_2$). 1,9-Pyrazolanthrones, like the anthrapyrimidines, can be regarded as heterocyclic analogues of benzanthrone. The parent tautomeric pyrazolanthrone system (6.102) is available from 1-aminoanthraquinone by diazotisation, reduction to the hydrazine with sodium bisulphite and ring closure in sulphuric acid. As with benzanthrone, dimerisation takes place on fusion with alkali. Improved resistance to alkali is achieved by alkylation. Thus the useful bluish red dye CI Vat Red 13 (6.103) is obtained by ethylation of the parent dimer. Several other valuable dyes also contain a pyrazolanthrone system, such as the navy blue dye CI Vat Blue 25 (6.104), which is prepared by condensing 3-bromobenzanthrone with pyrazolanthrone followed by treatment with alkali, and the grey dye CI Vat Black 8 (6.105), which is made in a similar manner from 3,9-dibromobenzanthrone, pyrazolanthrone and 1-aminoanthraquinone.



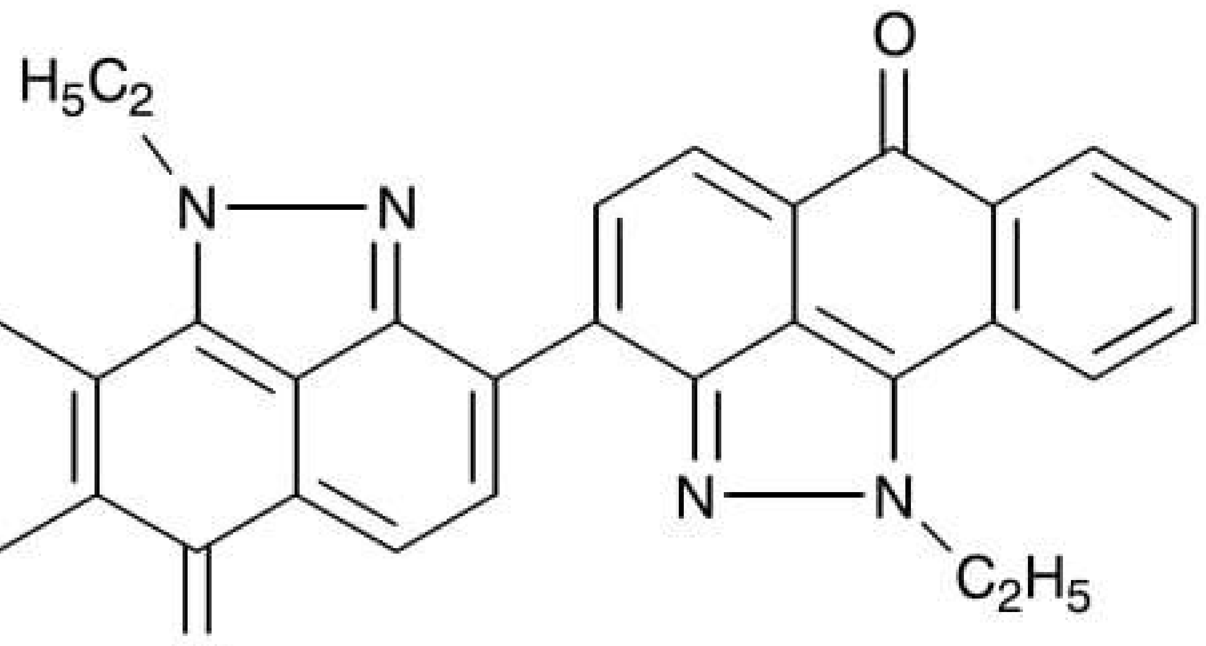
6.101

CI Vat Yellow 20



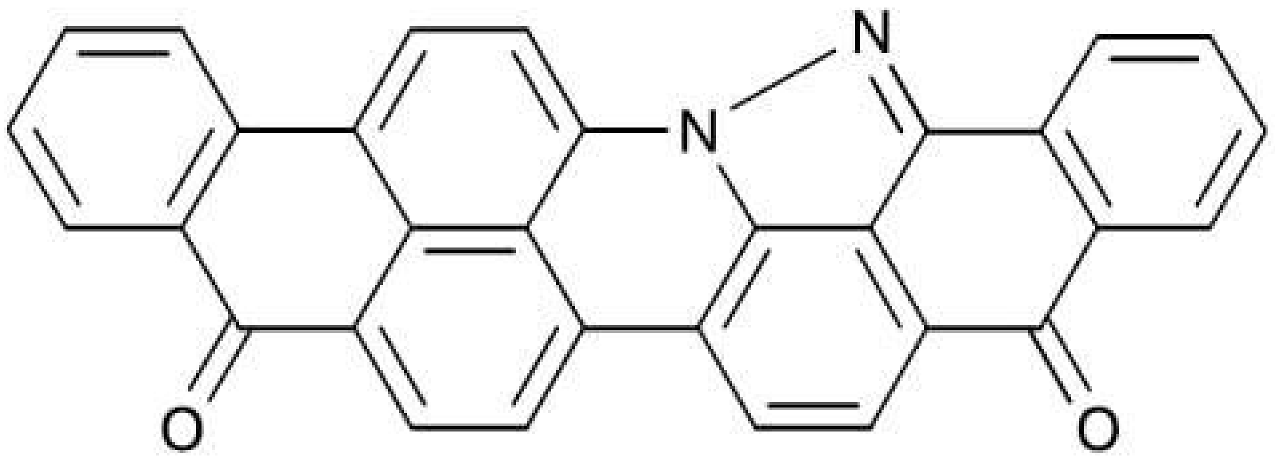
6.102

Pyrazolanthrone



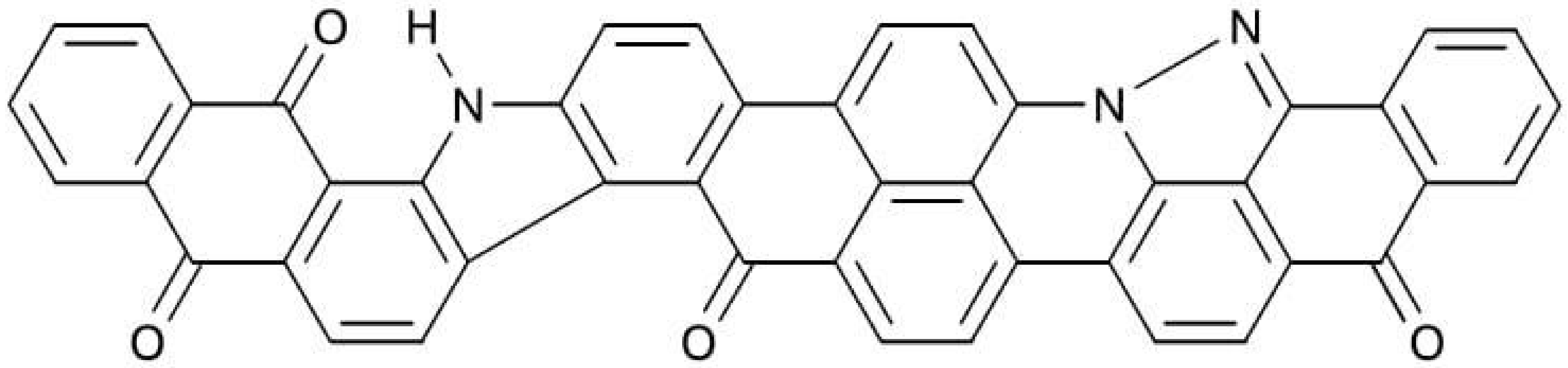
6.103

CI Vat Red 13



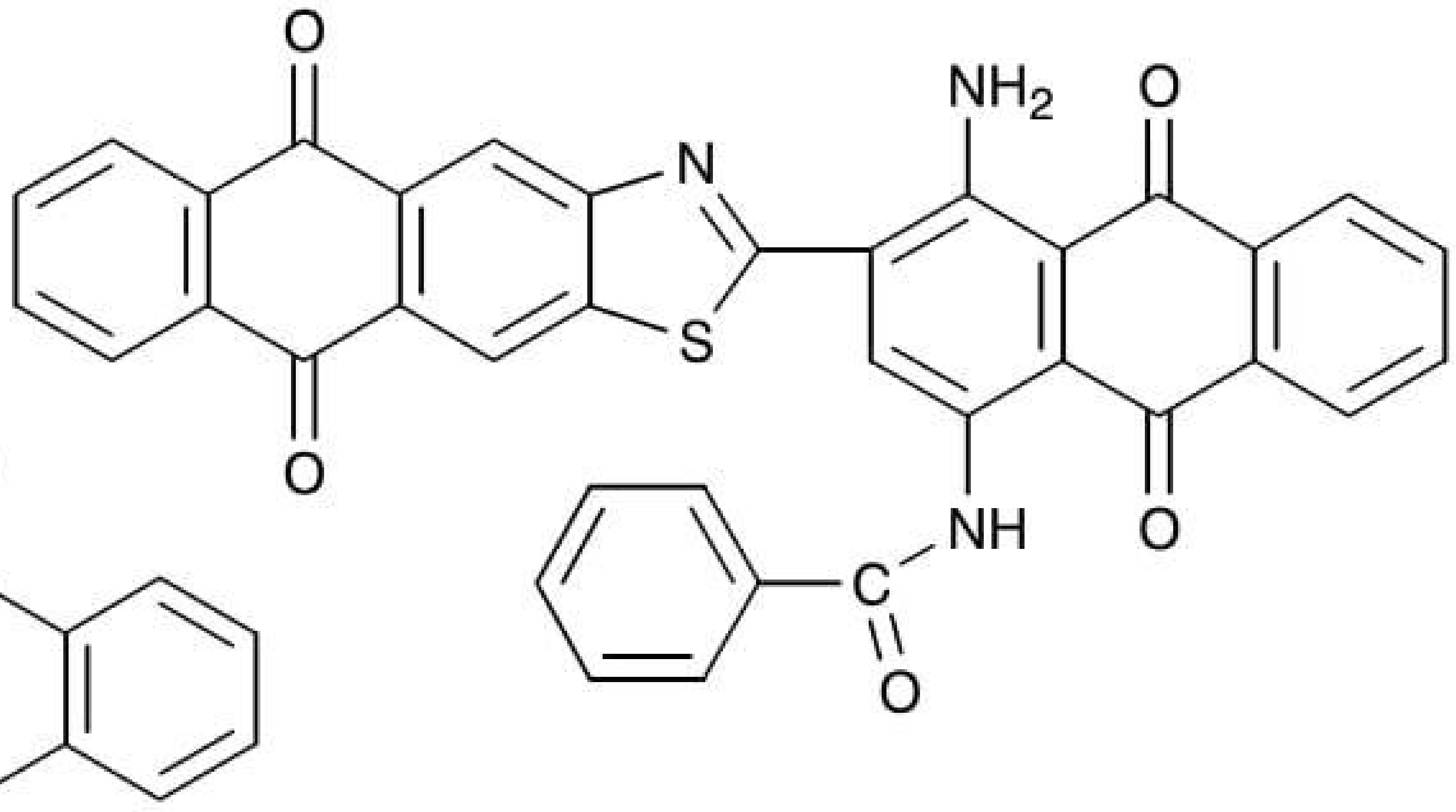
6.104

CI Vat Blue 25



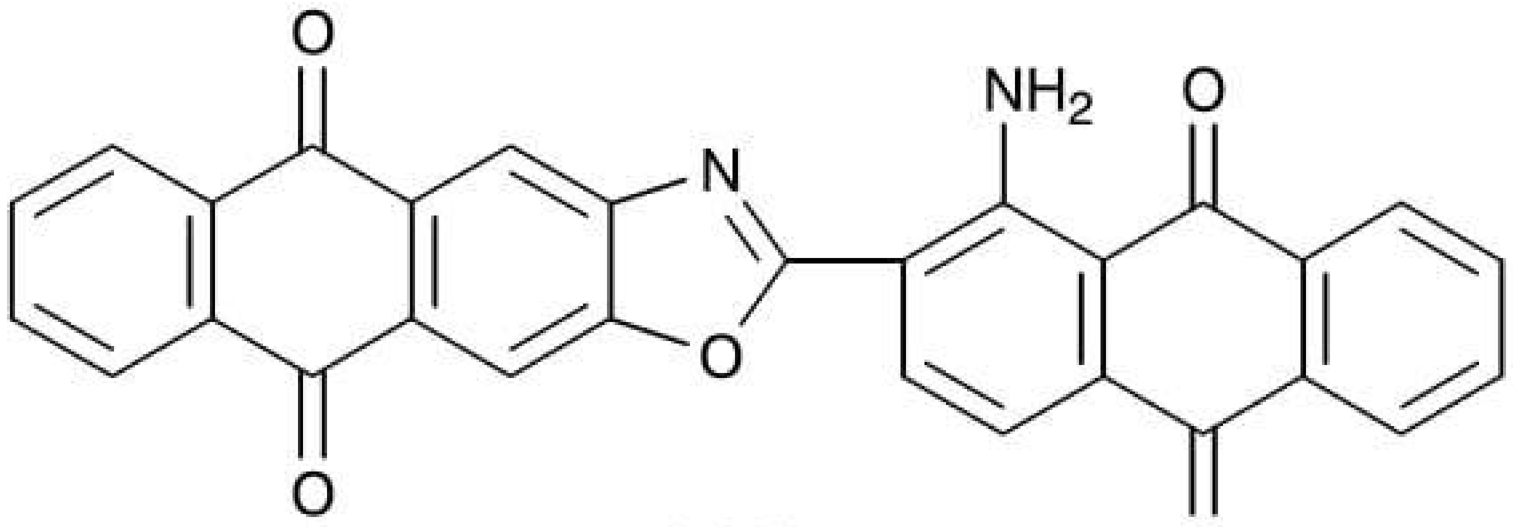
6.105

CI Vat Black 8



6.107

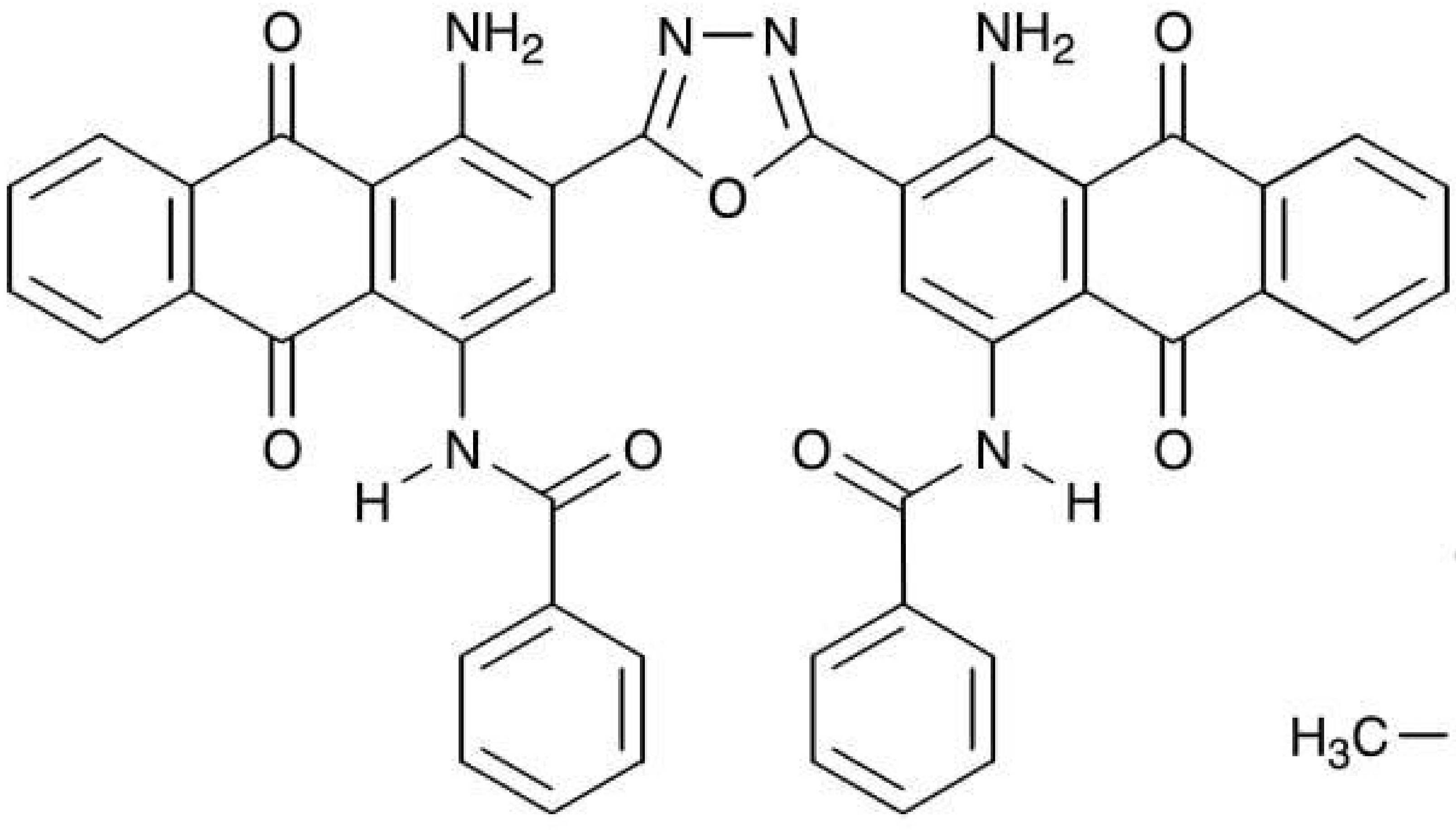
CI Vat Blue 31



6.106

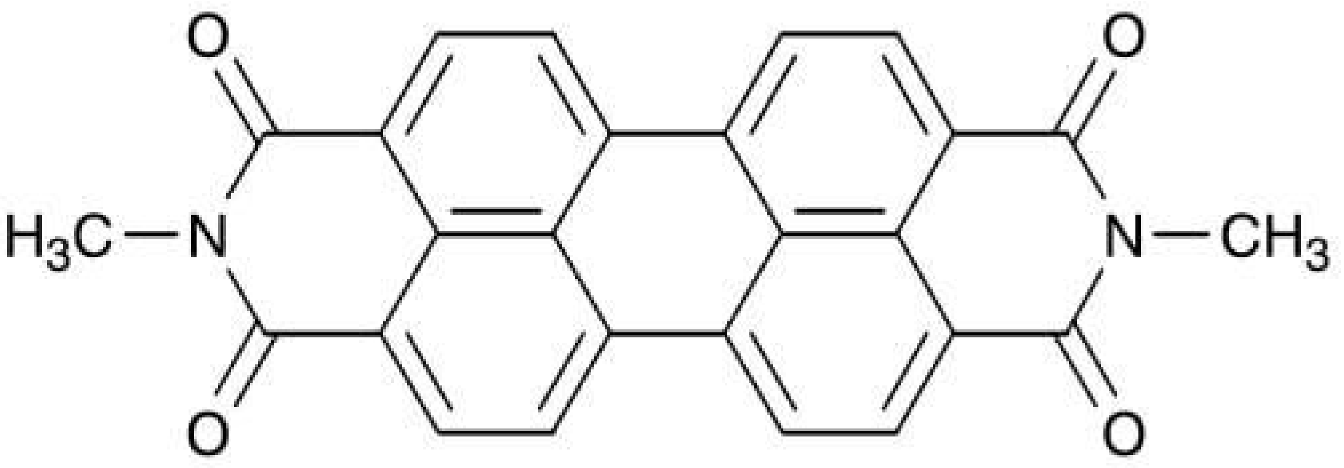
CI Vat Red 10

Heterocyclic ring systems are also used to connect two anthraquinone groups. Typical examples include CI Vat Red 10 (6.106), which is an oxazole derivative obtained from 2-amino-3-hydroxyanthraquinone and the appropriate acyl chloride, the similar thiazole derivative CI Vat Blue 31 (6.107) and the oxadiazole derivative CI Vat Blue 64 (6.108).



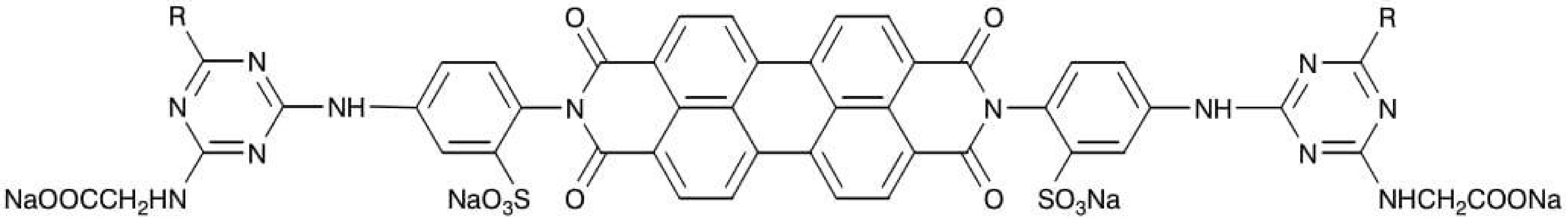
6.108

CI Vat Blue 64



6.109

CI Vat Red 23



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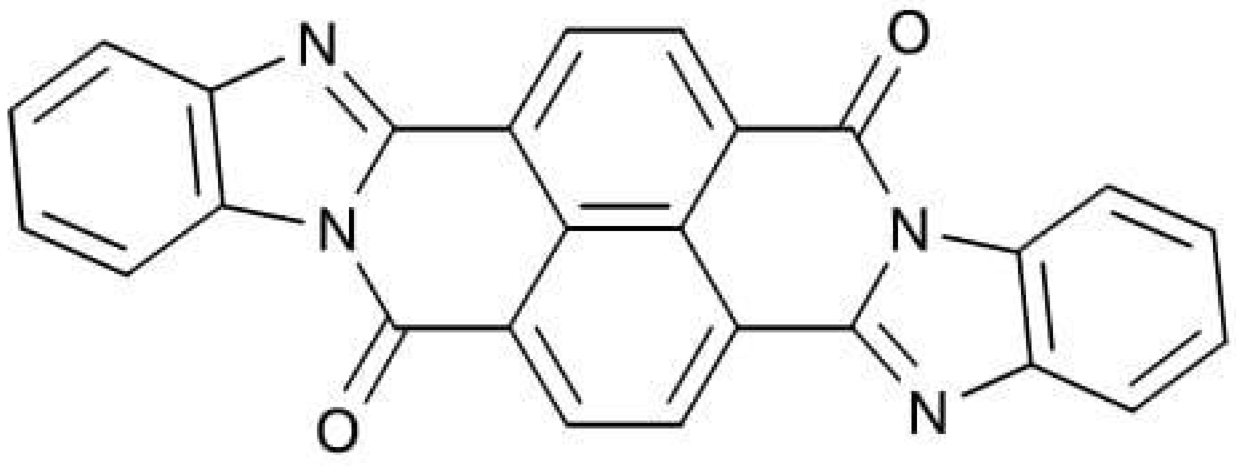
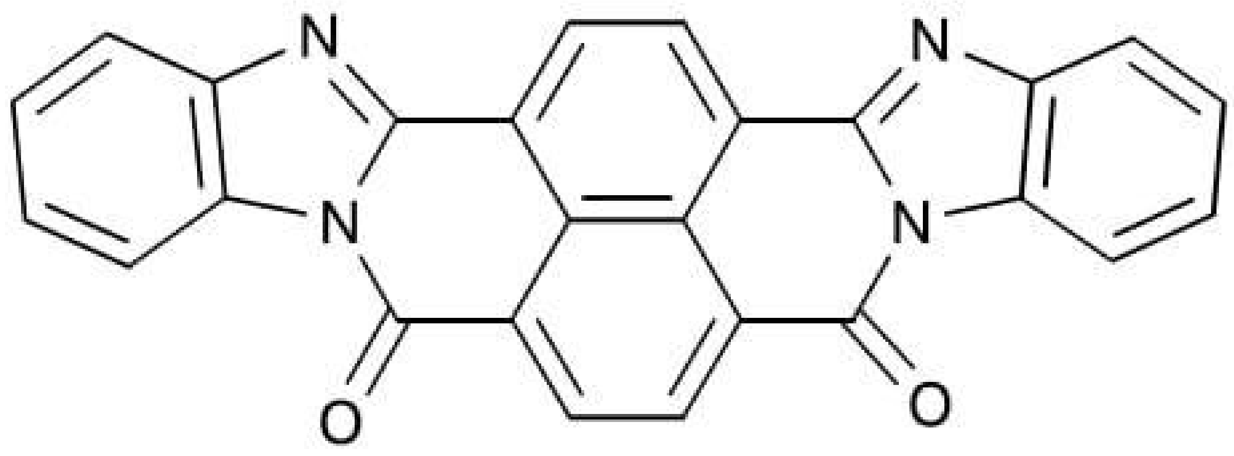


6.111

CI Vat Orange 7



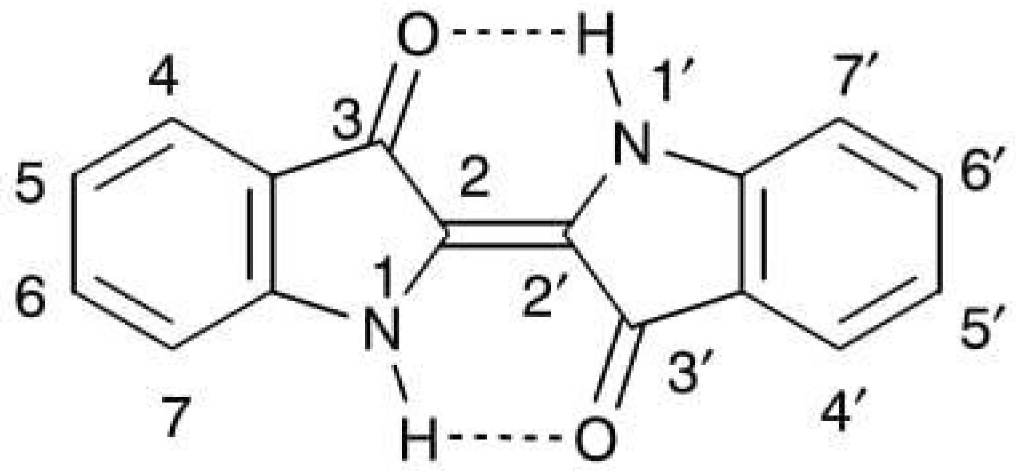
6.112

CI Vat Red 15

Although not anthraquinonoid, some related vat dyes derived from perylene-3,4,9,10-tetracarboxylic acid and from naphthalene-1,4,5,8-tetracarboxylic acid are worthy of mention. Thus, for example, when *N*-methylnaphthalimide is fused with alkali the resulting dimer is CI Vat Red 23 (6.109). This product is also useful as a pigment (CI Pigment Red 179). Dyes of this type also find an application in electrophotographic recording processes [36]. Water-soluble dyes of this class (6.110) have been patented recently by Clariant for ink-jet printing [37]. Treatment of naphthalene-1,4,5,8-tetracarboxylic anhydride with *o*-phenylenediamine gives rise to two isomeric diimidazoles, each of which is useful as a vat dye and as a pigment. The products are CI Pigment Orange 43 (6.111) and CI Pigment Red 194 (6.112). The two isomers can be seperated chromatographically or by treatment with ethanolic potassium hydroxide. Dichroic pigments of this type are also useful in liquid crystal display devices.

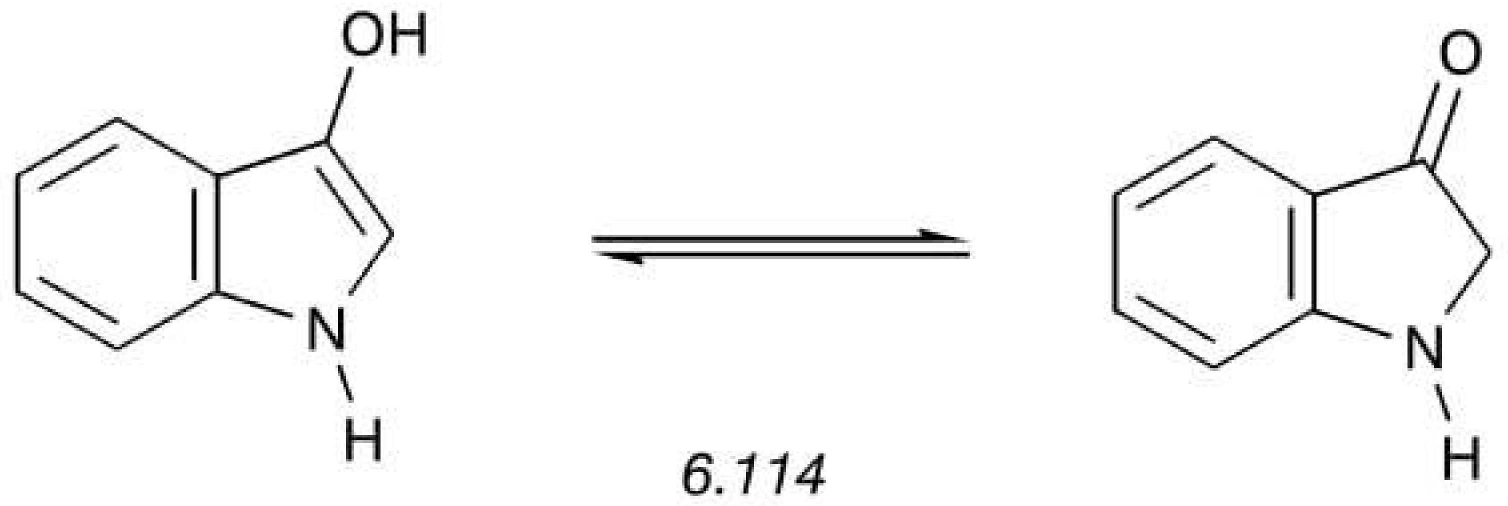
6.3 INDIGOID AND THIOINDIGOID DYES

The natural blue dye indigo (6.113; CI Vat Blue 1) has been known since antiquity; there are several plants from which indigo can be isolated. Of particular importance is the genus *Indigofera*, which can be grown in India, China and other tropical or subtropical regions [38]. Aqueous extraction of the indigo plant yields indican, the colourless glucoside of 3-hydroxyindole (6.114; indoxyl). Removal of the sugar residue in a fermentation process and air oxidation of the resulting indoxyl gives indigo. As well as the essential colouring matter, indigotin (6.113), natural indigo contains varying amounts of the isomeric by-product indirubin (6.115) and other compounds. In Europe the woad plant (*Isatis tinctoria*) was cultivated to provide indigo of lower purity in the guise of woad.



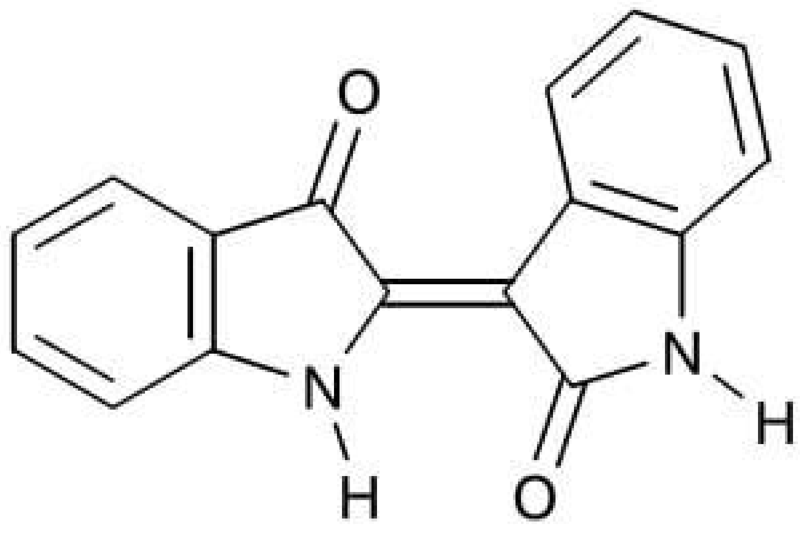
6.113

Indigotin



6.114

Indoxyl

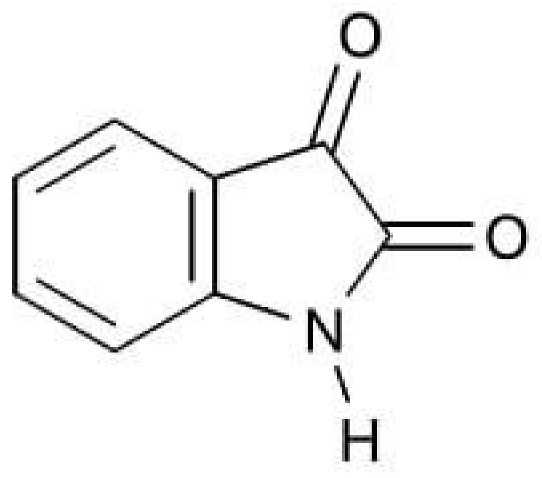


6.115

Indirubin

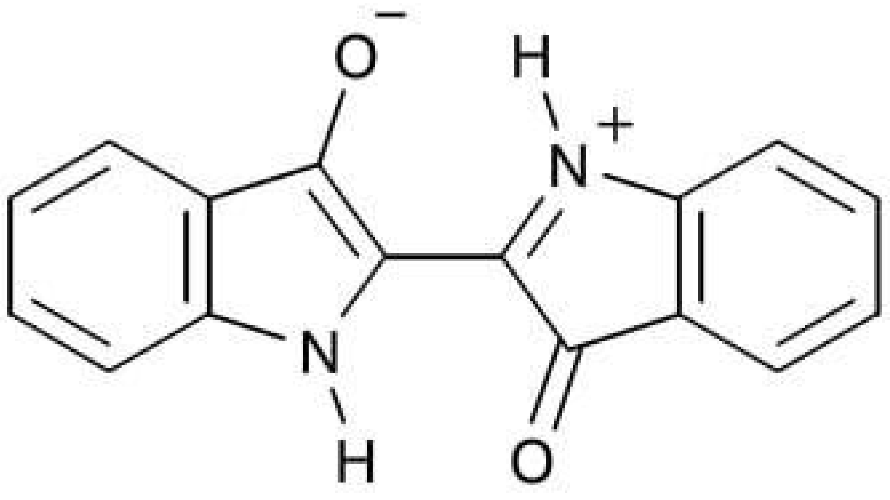
The constitution of indigotin was elucidated by Adolf von Baeyer between 1865 and 1883, on the basis of degradation and synthesis. It was already known that distillation of indigo gave aniline (*anil* is the Portuguese word for indigo). Among other conversions, von Baeyer showed that indigo could be reduced to indole and oxidised to isatin (6.116). The *cis* isomer (Z configuration) was proposed by von Baeyer for indigo. The correct *E* configuration (*trans* isomer) was eventually established in 1926 by Posner, using X-ray crystallography [39]. The indigo molecule is almost planar in the solid state and forms a hydrogen-bonded lattice in which each molecule is linked to four others. The observed bond lengths suggest some contribution to the ground state of the molecule from charge-separated structures such as the dipolar species 6.117. Not surprisingly, indigo has a high melting point (390–392 °C) and low solubility. Infrared studies have shown the existence of intermolecular hydrogen bonding in the parent compound and in many derivatives, but intramolecular hydrogen bonding (6.113) cannot be discounted. Unlike thioindigo, the *trans* isomer cannot readily be converted into the *cis* form although derivatives of the *cis* isomer are known, such as compound 6.118.

The colour of indigo depends dramatically upon its physical state and environment; for example, the vapour is red but the colour on the fibre is blue. The marked solvatochromism of indigo (Table 6.4) is attributable mainly to hydrogen bonding. A progressive bathochromic shift of the visible absorption band is observed as the solvent polarity

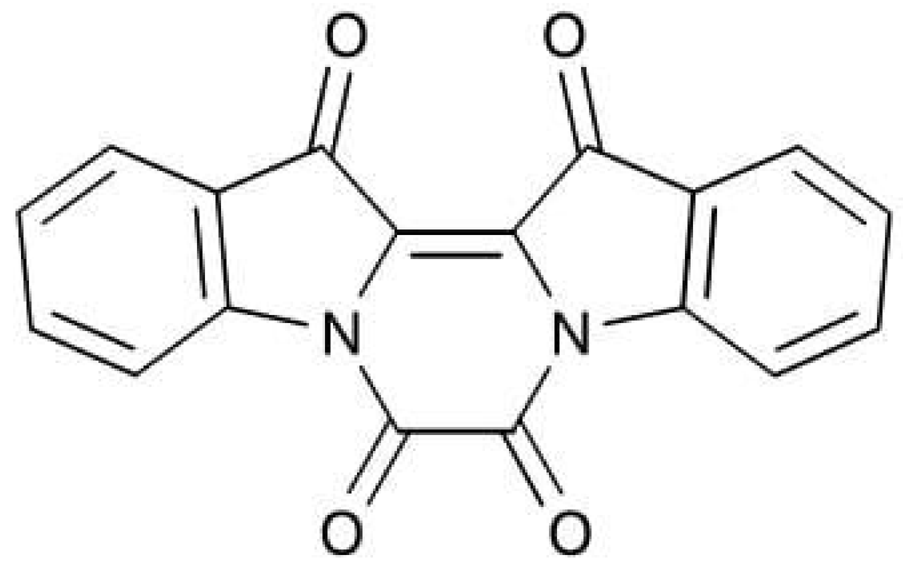


6.116

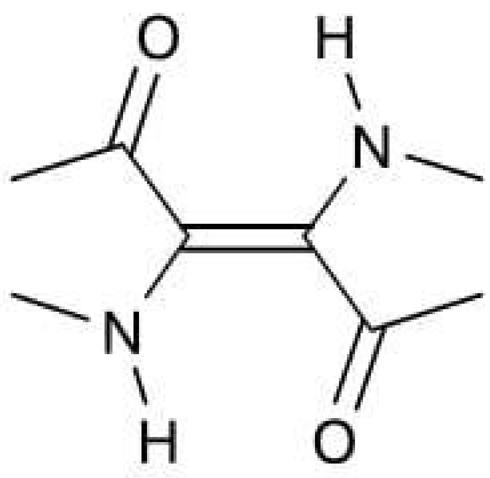
Isatin



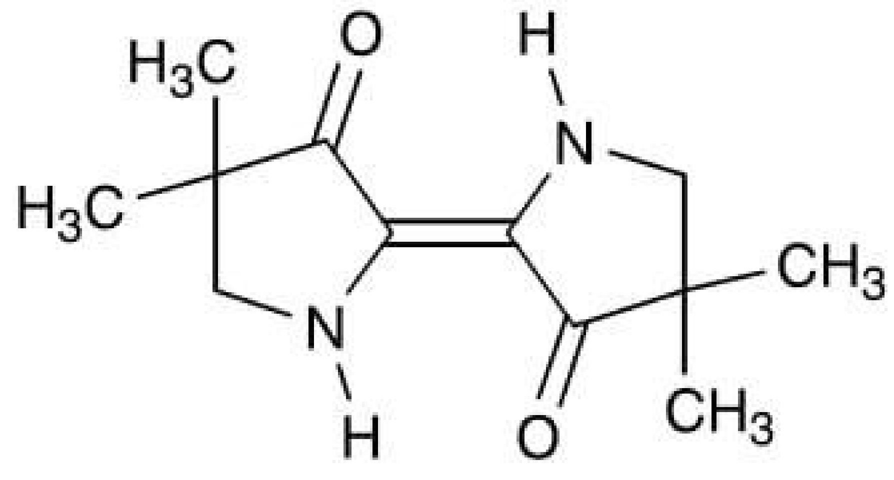
6.117



6.118



6.119



6.120

Table 6.4 Solvatochromism of indigo

Solvent	λ_{max} (nm)
Vapour	540
Carbon tetrachloride	588
Xylene	591
Ethanol	606
Dimethyl sulphoxide	642
Solid	660

(dielectric constant) increases. *N,N′*-Dimethylindigo and thioindigo, in which hydrogen bonding is absent, exhibit only small solvatochromic effects.

The isolated chromogen in indigo vapour, like that of thioindigo (λ_{max} 543 nm in DMF), is red. Klessinger and Lüttke have shown that the structural unit responsible for the red colour is the cross-conjugated H-shaped chromophore 6.119. The secondary role of the benzene rings in indigo has been established by the synthesis of simple analogues such as compound 6.120 [40]. PPP-MO calculations support the idea of an H chromogen [41]. Despite the relatively minor role of the benzene rings in the indigo molecule, the type and position of substituents in the chromogen are important for determining the colour of a derivative. In general, electron-donating groups at the 5,5′- and 7,7′-positions bring about bathochromic shifts, whereas electron-withdrawing substituents at these sites cause hypsochromic shifts. Qualitatively, a donor substituent that is *para* or *ortho* to the donor NH group will stabilise the first excited state whereas an acceptor group has a destabilising effect. The reverse situation obtains at 4,4′- and 6,6′-positions that are *ortho* or *para* to the acceptor carbonyl group. The VB explanation is supported by PPP-MO calculations [39].

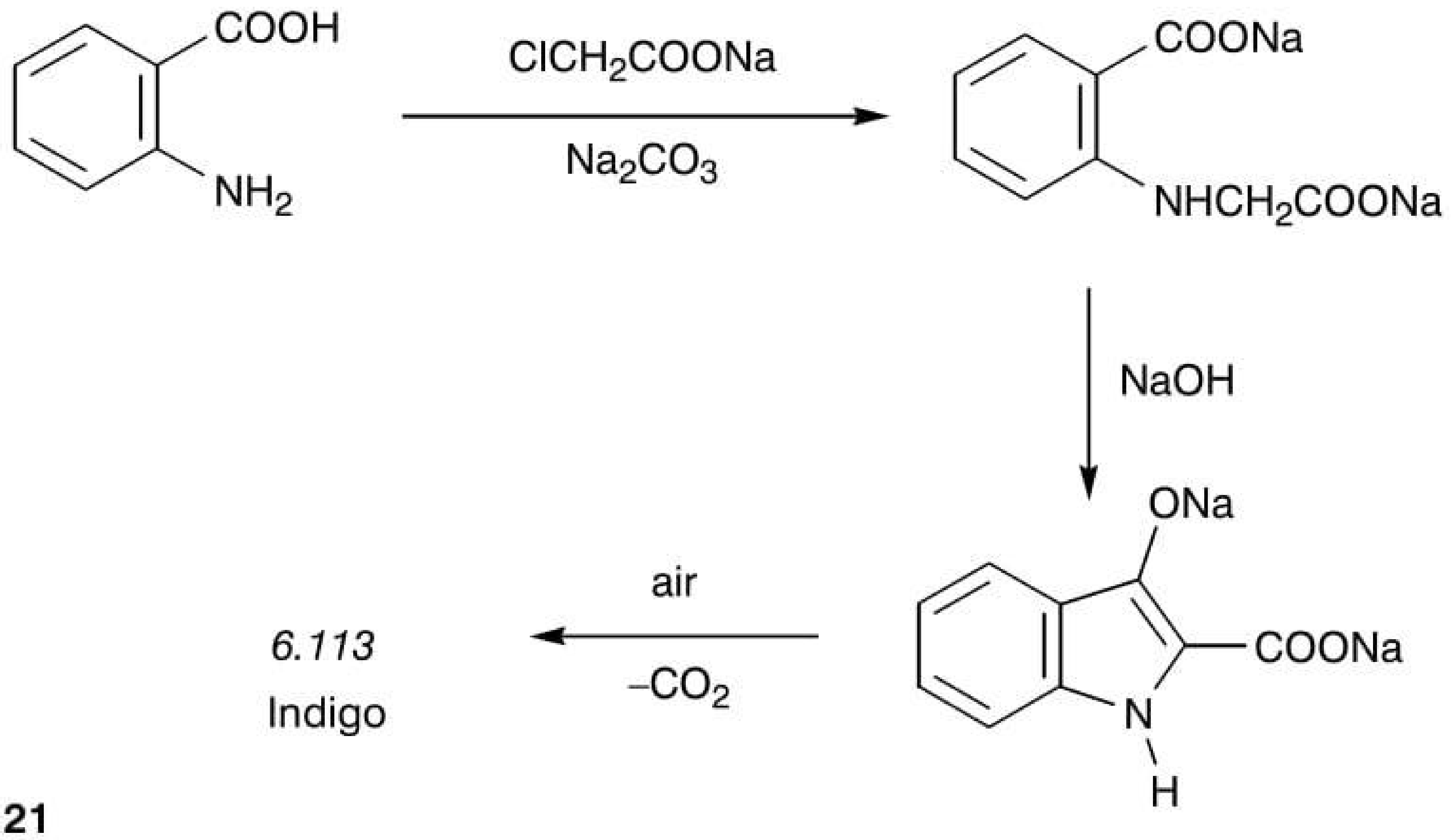
Indigo is still of considerable commercial importance, especially in warp dyeing for woven cotton denim, and finds use as a pigment, CI Pigment Blue 66. Light fastness of indigo dyeings is only moderate but it fades on tone to a pale blue. Photofading of indigo probably involves attack by singlet oxygen at the central double bond [42]. Indigoid vat dyes have gradually declined in importance relative to anthraquinone derivatives.

6.3.1 Methods of synthesis

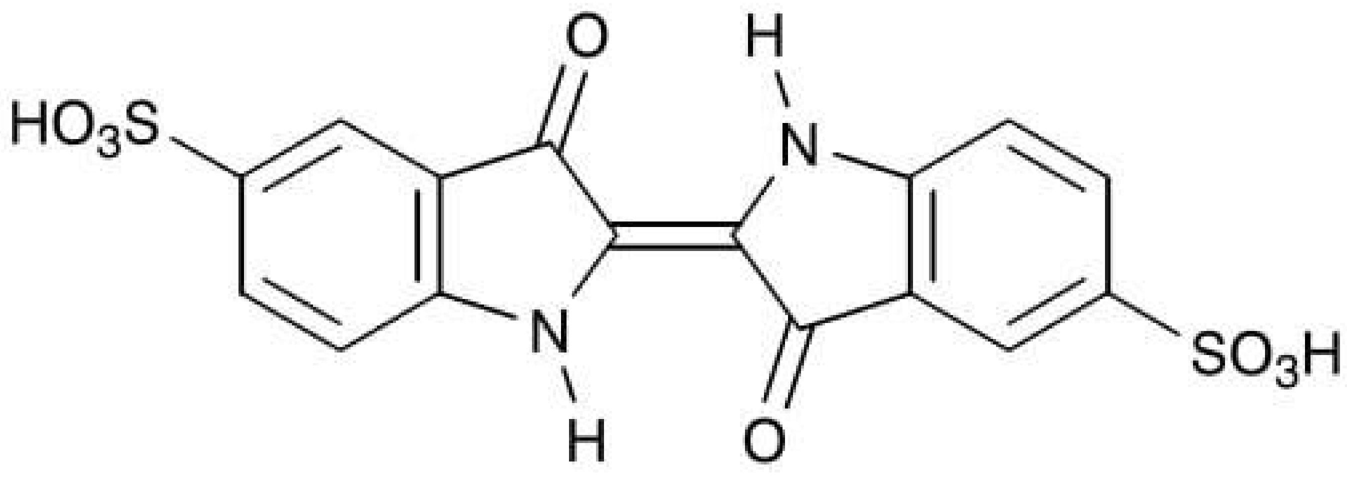
The synthesis of indigo was much more difficult than that of alizarin (6.2) [43]. In 1865 von Baeyer first attempted to obtain indigo by reductive dimerisation of isatin (6.116); he finally achieved a seven-step synthesis from phenylglycine via isatin in 1878. Many syntheses have been developed subsequently for indigo, but very few of these have achieved industrial importance.

In 1890 Heumann obtained a low yield of indoxyl (6.114) by fusing phenylglycine with potassium hydroxide at 300 °C. Indoxyl, once formed, is readily oxidised by atmospheric oxygen to give indigo. An improved yield was obtained at a lower fusion temperature (200 °C) from 2-carboxyphenylglycine, starting from anthranilic acid (Scheme 6.21). The initial cyclisation is like a Dieckmann condensation [44]. This route was adopted by BASF when synthetic indigo was first marketed in 1897. The advent of synthetic indigo soon led to a rapid decline in demand for the relatively impure natural product. At the time the route to anthranilic acid was difficult and relatively expensive [45]. In 1901 Pfleger found that it is possible to cyclise phenylglycine efficiently by adding sodamide at 190 °C to a low-melting eutectic mixture of sodium and potassium hydroxides. This discovery enabled aniline to be used as a cheaper starting material. Pfleger's route is still used today, except that the required phenylglycine is produced via the *N*-cyanomethyl derivative obtained by the condensation of aniline with sodium formaldehyde–bisulphite and sodium cyanide; alkaline hydrolysis then gives sodium phenylglycinate.

Derivatives of indigo can be made by synthesis or by direct substitution. Sulphonation of indigo using oleum gives mainly the 5,5′-disulphonic acid (6.121) together with the 5,7′-isomer. This colorant is of interest as a food dye (CI Food Blue 1) and as an acid dye (CI Acid Blue 74); the aluminium salt is a pigment (CI Pigment Blue 63). Several halogenated dyes have been marketed, exemplified by CI Vat Blue 5 (6.122), which is obtained from indigo by bromination in an organic solvent such as nitrobenzene. The natural dye Tyrian purple (CI Natural Violet 1) is 6,6′-dibromoindigo [46].

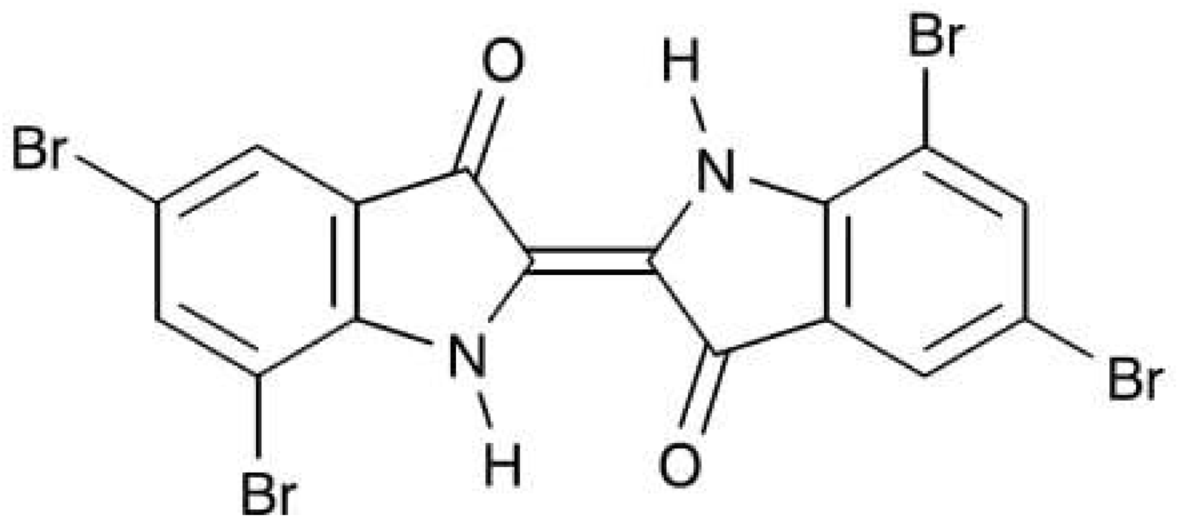


Scheme 6.21



6.121

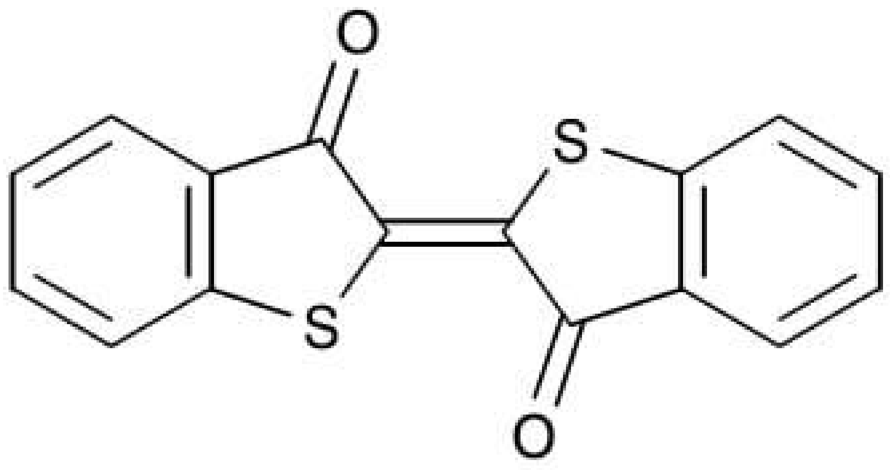
CI Food Blue 1



6.122

CI Vat Blue 5

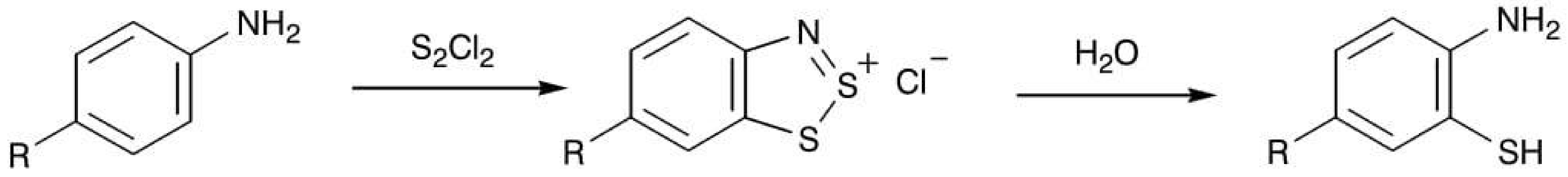
The sulphur analogue of indigo, thioindigo (6.123), was first synthesised in 1905 by Friedländer from anthranilic acid, using a reaction sequence similar to the earlier Heumann synthesis of indigo (Scheme 6.21); the amino group was first converted into a thiol by diazotisation, followed by treatment with sodium disulphide and reduction of the intermediate diphenyl disulphide. Reaction of the thiol with chloroacetic acid and subsequent cyclisation gives thioindoxyl, which is then oxidised, usually with sulphur. The final oxidation step, as in the case of indigo, may proceed by a hydride transfer mechanism or by a free-radical coupling reaction [44]. Thioindigo (CI Vat Red 41) is a bright red dye that is still available commercially. Unlike indigo, it is photochromic; on exposure to light the *trans* stereoisomer (λ_{max} 546 nm in chloroform) is converted into the more hypsochromic *cis* compound (λ_{max} 490 nm in chloroform) giving a marked change of colour from violet to yellowish red.



6.123

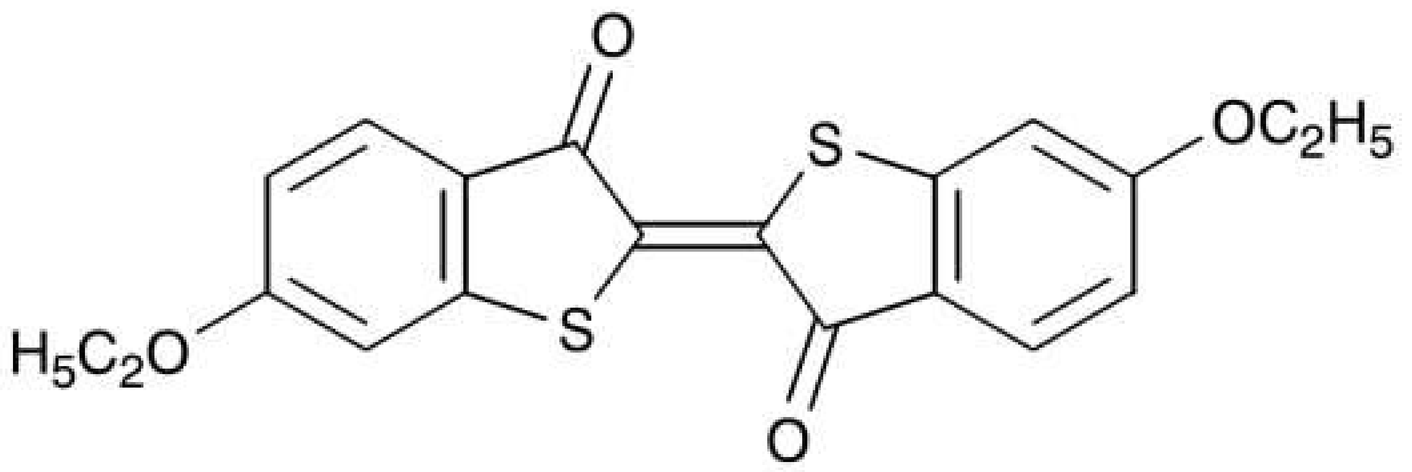
Thioindigo

Substituted thioindigoid dyes are usually obtained via the appropriate benzenethiol in a Heumann-type synthesis. The final cyclisation of the phenylthioglycolic acid derivative can often be achieved in concentrated sulphuric acid or by using chlorosulphonic acid. Several routes make use of the Herz reaction (Scheme 6.22), in which a substituted aniline is converted into the corresponding *o*-aminothiophenol by reaction with sulphur monochloride followed by hydrolysis of the intermediate dithiazolium salt [47]. After reaction between the thiol and chloroacetic acid, the amino group is converted into a nitrile group by a Sandmeyer reaction. Hydrolysis of the nitrile leads to the formation of the required thioindoxyl derivative.



Scheme 6.22

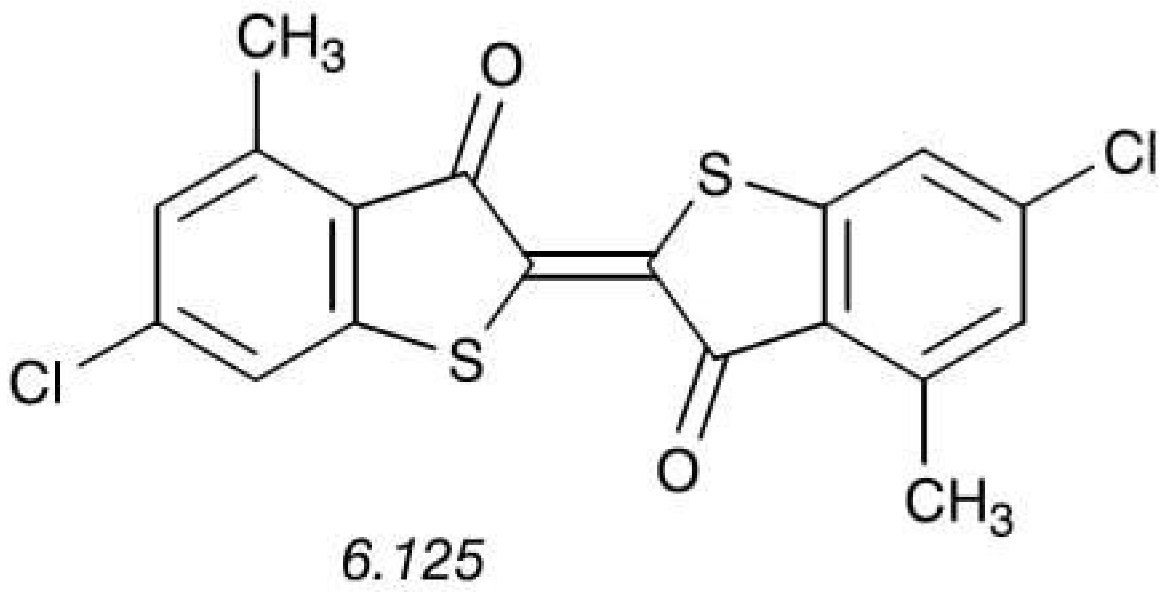
The colour of the thioindigo chromogen is more sensitive to the effects of substituents than that of indigo. Several derivatives of thioindigo are of commercial significance. The presence of donor substituents *para* to the carbonyl groups leads to a pronounced hypsochromic shift, as in the case of CI Vat Orange 5 (6.124).



6.124

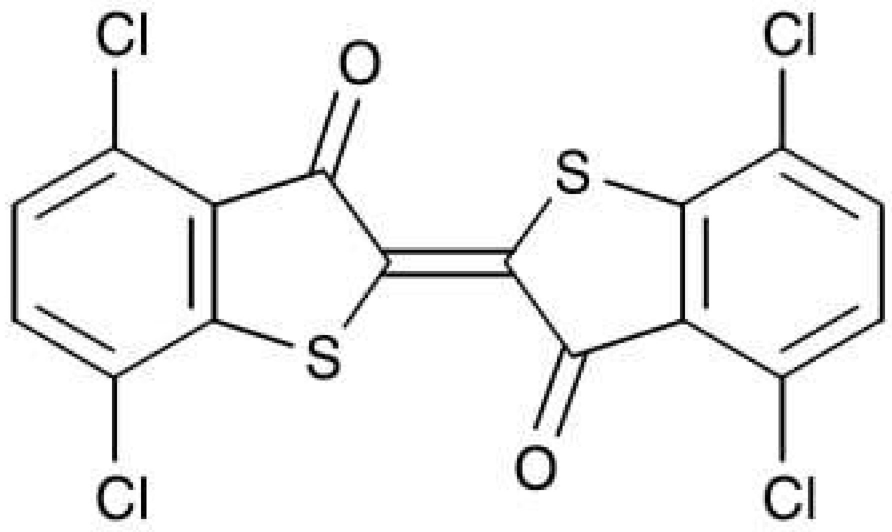
CI Vat Orange 5

Colorants containing chloro and methyl substituents are of importance, particularly as pigments [27]. Thus, CI Vat Red 1 (6.125) also finds use as a pigment, CI Pigment Red 181. Tetrachlorothioindigo (6.126) is widely used as a reddish violet pigment (CI Pigment Red 88). A naphthalene analogue of thioindigo (6.127; CI Vat Brown 5) can be prepared from naphthalene-2-thiol and is used for textile printing. A few unsymmetrically-substituted thioindigo dyes are also produced; CI Vat Red 2 (6.128) is an example.



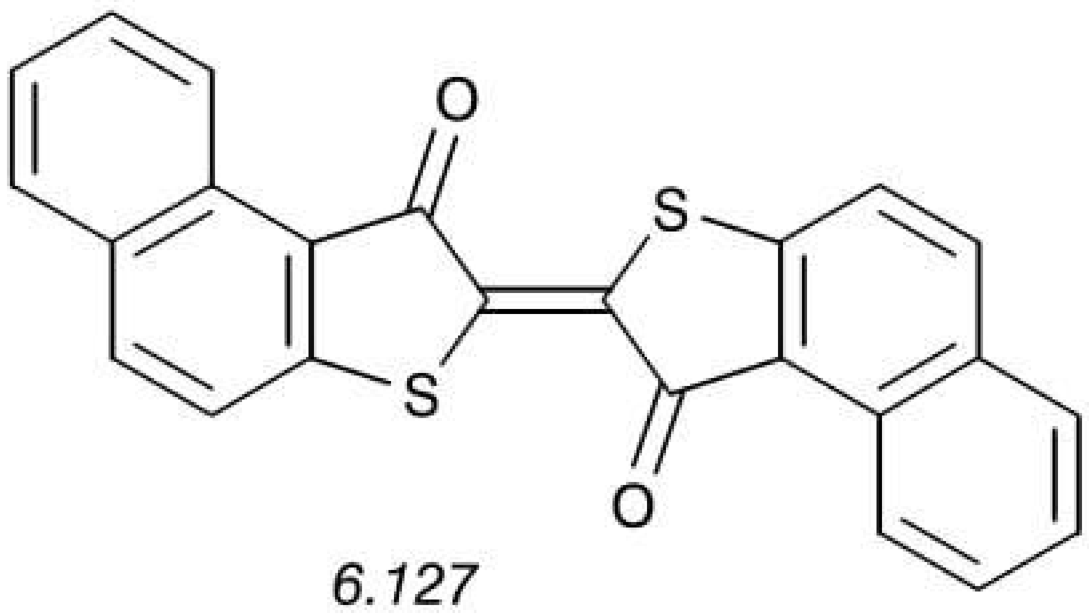
6.125

CI Vat Red 1



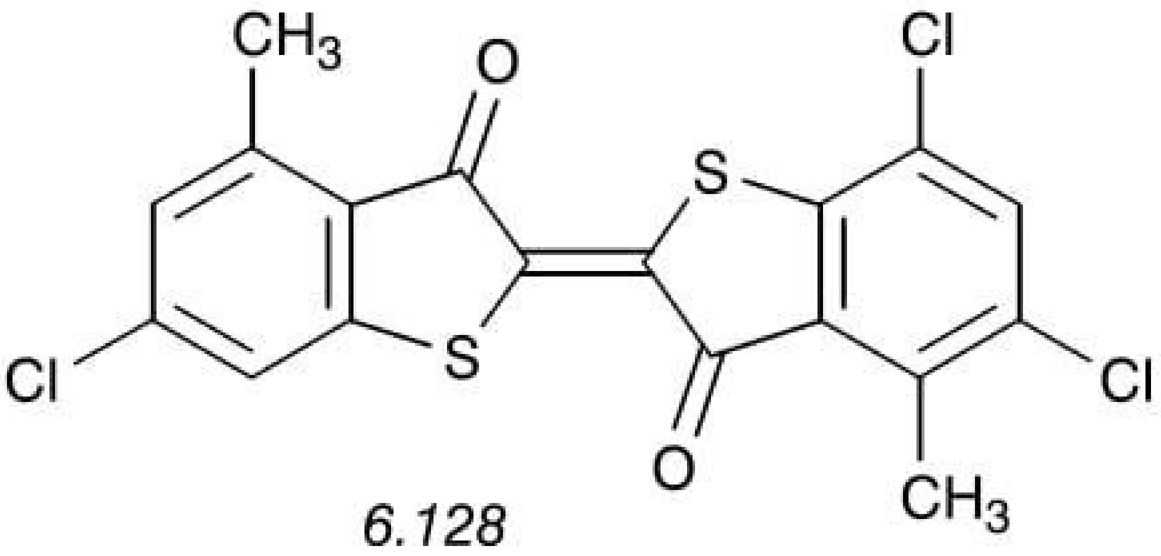
6.126

CI Pigment Red 88



6.127

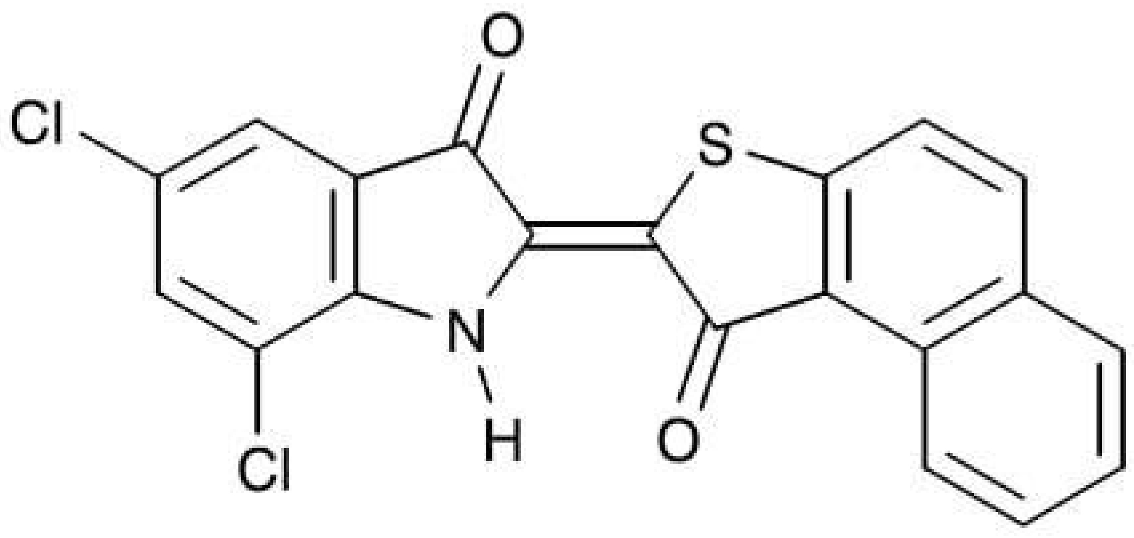
CI Vat Brown 5



6.128

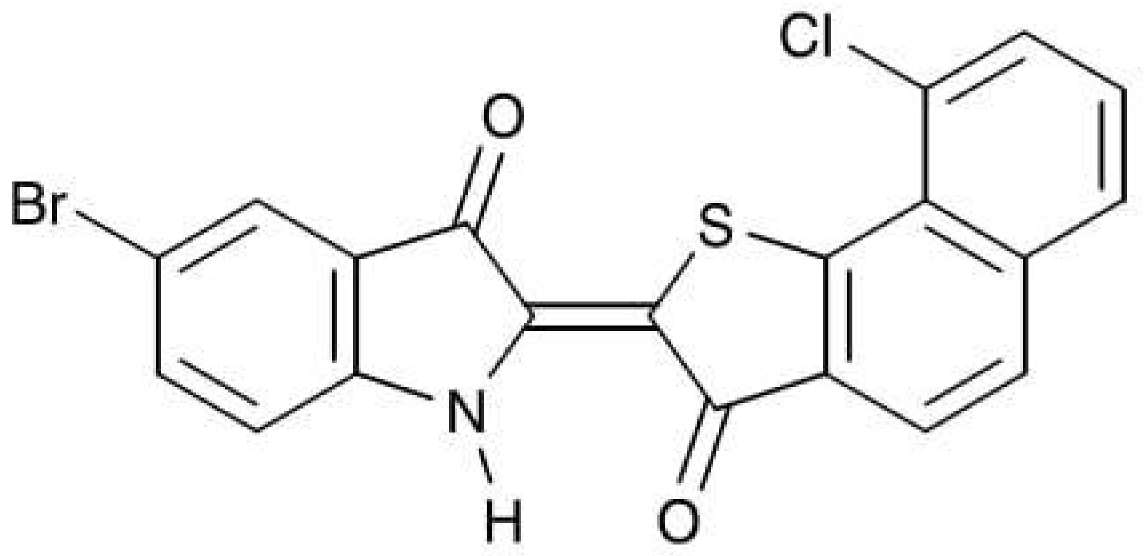
CI Vat Red 2

Dull tertiary hues are available from mixed indigoid-thioindigoid dyes, such as CI Vat Brown 42 (6.129) and CI Vat Black 1 (6.130). Hybrid dyes of this kind are relatively difficult to prepare. In one method of synthesis a suitable indoxyl or thioindoxyl reacts with 4-nitroso-*N,N*-dimethylaniline to form an anil at the 2-position (keto tautomer). Further condensation between the anil and a different thioindoxyl or indoxyl gives the unsymmetrical dye.



6.129

CI Vat Brown 42



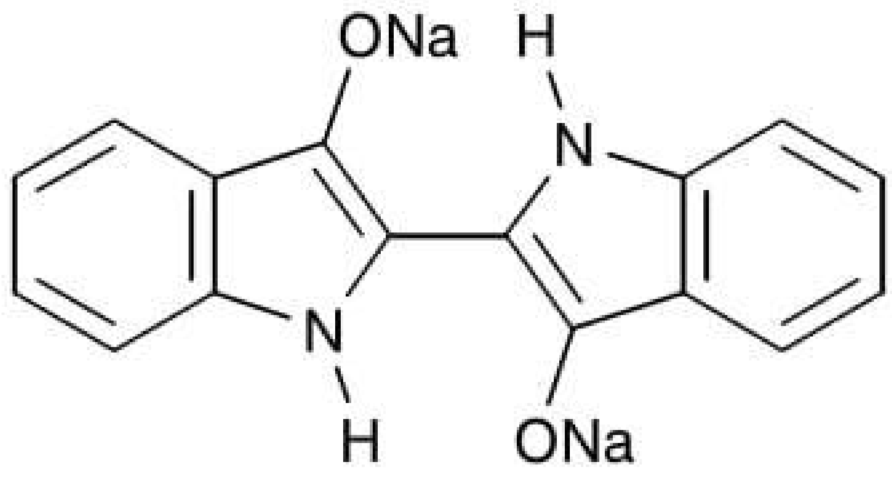
6.130

CI Vat Black 1

6.3.2 Application

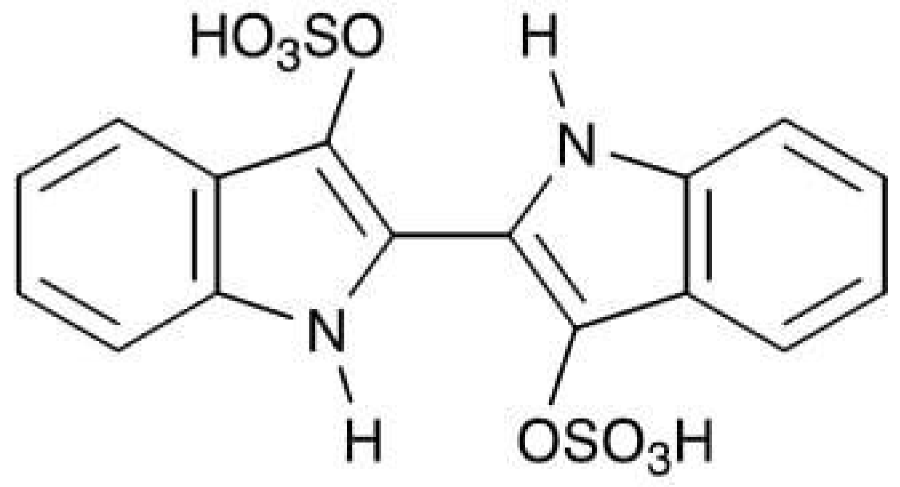
Vat dyes in general have the disadvantage that reduction to a water-soluble form is necessary before application to cellulosic textiles. Traditionally sodium dithionite in alkaline solution serves as the reducing agent. An alternative sometimes used in vat printing is thiourea dioxide, which is converted into formamidine sulphinate in alkaline solution (section 12.9.1).

Indigo and its derivatives are readily reduced under weakly alkaline conditions to the water-soluble leuco form. The disodium salt Indigo white (6.131) is classified in the *Colour Index* as CI Reduced Vat Blue 1 and is the form in which it is absorbed by cellulosic fibres. Acidification of Indigo white gives the more stable acid leuco form. The related leuco disulphuric ester (6.132; CI Solubilised Vat Blue 1) was mainly used for wool dyeing. As mentioned in section 6.2, reduction and esterification can be carried out without isolating the leuco compound by using pyridine and iron together with chlorosulphonic acid. Indirect electrolysis can also be used as a reduction technique in indigo dyeing [48].



6.131

Indigo white



6.132

CI Solubilised Vat Blue 1

Nearly all the commercially produced indigoid and thioindigoid vat dyes have been marketed in their solubilised forms. Thus, for example, CI Vat Blue 5 is also available as CI Solubilised Vat Blue 5. In addition, several vat dyes have been sold only as their solubilised derivatives. Usage of these expensive derivatives has declined in recent years.

6.4 SULPHUR AND THIAZOLE DYES

Although many types of dye contain sulphur other than in sulphonic acid groups, sulphur dyes are usually considered to be those dyes that are best applied from a sodium sulphide dyebath. Like vat dyes, sulphur dyes are water-insoluble before and after application to cellulosic fibres. Disulphide linkages in the dye molecules are readily reduced by sodium sulphide to give alkali-soluble thiol groups. The more environmentally friendly thiourea dioxide can be used as a substitute for sodium sulphide [49]. The resulting leuco dye has substantivity for cellulose. Subsequent oxidation within the fibre by exposure to air and oxidising agents such as hydrogen peroxide leads to the regeneration of di- and polysulphide linkages between aromatic ring systems. The dyeings generally possess good wet fastness and satisfactory light fastness. The fastness to bleaching of sulphur dyes is poor and the dyes are often sensitive to acid attack with the evolution of hydrogen sulphide. Nevertheless they are relatively cheap to produce and offer a full range of hues from yellow to black, albeit rather dull colours. The blues and blacks are of greatest importance, especially CI Sulphur Black 1, which is manufactured on a very large scale [50]. Environmental legislation imposes increasing constraints on the use of dyes. Sulphur dye effluents contain, in particular, harmful sulphides which cannot be discharged into sewerage treatment systems directly. The preferred method of removing sulphides is by air oxidation using efficient aerators, known as helixors, to produce thiosulphates [51].

The first commercial sulphur dye was discovered accidentally in 1873 by Croissant and Bretonnière who heated lignin-containing organic waste, such as sawdust, with sodium polysulphide at about 300 °C; the product was sold under the name Cachou de Laval [52]. Even today an equivalent dye (CI Sulphur Brown 1) is derived from lignin sulphonate, which is readily available from waste liquors from wood pulp manufacture. The real pioneer of sulphur dyes was Vidal, the first chemist to obtain dyes of this type from specific organic compounds. In particular, Sulphur Black T (CI Sulphur Black 1) was made from 2,4-dinitrophenol in 1899. At the turn of the century many of the intermediates available were subjected to sulphurisation (thionation), that is, treatment with sulphur, sodium sulphide or sodium polysulphide to introduce sulphur linkages.

6.4.1 Methods of formation

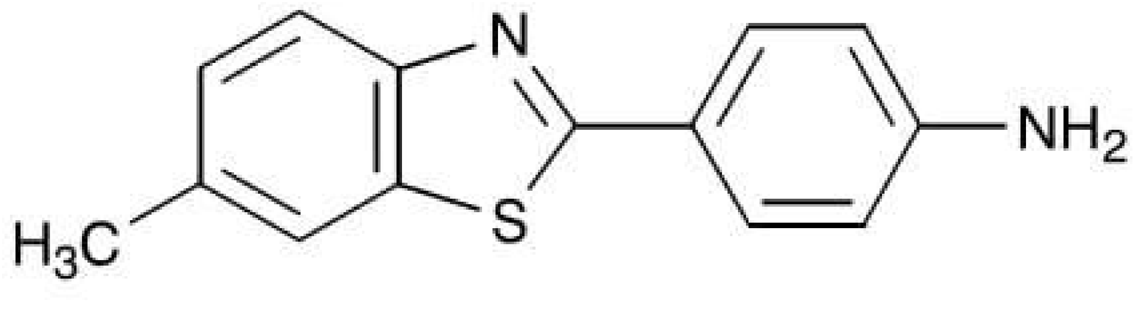
Two basic methods are used for the manufacture of sulphur dyes. In one, the starting materials are baked either with sulphur alone or with sulphur and sodium sulphide at a temperature between 180 and 350 °C. Alternatively the intermediates are heated under reflux in aqueous or alcoholic sodium polysulphide; this process may also be carried out under pressure at temperatures up to about 130 °C. Following sulphurisation the dye is precipitated by means of air or chemical oxidation, acidification or a combination of these methods. The sulphurisation process results in the evolution of hydrogen sulphide, which is usually absorbed in aqueous sodium hydroxide for use elsewhere – in the reduction of nitro compounds, for example.

The commercially available sulphur dyes can be divided into three categories. The conventional CI Sulphur dyes are water-insoluble, polymeric products, which can also be produced in a finely dispersed form [50]. CI Leuco Sulphur dyes are obtained by treating sulphur dyes with, typically, an alkaline mixture of sodium sulphide and sodium hydrosulphide. These dyes are suitable for direct application and are available in concentrated solutions (liquid dyes). Liquid dyes are also produced directly from the thionation mixture without isolation; powder or granular products can be made by drying a slurry of the dye together with a reducing agent. CI Solubilised Sulphur dyes, which are thiosulphonic acid derivatives of sulphur dyes, are obtained by the action of sodium sulphite or bisulphite on the parent dye. These products are highly water-soluble but possess only low substantivity for cotton until they have been converted into the leuco form with sodium sulphide. After application an oxidative treatment converts the thiol groups into disulphide bonds, leading to dimeric or polymeric dyes [53]. The thiosulphate dyes ($ArSSO_3Na$) belong to a group of compounds known as Bunte salts [54].

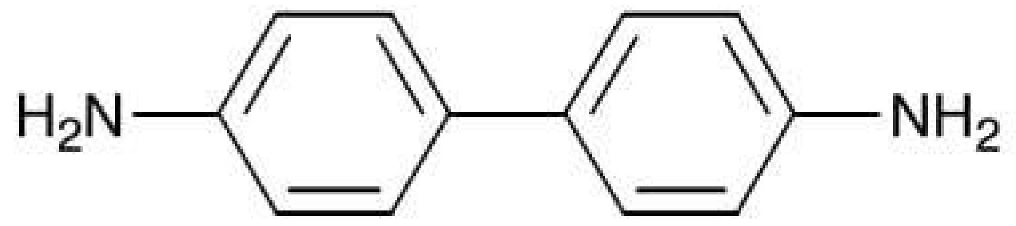
In the *Colour Index* both conventional sulphur dyes and their leuco counterparts are allocated the same CI constitution number; a different number is given to the related solubilised version. Thus, for example, CI Sulphur Black 1 and CI Leuco Sulphur Black 1 have the reference CI 53185 whereas CI Solubilised Sulphur Black 1 appears under CI 53186. Because of the complexity of the final products, sulphur dyes are classified according to the chemical structure of the organic starting material that predominates in the manufacturing process. Typical intermediates include aromatic amines, with or without nitro and phenolic groups, and diphenylamine derivatives.

6.4.2 Structural features

The dry baking procedure generally results in yellow, orange or brown sulphur dyes, many of which are known to contain benzothiazole groups. For example, CI Sulphur Yellow 4 can be obtained from a melt of 2-(4′-aminophenyl)-6-methylbenzothiazole (6.133; dehydrothio-*p*-toluidine) 4,4′-diaminobiphenyl (6.134; benzidine) and sulphur. The thiazole intermediate is obtained when *p*-toluidine is heated with sulphur. Further sulphurisation gives the dithiazole derivative primuline base, sulphonation of which led to the discovery of primuline (CI Direct Yellow 59) by Green in 1887. Primuline base is now known to contain three related components having one, two or three benzothiazole units, respectively [55]. Benzidine (a carcinogen) is no longer used by European manufacturers but sulphur dyes derived from this intermediate are still available commercially in other parts of the world. The structure of CI Sulphur Yellow 4 was investigated in 1948 by Zerweck *et al.* [56]. These workers degraded the dye in a potassium hydroxide melt and obtained various *o*-aminothiophenols, which were condensed with chloroacetic acid to produce identifiable lactams. From the ratio of lactams obtained, it was deduced that CI Sulphur Yellow 4 was a mixture of four main components, exemplified by structure 6.135; these were all synthesised and gave, on admixture, a product that was effectively identical with the commercial dye.

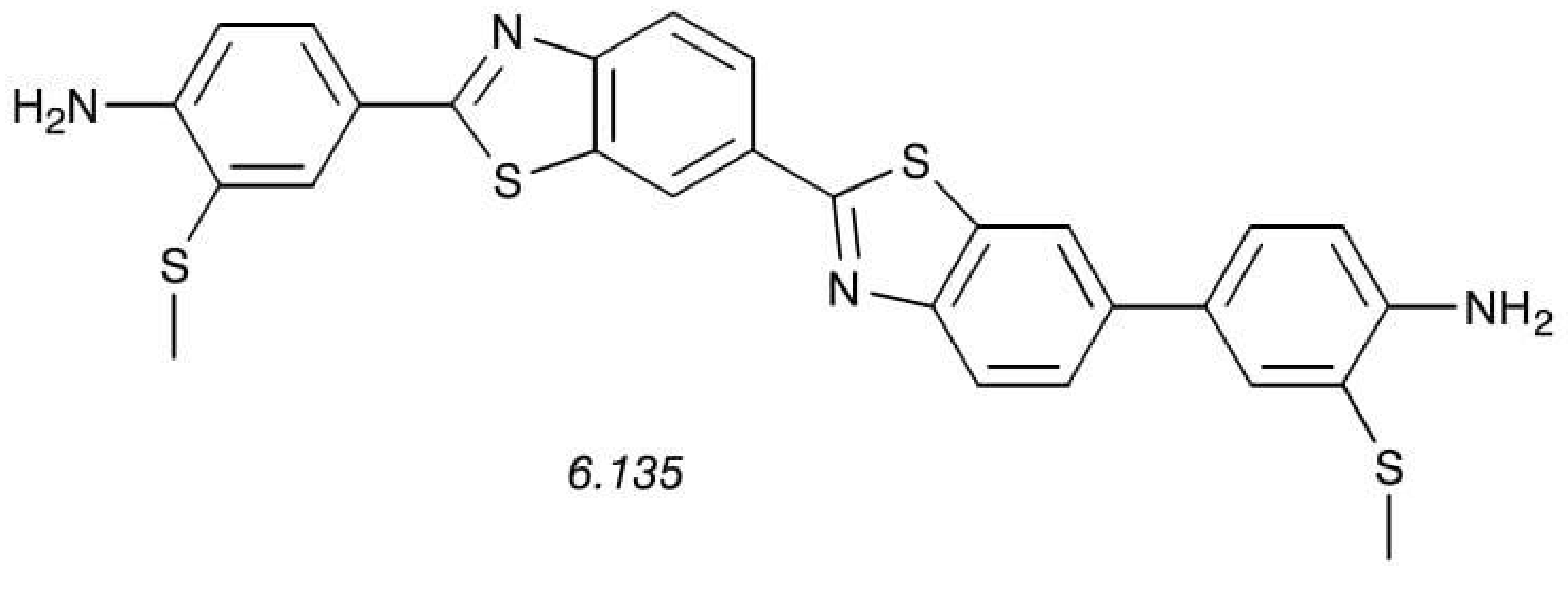


6.133



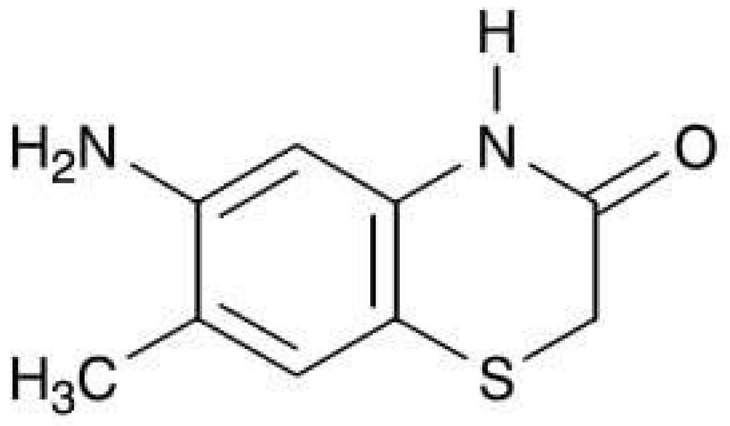
6.134

Benzidine

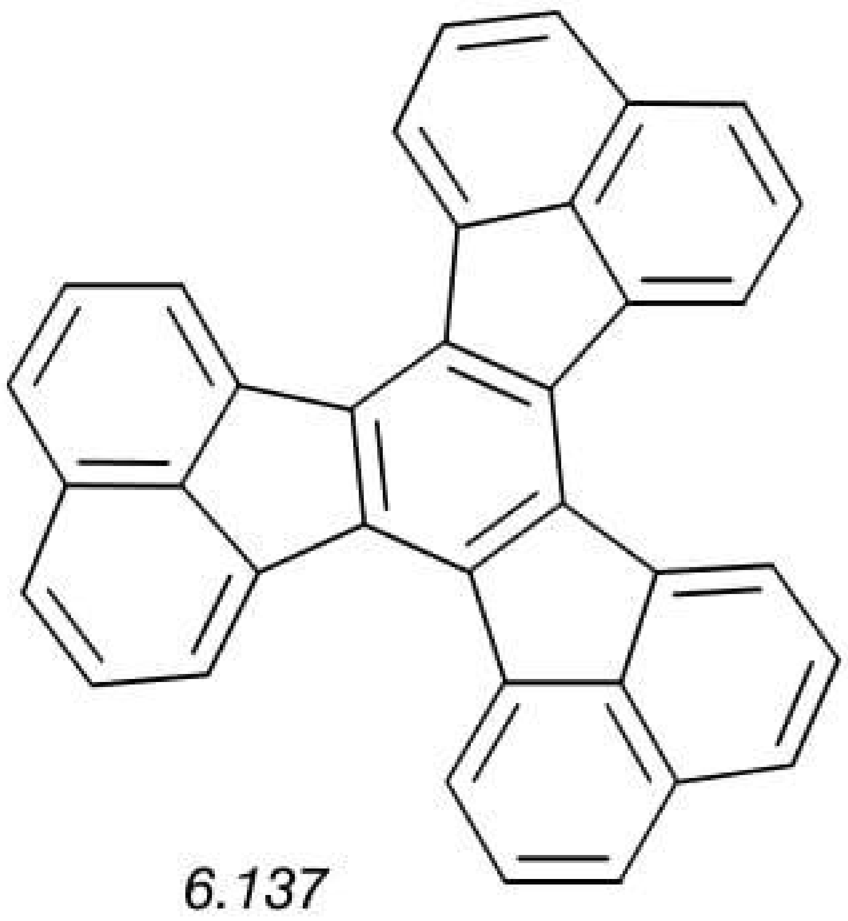


6.135

A similar study of the dye CI Sulphur Orange 1, obtained by heating 2,4-diaminotoluene with sulphur, led to the isolation of compound 6.136 after reaction of the alkali melt of the dye with chloroacetic acid. It was concluded that the commercial dye is a polybenzothiazole. The final hue of the product depends on the temperature and the duration of the sulphurisation; the use of a smaller proportion of sulphur produces CI Sulphur Brown 10. A similar product (CI Sulphur Brown 8) is obtained when 2,4-dinitrotoluene is baked with sodium polysulphide. A brown sulphur dye of high fastness to light (CI Sulphur Brown 52) results when the polycyclic hydrocarbon decacyclene (6.137) is baked with sulphur at 350 °C [57].

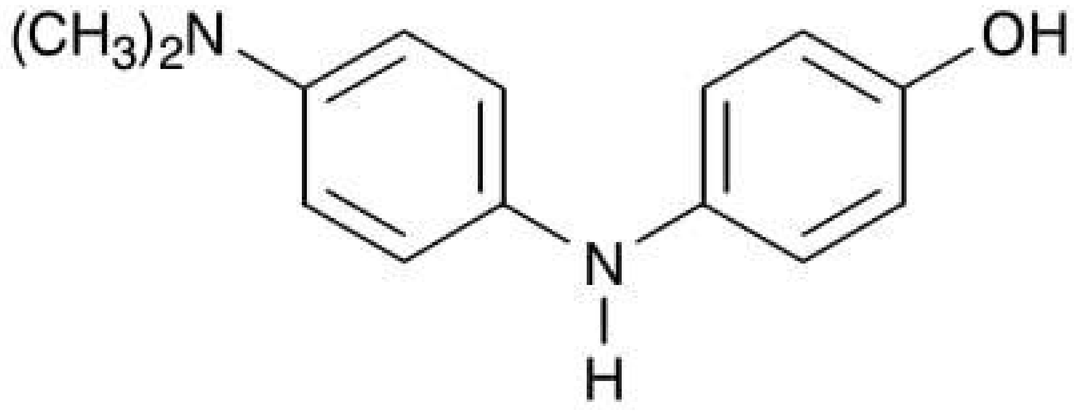


6.136

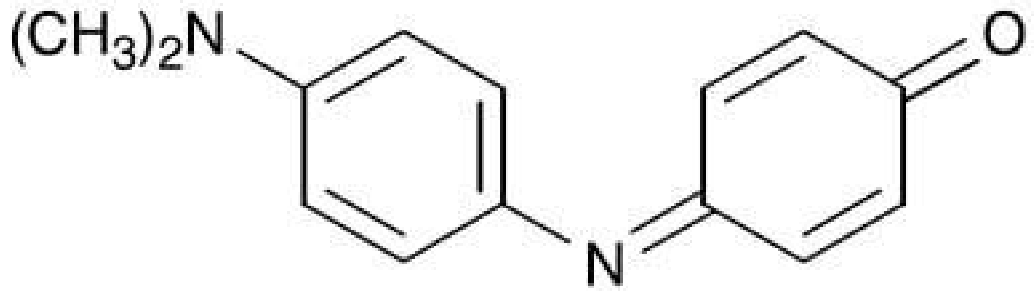


6.137
Decacyclene

The use of intermediates capable of forming quinonimine ring systems leads to the synthesis of red, blue, green and black sulphur dyes on treatment with aqueous or alcoholic sodium polysulphide. Thus, for example, condensation of *N,N*-dimethyl-*p*-phenylenediamine with phenol gives a diphenylamine intermediate (6.138), which on sulphurisation in alcoholic sodium polysulphide first yields an indoaniline oxidation product (6.139). This quinonimine in turn undergoes thionation to form a phenothiazone chromogen (6.140). Further reaction leads to the synthesis of CI Sulphur Blue 9. A similar sequence can be envisaged using indophenol derivatives. For example, the simple indophenol 6.141, which is made by oxidising a mixture of 4-aminophenol and phenol with sodium hypochlorite, gives CI Sulphur Blue 14 on sulphurisation with aqueous sodium polysulphide. Similar blue dyes are available from related intermediates. For example, condensation of diphenylamine with 4-nitrosophenol in sulphuric acid gives compound 6.142; this intermediate reacts with aqueous sodium polysulphide to form CI Sulphur Blue 13. The incorporation of a naphthalene ring system enables green dyes to be produced. The important dye CI Sulphur Green 3, for example, is made by heating compound 6.143 with aqueous sodium polysulphide under reflux in the presence of copper(II) sulphate. CI Sulphur Green 14 is based on copper phthalocyanine [50].



6.138



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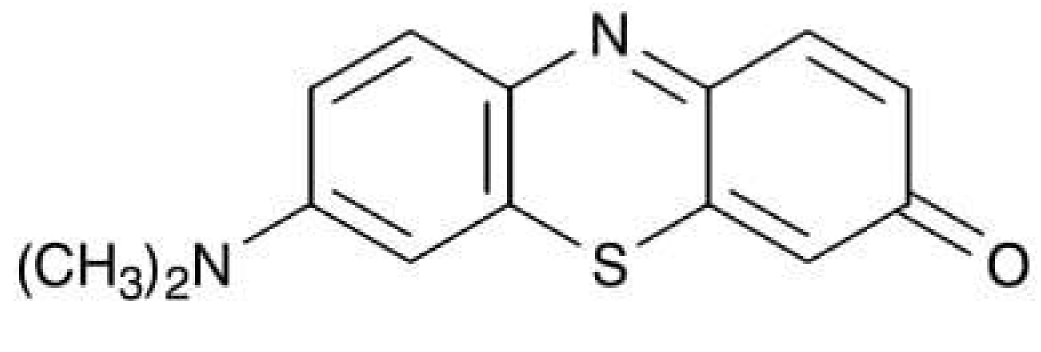

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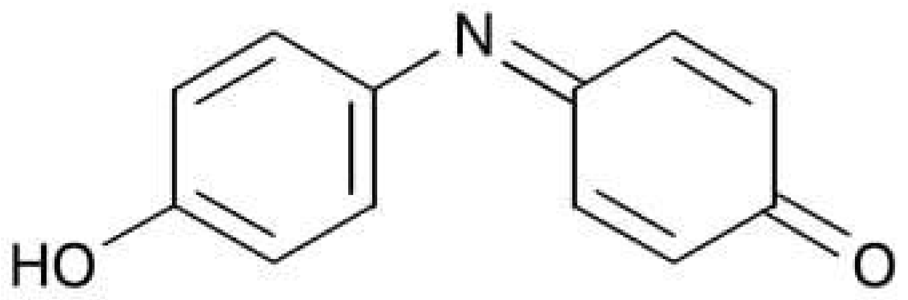
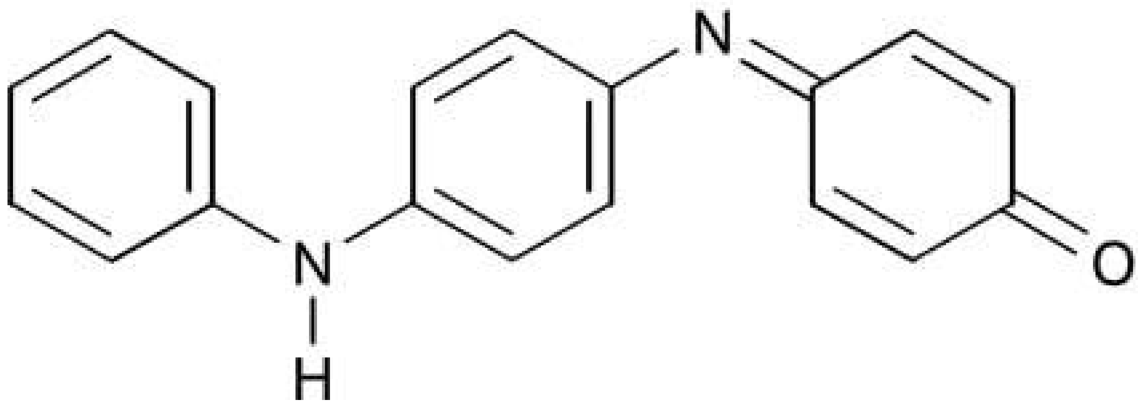
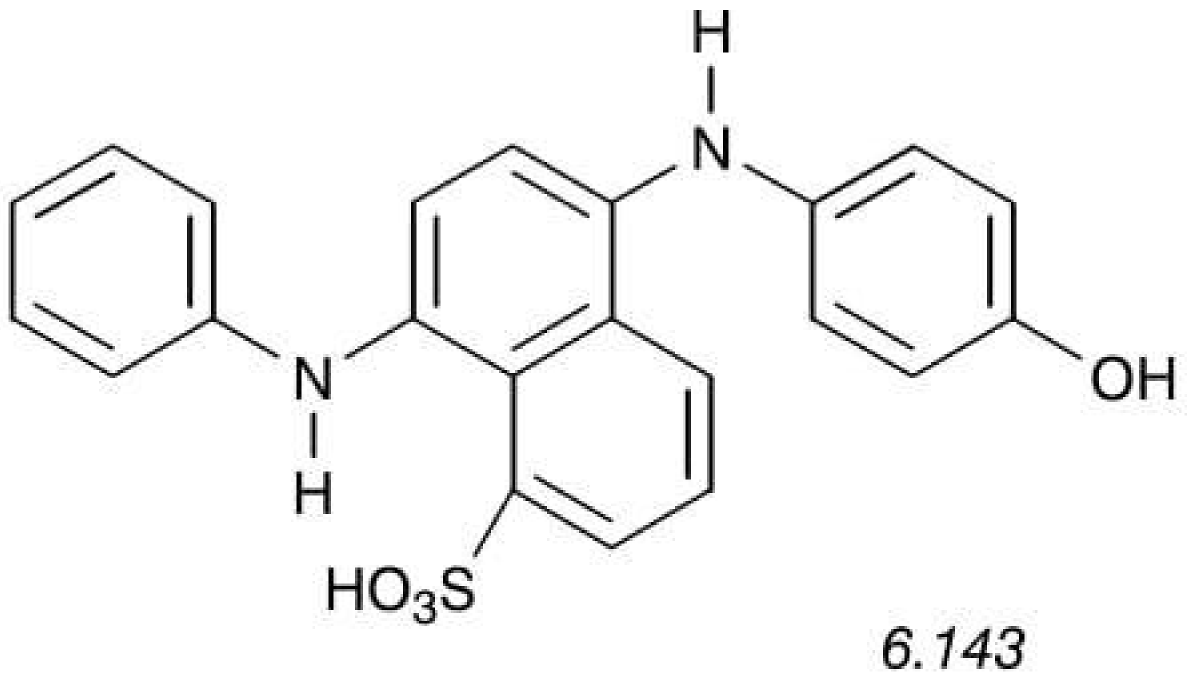


6.141



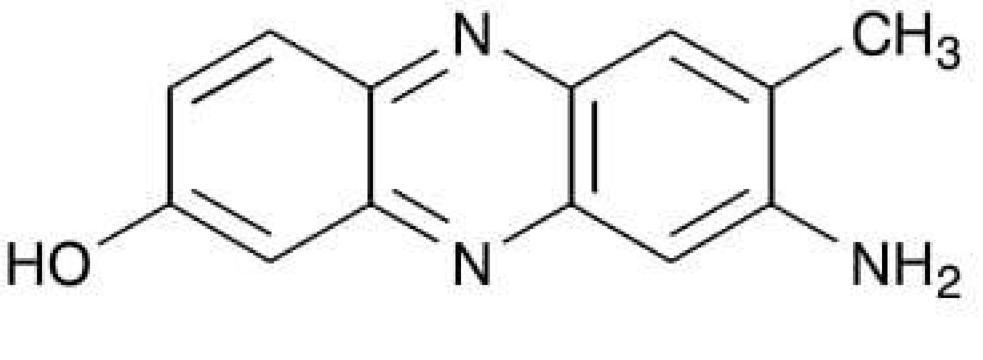
6.142



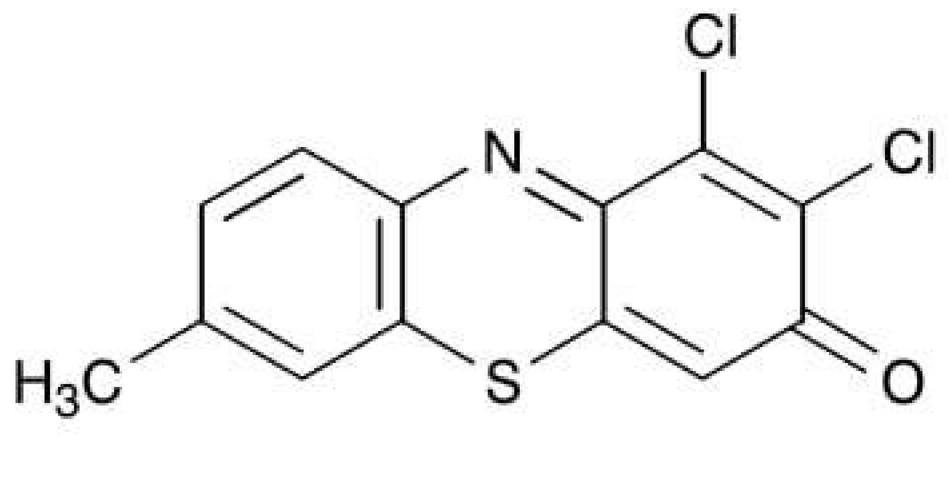
6.143

Sulphurisation of 4-hydroxydiphenylamine in a glycol solvent gives CI Sulphur Red 10. A useful red dye (CI Sulphur Red 6) is prepared by heating 3-amino-6-hydroxy-2-methylphenazine (6.144) with aqueous sodium polysulphide. The phenazine derivative can be made by oxidising the condensation product of 2,4-diaminotoluene and 4-aminophenol. The substituted phenothiazone 6.145 gives CI Sulphur Red 5 on treatment with aqueous sodium polysulphide in the presence of glycerol. Zerweck *et al.* [56] showed that the chlorine atoms in compound 6.145 could be displaced stepwise by mercapto groups. The resulting polymeric dye was found to be essentially the same as that generated by sulphurisation of the parent 4-hydroxy-4′-methyldiphenylamine. It can therefore be deduced that sulphur dyes of this type contain structural units similar to that shown in structure 6.146, which possesses a central thianthrene ring system isosteric with indanthrone (6.65).

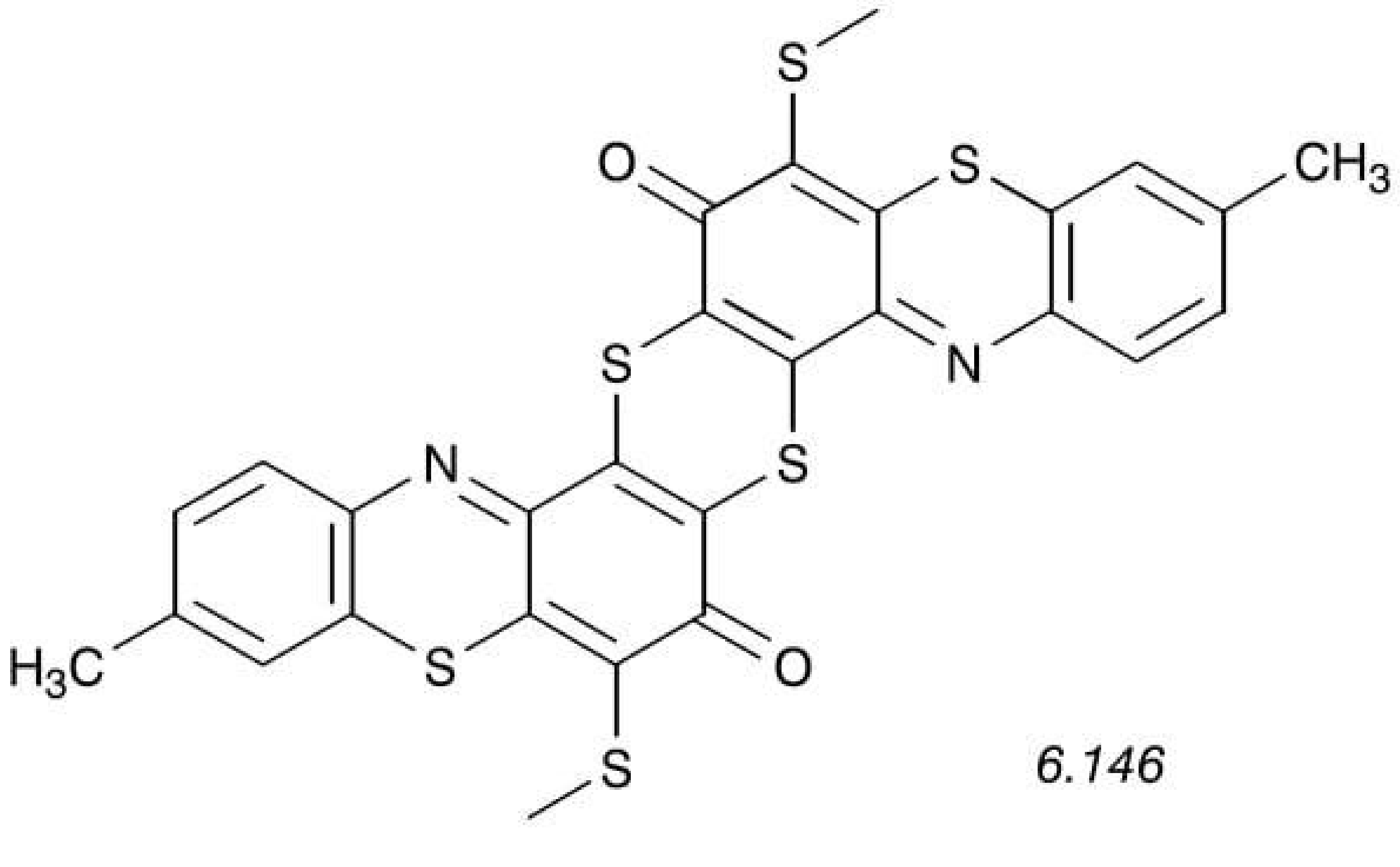
Only one violet sulphur dye is commercially available: CI Sulphur Violet 1, obtained from the substituted indoaniline 6.147. Several black sulphur dyes are currently in use, especially



6.144



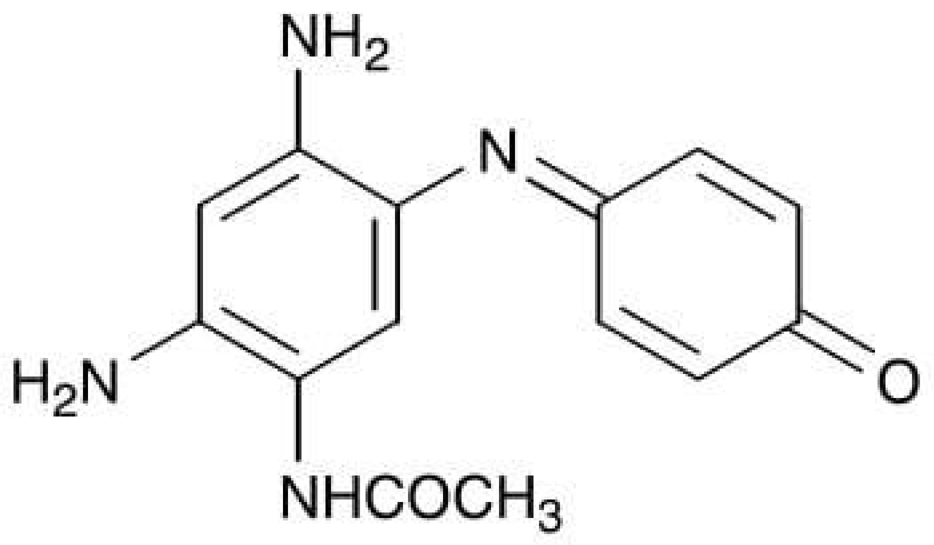
6.145



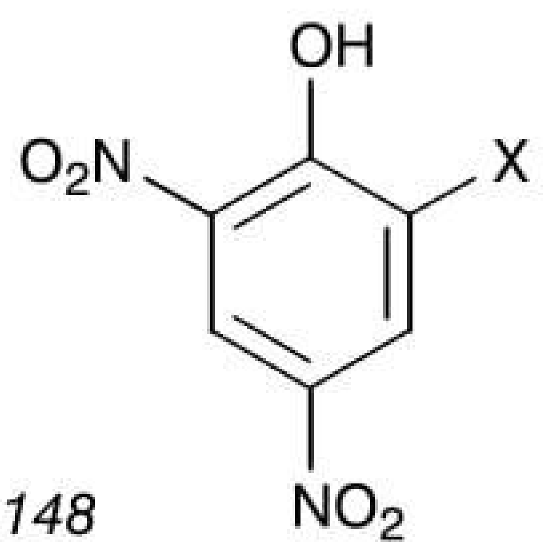
6.146

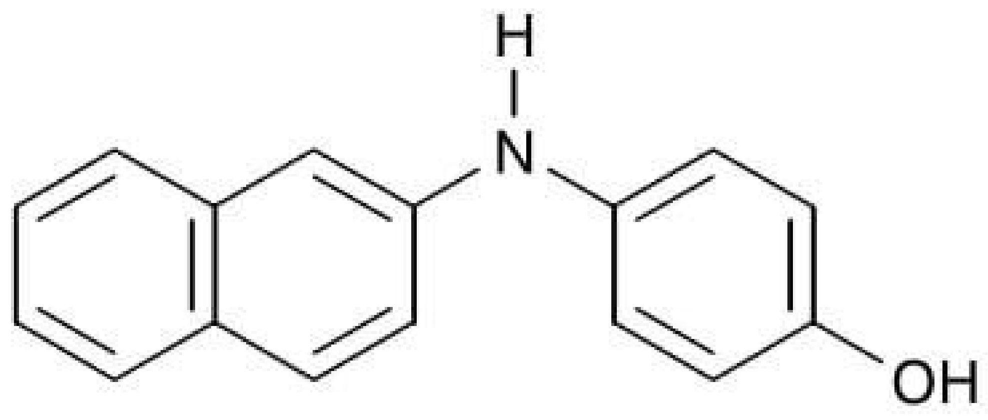
CI Sulphur Black 1, which is produced from the relatively simple intermediate 2,4-dinitrophenol and aqueous sodium polysulphide. A similar product (CI Sulphur Black 2) is obtained from a mixture of 2,4-dinitrophenol and either picric acid (6.148; X = NO_2) or picramic acid (6.148; X = NH_2). A black dye possessing superior fastness to chlorine when on the fibre (CI Sulphur Black 11) can be made from the naphthalene intermediate 6.149 by heating it in a solution of sodium polysulphide in butanol. An equivalent reaction using the carbazole intermediate 6.150 gives rise to the reddish blue CI Vat Blue 43 (Hydron blue). This important compound, which also possesses superior fastness properties, is classified as a sulphurised vat dye because it is normally applied from an alkaline sodium dithionite bath. Interestingly, inclusion of copper(II) sulphate in the sulphurisation of intermediate 6.150 leads to the formation of the bluish black CI Sulphur Black 4.

The many sulphur dyes synthesised via quinonimine intermediates are polymeric products containing numerous disulphide crosslinkages that can be broken by reduction in aqueous sodium sulphide; thioether groups survive the reduction process. The smaller thiolate-containing molecules formed are substantive to cellulose. Although the actual structures of such dyes are complex, their essential features can be illustrated in an idealised model (Scheme 6.23), in which X = S, NH or O, and R indicates substituents or annelated rings.

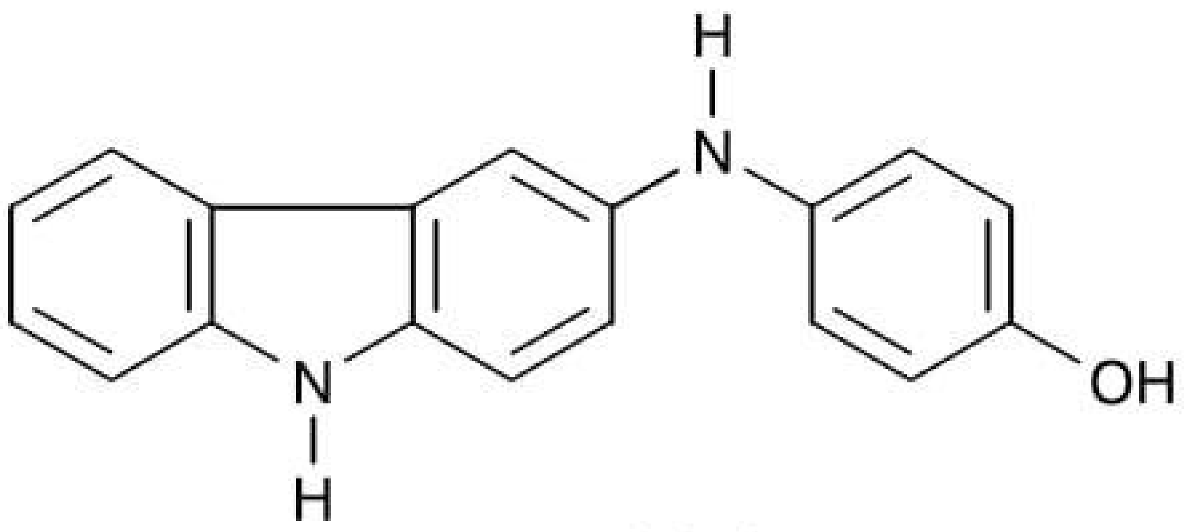


6.147

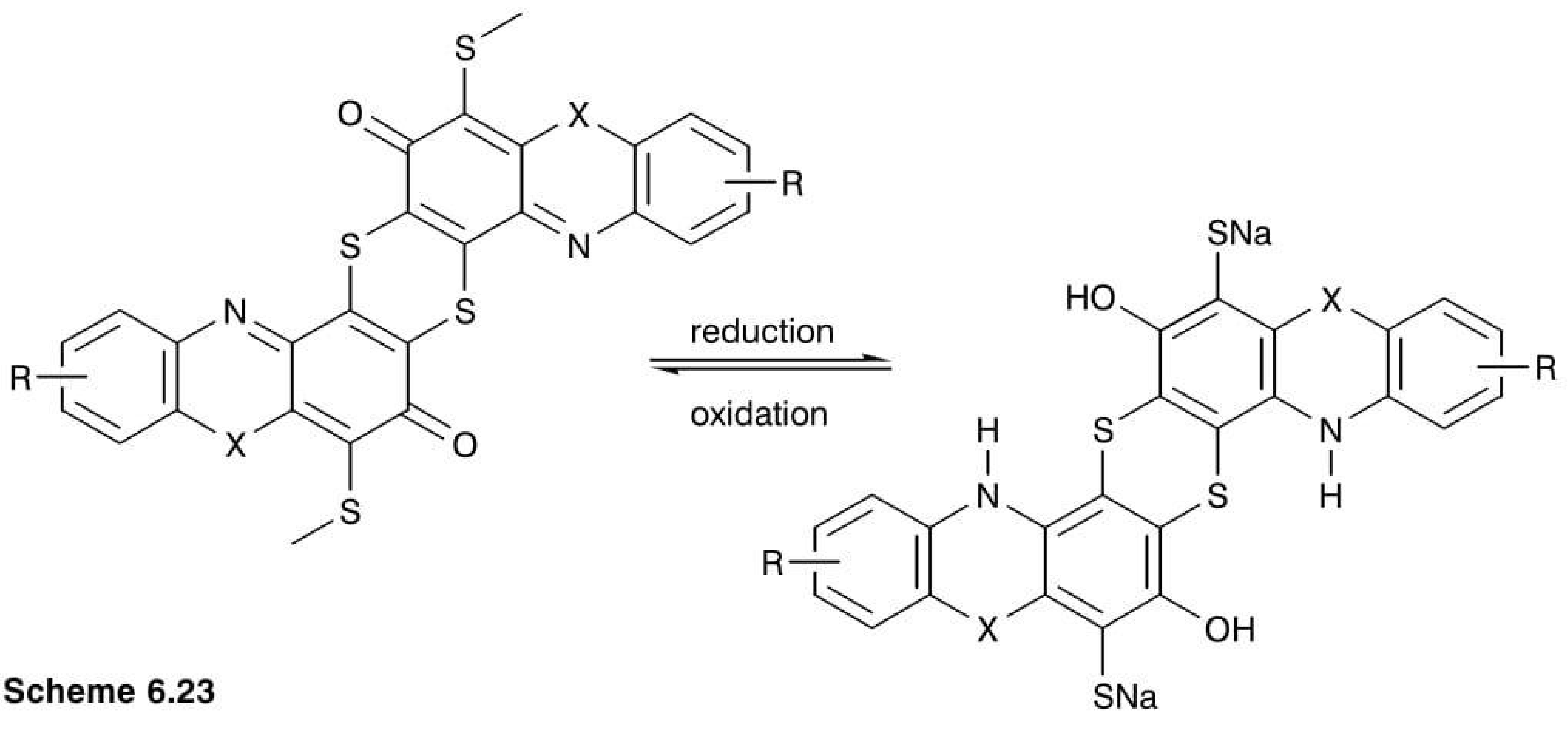




6.149



6.150

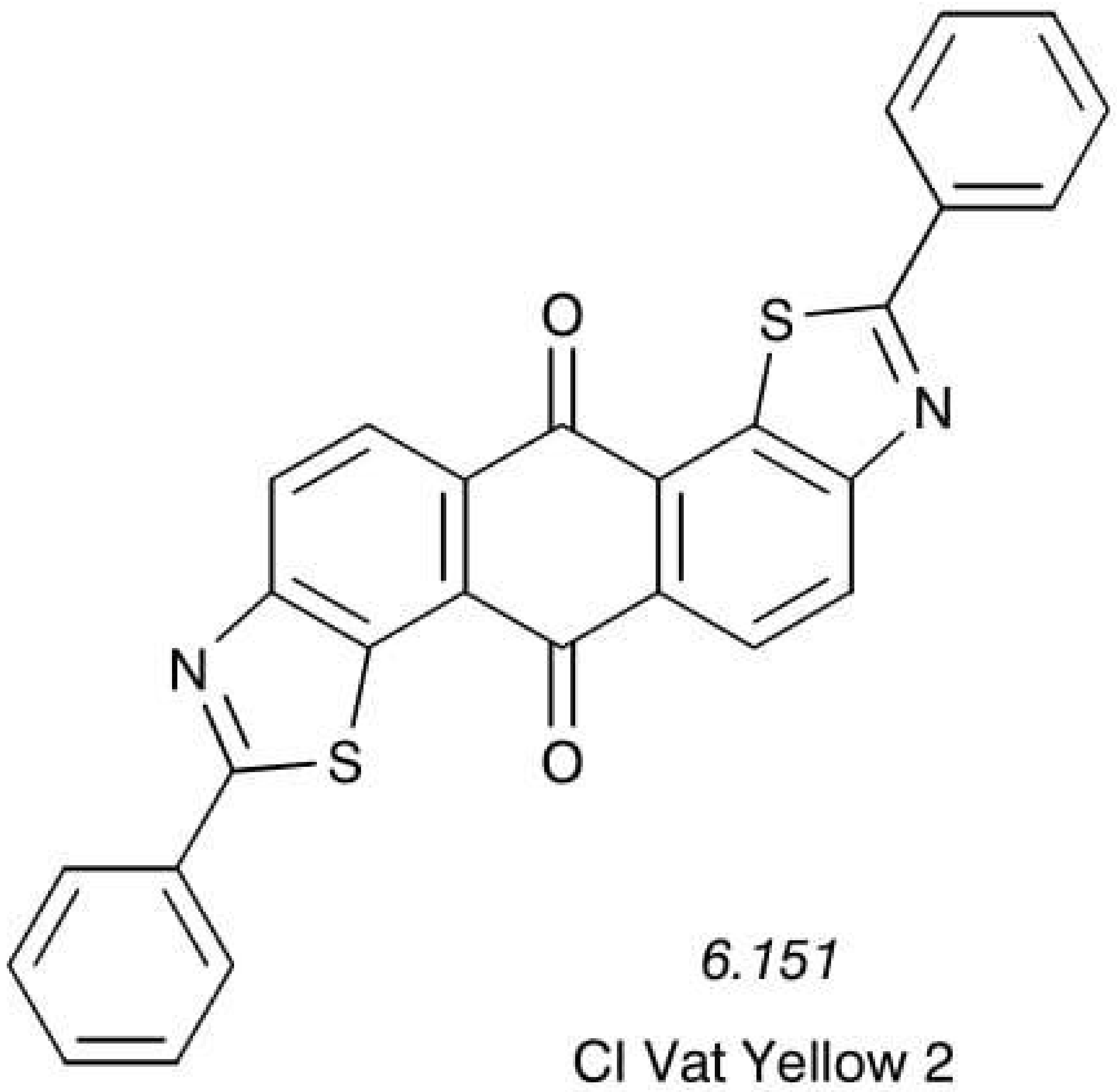


Scheme 6.23

6.4.3 Sulphurised vat dyes and thiazole derivatives

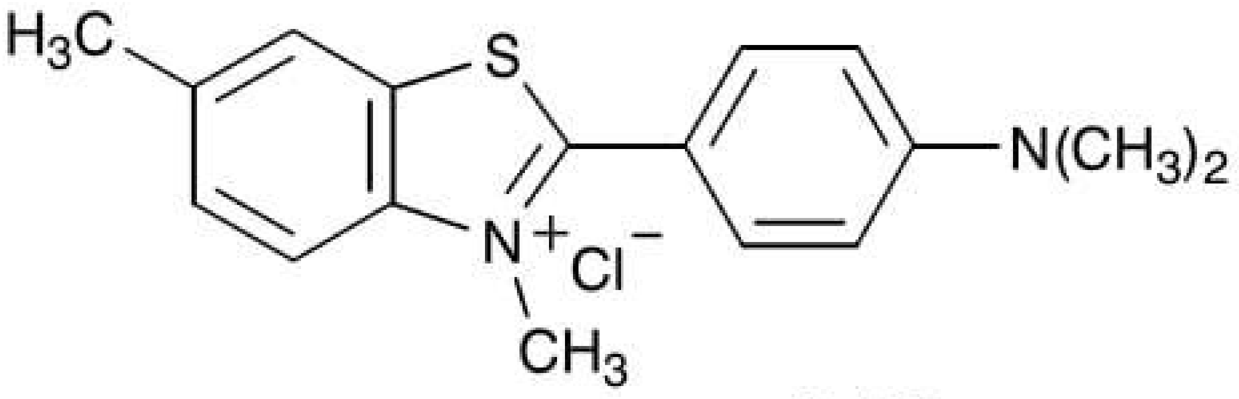
CI Vat Blue 43 and the equivalent dye derived from *N*-ethylcarbazole (CI Vat Blue 42) are sometimes referred to as sulphurised vat dyes. This term is also applied to some anthraquinonoid thiazole derivatives, such as CI Vat Yellow 2 (6.151). This compound can be made by the reaction of 2,6-diamino-1,5-dichloroanthraquinone with benzaldehyde and sulphur. Another anthraquinonoid vat dye containing a thiazole ring system (6.107) has already been mentioned.

The thiazole ring system is found in many types of dye. Thiazole-containing sulphur dyes and primuline were considered in section 6.4.2. Quaternised dehydrothio-*p*-toluidine 6.133 is available as CI Basic Yellow 1 (6.152). Other derivatives of this intermediate are used as direct dyes, such as CI Direct Yellow 8 (4.58). The benzothiazole ring appears in various azo disperse dyes [14], quaternisation of which gives useful cationic dyes, an important example being CI Basic Blue 41 (4.99). Another example containing a quaternised thiazole ring is CI Basic Red 29 (4.102).



6.151

CI Vat Yellow 2



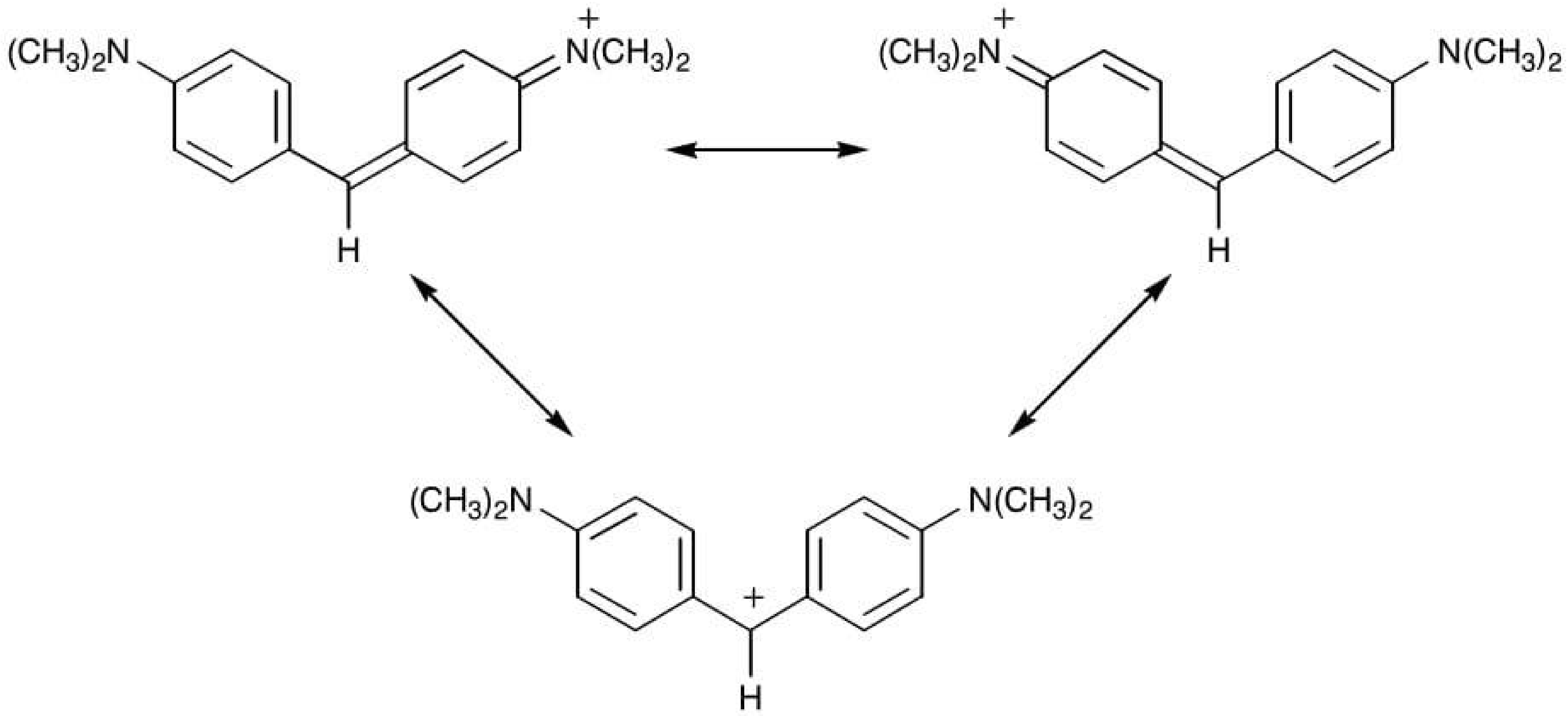
6.152

CI Basic Yellow 1

6.5 DIARYLMETHANE AND TRIARYLMETHANE DYES

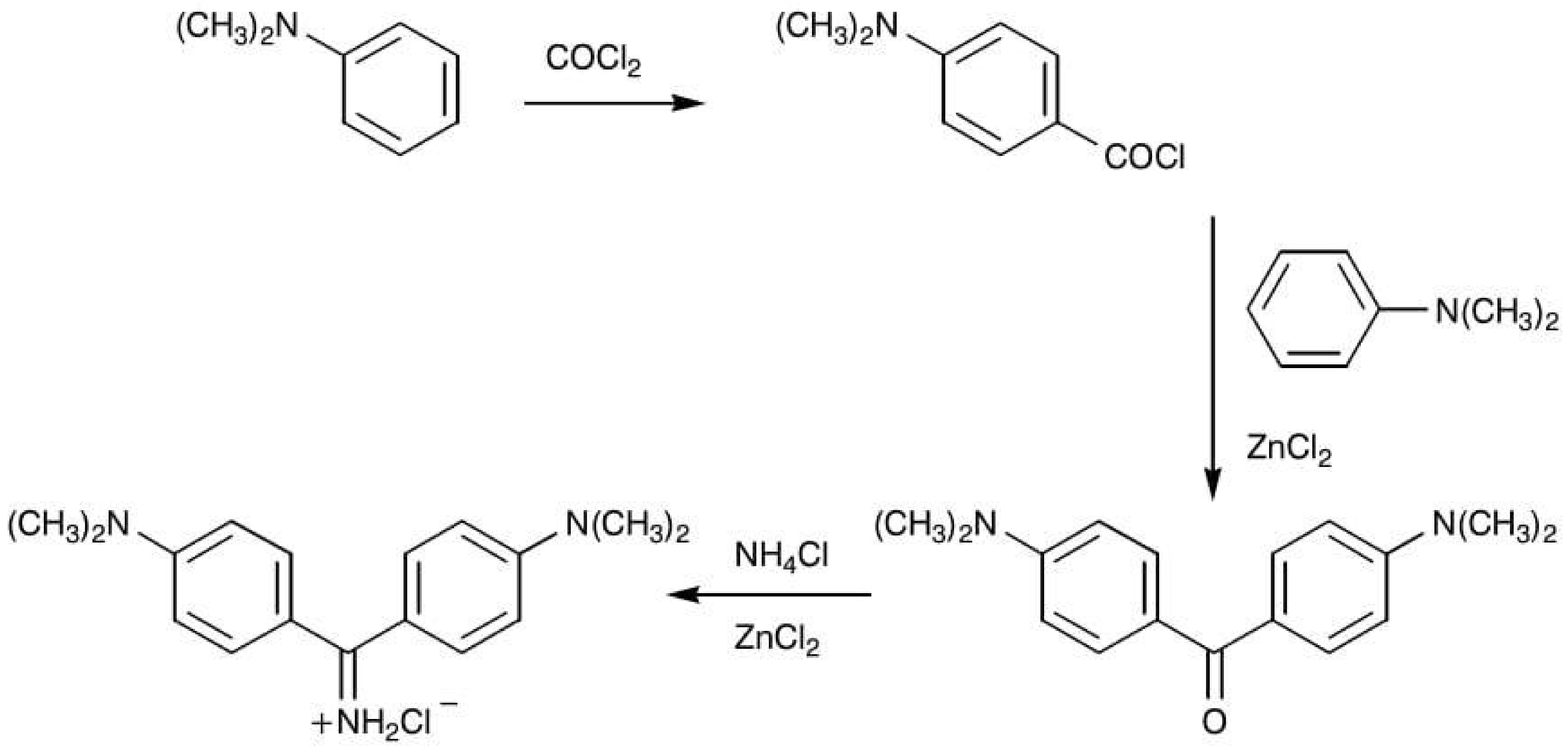
Derivatives of triphenylmethane were among the earliest synthetic colorants, and are still in demand where bright, intense colours are needed without the necessity for outstanding fastness to light and chemical reagents. Basic dyes of this type, as well as other cationic dyes, are suitable for dyeing conventional acrylic fibres, on which they show better fastness properties than on natural fibres. The photodegradation of triphenylmethane dyes has been reviewed [42].

Traditionally dyes in this category are referred to as triarylmethane dyes; carbocyclic ring systems other than benzene, particularly naphthalene, and various heterocyclic systems are also encountered. Few diarylmethane dyes are of commercial significance, although some heterocyclic derivatives and analogues are of interest. Di- and tri-arylmethane dyes are mesomeric cations (charge-resonance systems) in which the positive charge is localised mainly on the terminal nitrogen atoms, as in the case of Michler's Hydrol Blue (Scheme 6.24). One of the resonance canonical forms (6.153) is a carbonium ion, so that dyes of this kind are sometimes referred to as di- or tri-arylcarbonium ions [58]. Since the central carbon atom in these systems is sp^2 hybridised, Zollinger suggests that the terms di- and tri-arylmethine dyes are more appropriate [59]; this class of dyes is structurally similar to the polymethine dyes.



6.153
Michler's Hydrol Blue

Scheme 6.24

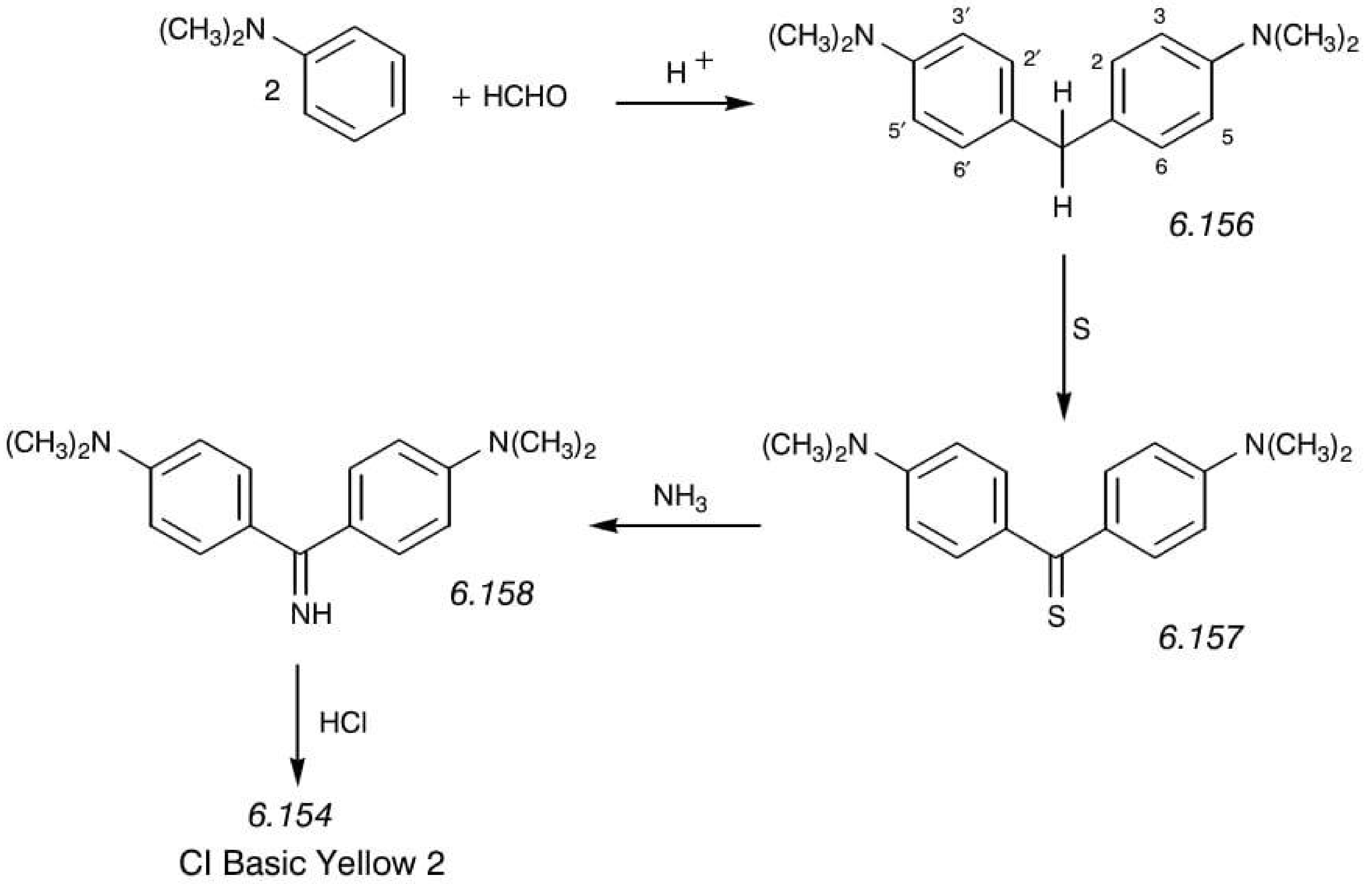


6.154
CI Basic Yellow 2

6.155
Michler's ketone

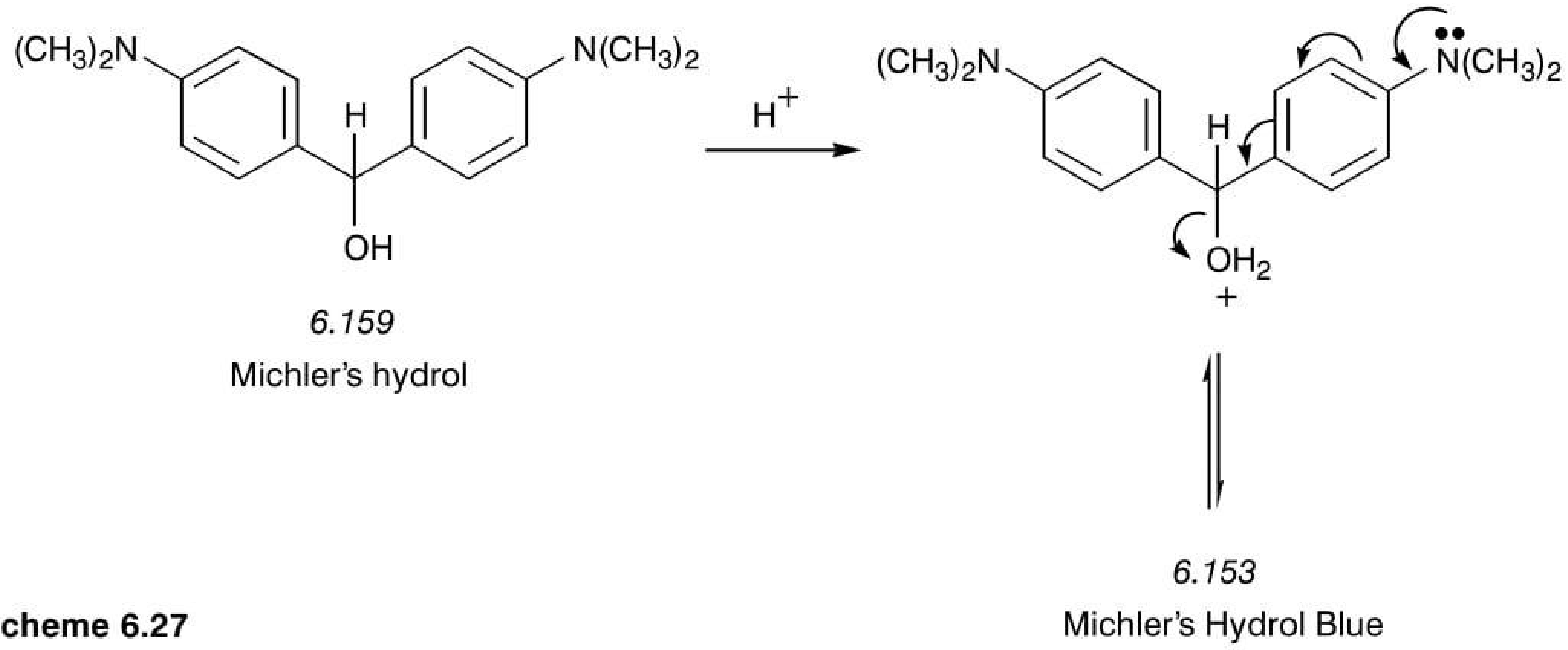
Scheme 6.25

Michler's Hydrol Blue absorbs at 607.5 nm ($\varepsilon = 147\ 500$) in 98% acetic acid [60]. This bright blue dye and related diphenylmethane derivatives have poor fastness properties and are not of commercial importance. Attachment of an amino group to the central carbon atom of Michler's Hydrol Blue gives the yellow dye Auramine (6.154; CI Basic Yellow 2), which absorbs at 434 nm in ethanol and is used in the dyeing of paper and in other applications, although the dye is a known carcinogen. The electron-donating amino group produces a very marked hypsochromic shift. Auramine is somewhat more stable than Michler's Hydrol Blue but, being a ketimine, it is hydrolysed in boiling water to form Michler's ketone (6.155) and ammonia. The dye was first obtained in 1883 by Kern and Caro who heated Michler's ketone with ammonium chloride and zinc chloride. The synthesis first requires the formation of the important ketone intermediate by a Friedel–Crafts acylation (Scheme 6.25). An improved route was devised in 1889 by Sandmeyer, involving the corresponding thioketone (6.157). Condensation of *N,N*-dimethylaniline with formaldehyde gives 4,4′-bis(dimethylamino)diphenylmethane (6.156), which is then heated with sulphur and ammonium chloride, with sodium chloride as diluent, in an atmosphere of ammonia (Scheme 6.26). The resulting Auramine base (6.158) gives Auramine when treated with hydrochloric acid. The ethyl analogue of Auramine is CI Basic Yellow 37.



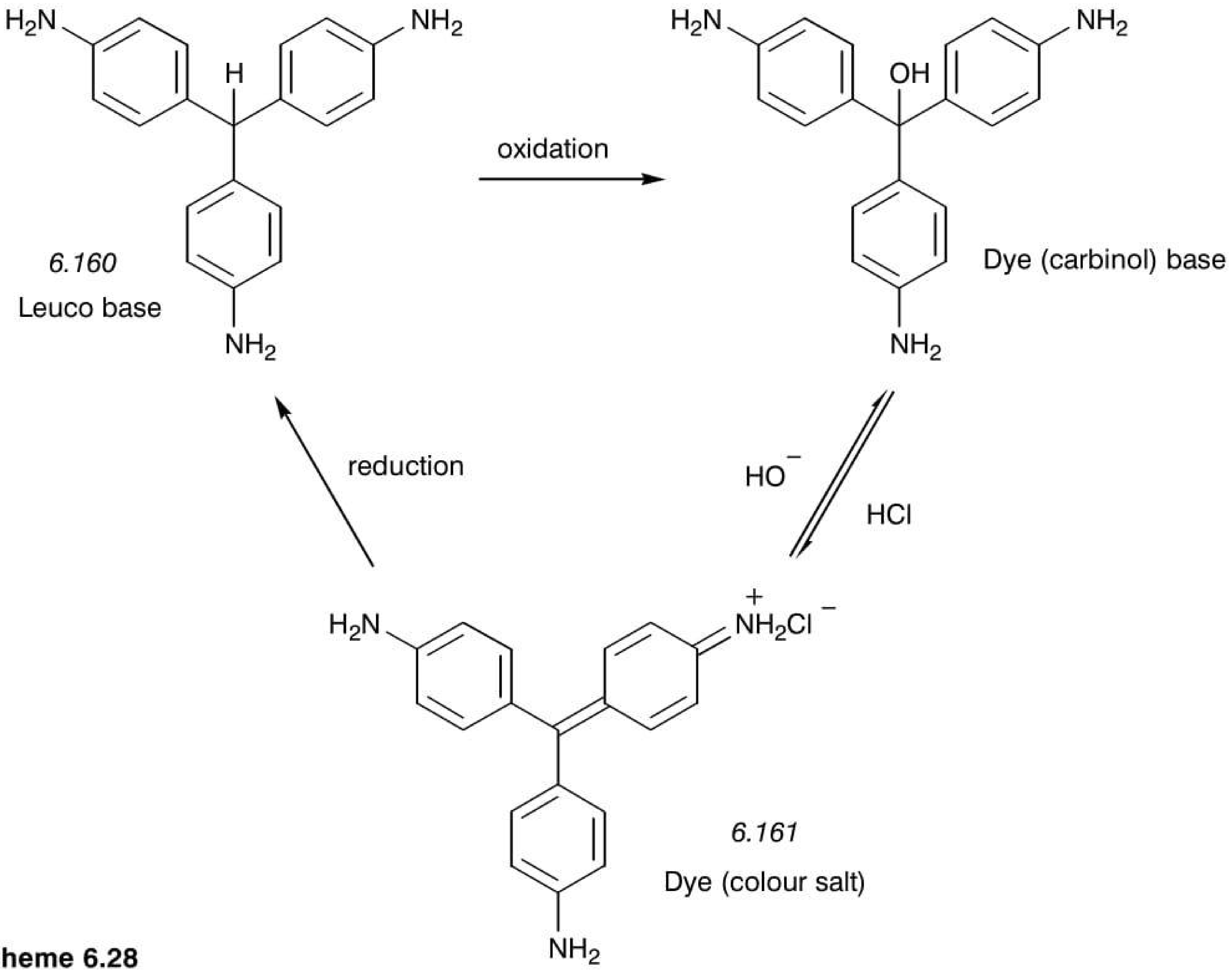
Scheme 6.26

Reduction of Michler's ketone gives Michler's hydrol (6.159), which forms Michler's Hydrol Blue in the presence of acid (Scheme 6.27). Michler's hydrol is produced industrially by the oxidation of the diphenylmethane precursor (6.156); further oxidation to give Michler's ketone takes place readily.



Scheme 6.27

The more important triphenylmethane dyes probably date from 1834, when Runge obtained red compounds of unknown constitution from crude phenol and from crude aniline. Shortly after Perkin's discovery of mauveine (section 6.6.1) in 1856 Natanson obtained the triphenylmethane dye magenta from crude aniline by oxidation. Although many related dyes were made empirically over the following two decades, it was not until 1880 that Fischer was able to establish structural relationships within this group of dyes. The essential triphenylmethane ring system was identified by its conversion (Scheme 6.28) into 4,4′,4″-triaminotriphenylmethane (6.160), the source of pararosaniline (6.161; CI Basic Red 9).



Scheme 6.28

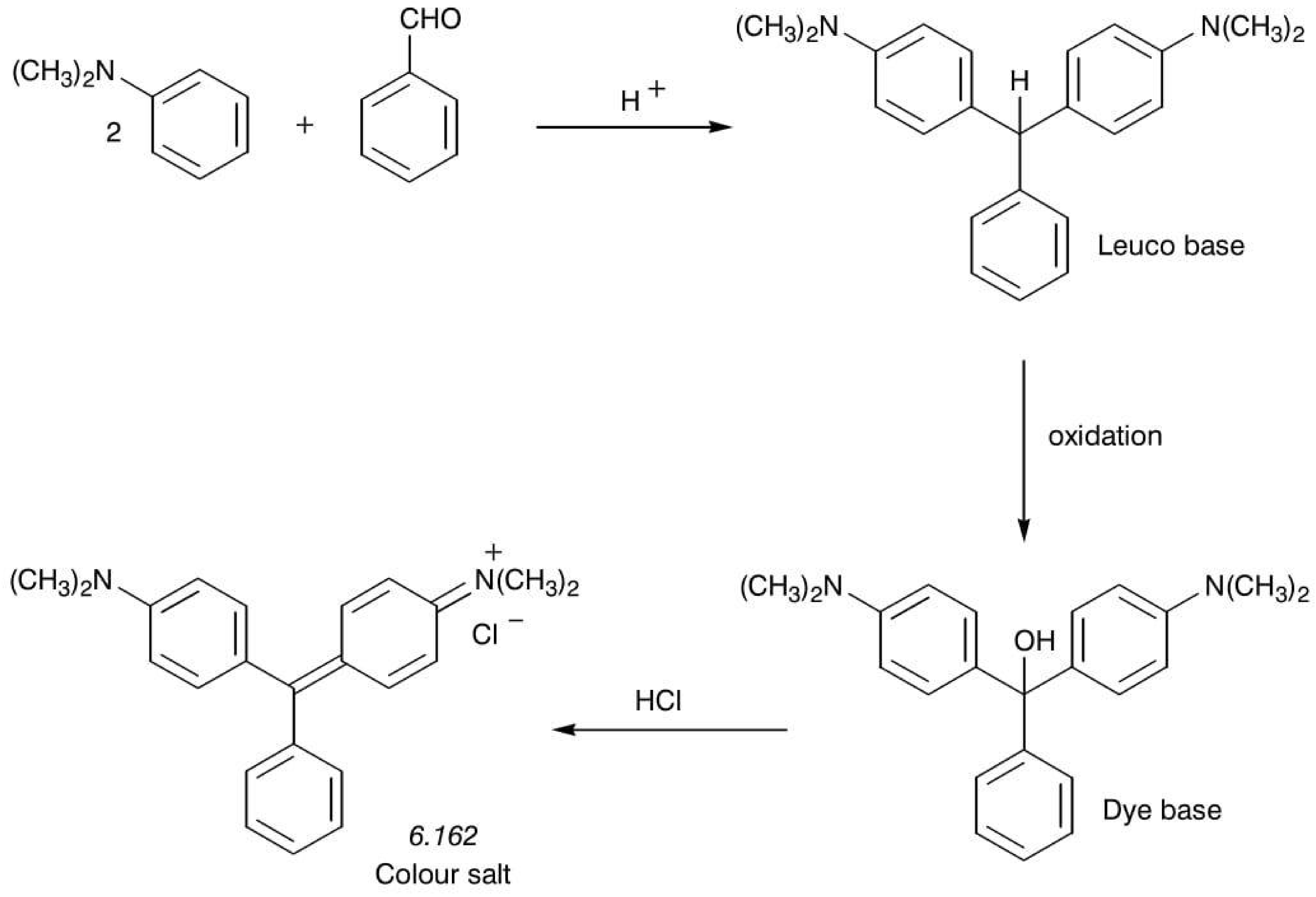
Nearly all commercial triarylmethane dyes contain two or three electron-donor substituents at *para* sites. In general, dyes containing two *p*-amino groups (the malachite green series) are green or greenish blue, whereas those with three *p*-amino groups (the crystal violet series) are reddish to bluish violet. Of lesser importance are monoamino structures containing alkoxy groups, although these orange or red dyes have very good light fastness on acrylic and modacrylic fibres [22].

6.5.1 Methods of synthesis

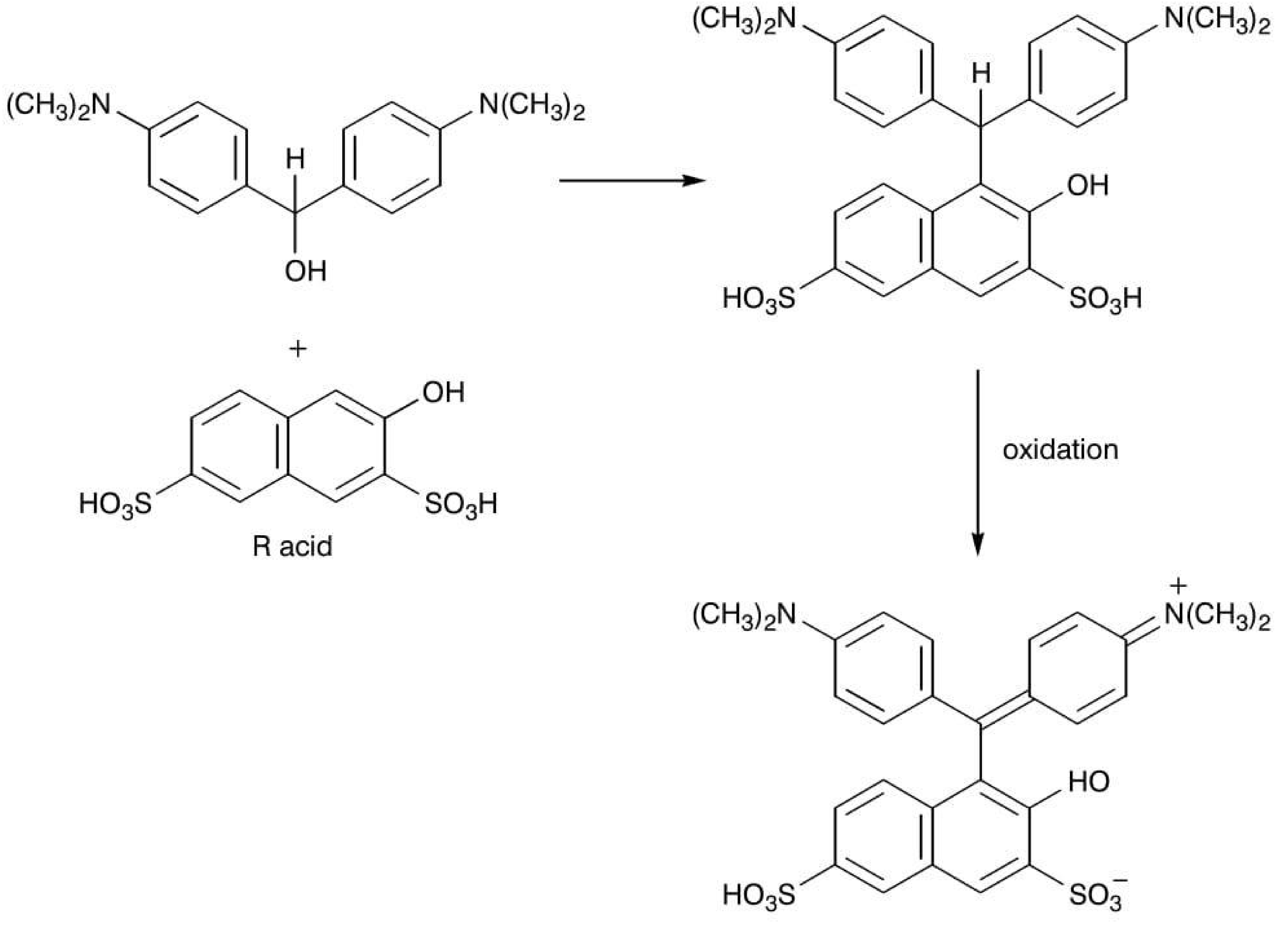
In the synthesis of the triarylmethane skeleton the central carbon atom is provided either by a simple compound, such as formaldehyde or phosgene, or as part of an aromatic intermediate. Depending on the oxidation state of the component used, the resulting dye is obtained directly or as the leuco base. The various reactions involved are essentially electrophilic aromatic substitutions in which, usually, the *para* position is activated by a powerful electron-donor substituent such as a dialkylamino group.

The leuco base of the dye is produced by condensation of one mole of an aromatic aldehyde with two moles of an aromatic amine having an unsubstituted *para* position (*the aldehyde synthesis*) in the presence of a mineral acid or a Friedel–Crafts catalyst. Schiff bases are obtained with primary aromatic amines devoid of crowding substituents adjacent to the amino group. The aldehyde method is illustrated by the classical synthesis of malachite green (6.162; CI Basic Green 4), first carried out in 1877 by Fischer (Scheme 6.29). The resulting leuco base is readily oxidised to the dye base and thence to the colour salt. For many years lead(IV) oxide has been used as the oxidising agent but more recently, for environmental reasons, lead-free processes have been used. Of particular interest is oxidation by chloranil (tetrachloro-*p*-benzoquinone) or by air in the presence of catalysts. Mechanistically it is likely that the conversion involves hydride abstraction in the case of chloranil, so that the dye is formed directly from the leuco base [61]. The chemistry of leuco triarylmethanes has been reviewed [62].

Condensation of a diphenylmethanol derivative, such as Michler's hydrol (6.159), with a reactive aryl component under acid conditions (*the hydrol synthesis*) also provides a leuco base. The dye 6.163 (CI Acid Green 50) is made by reacting Michler's hydrol with R acid (2-naphthol-3,6-disulphonic acid) and oxidising the resulting leuco compound (Scheme 6.30).

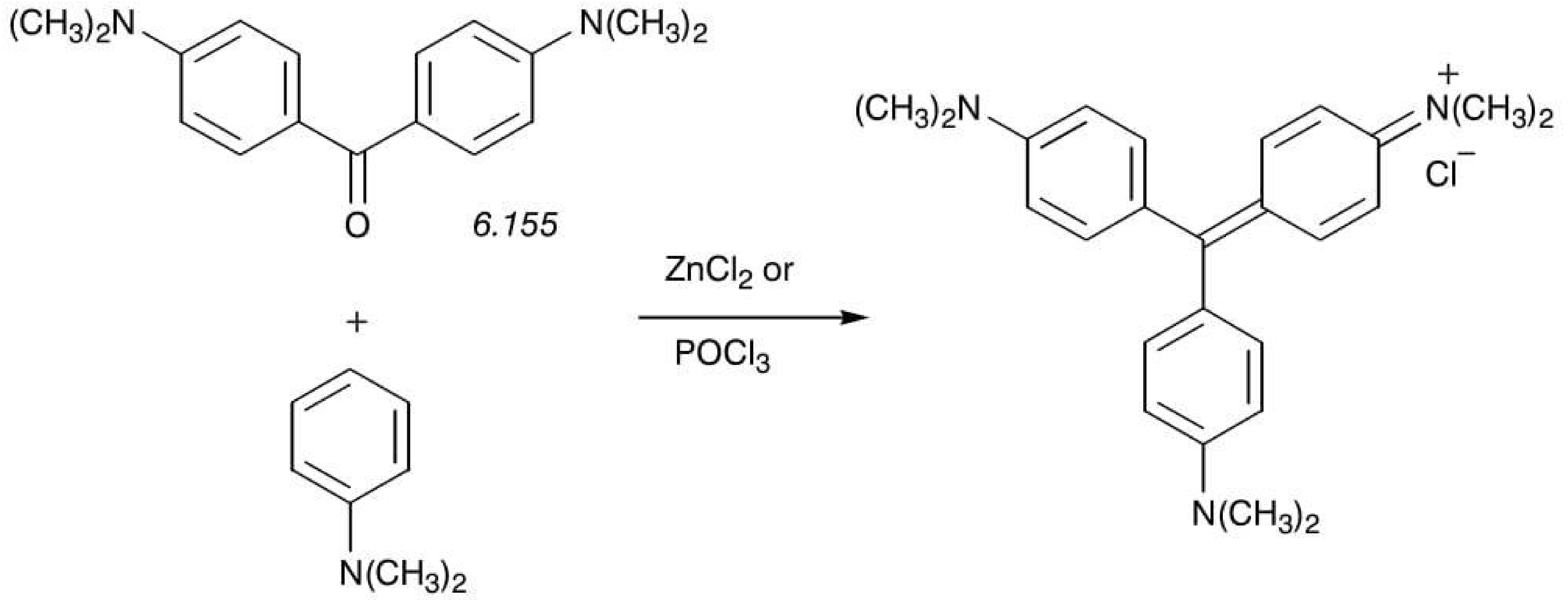


Scheme 6.29



6.163
CI Acid Green 50

Scheme 6.30

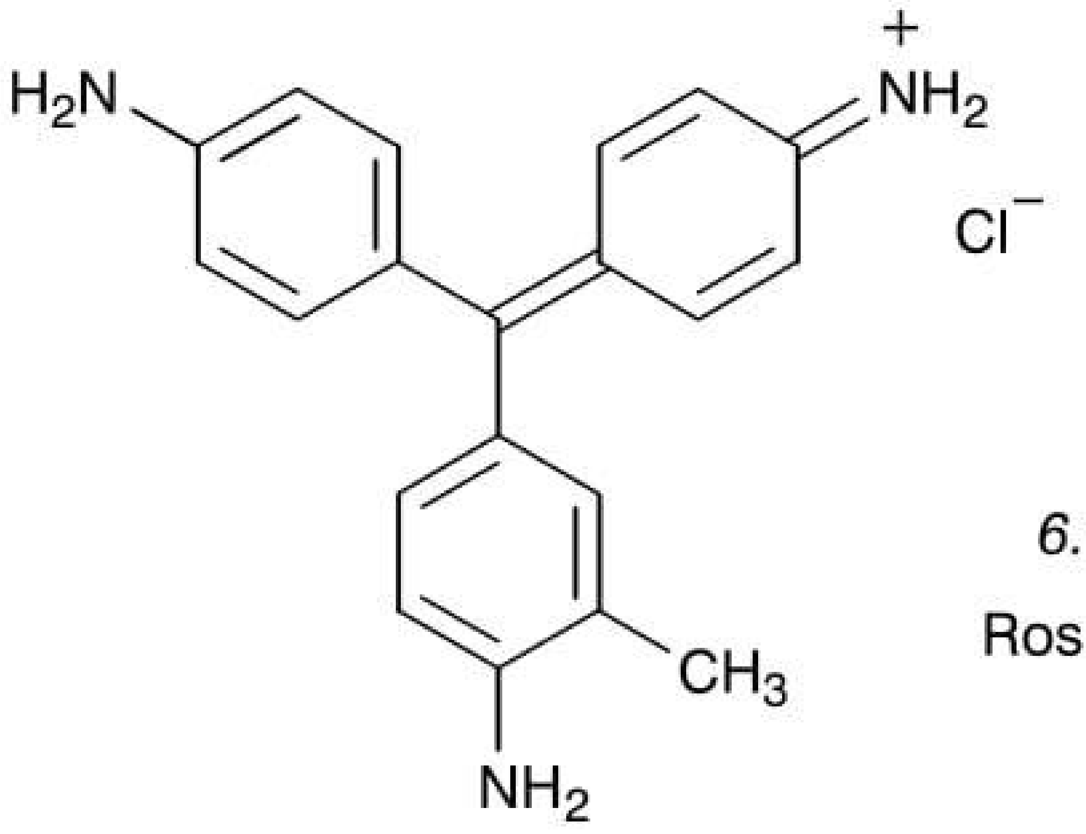


6.164
CI Basic Violet 3

Scheme 6.31

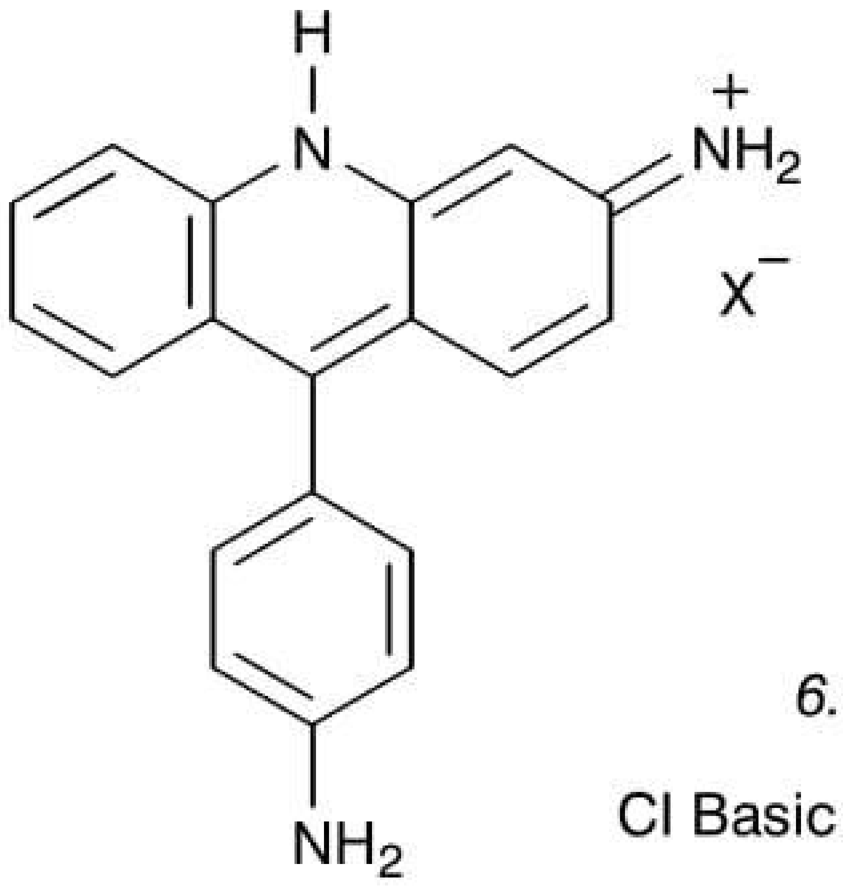
Michler's ketone (6.155) and related carbonyl compounds can be used to obtain colour salts directly by reaction with a reactive intermediate such as an aromatic amine (*the ketone synthesis*), as in the case of crystal violet (6.164; CI Basic Violet 3) shown in Scheme 6.31.

A few triphenylmethane dyes are still obtained by empirical methods first used in the early processes of dye manufacture. For example, in the production of magenta (CI Basic Violet 14), a mixture of aniline, toluidines and nitrotoluenes is heated with zinc and iron(II) chlorides for several hours. It is likely that the reaction involves initially the oxidation of a methyl group to an aldehyde group. Condensation to form triphenylmethane derivatives, not surprisingly, leads to mixtures. It is now known that magenta is carcinogenic. The main components of magenta are rosaniline (6.165) and pararosaniline (6.161). The yellowish brown by-product chrysaniline (6.166; CI Basic Orange 15), an acridine dye, is present in the mother liquors of magenta manufacture. In the manufacture of methyl violet (CI Basic Violet 1), air oxidation of *N,N*-dimethylaniline in the presence of a copper(II) salt gives a mixture of the more highly methylated pararosanilines.



6.165

Rosaniline



6.166

CI Basic Orange 15

In the laboratory pure dye bases can be prepared by the reaction of diaryl ketones, such as Michler's ketone (6.155), with appropriate Grignard reagents or organolithium compounds. These tertiary alcohols are also available from related reactions between aryl esters and organometallic reagents. A new method of synthesis has been reported which involves displacement of benzotriazole in diarylbenzothiazolylmethanes by aryl Grignard reagents [63].

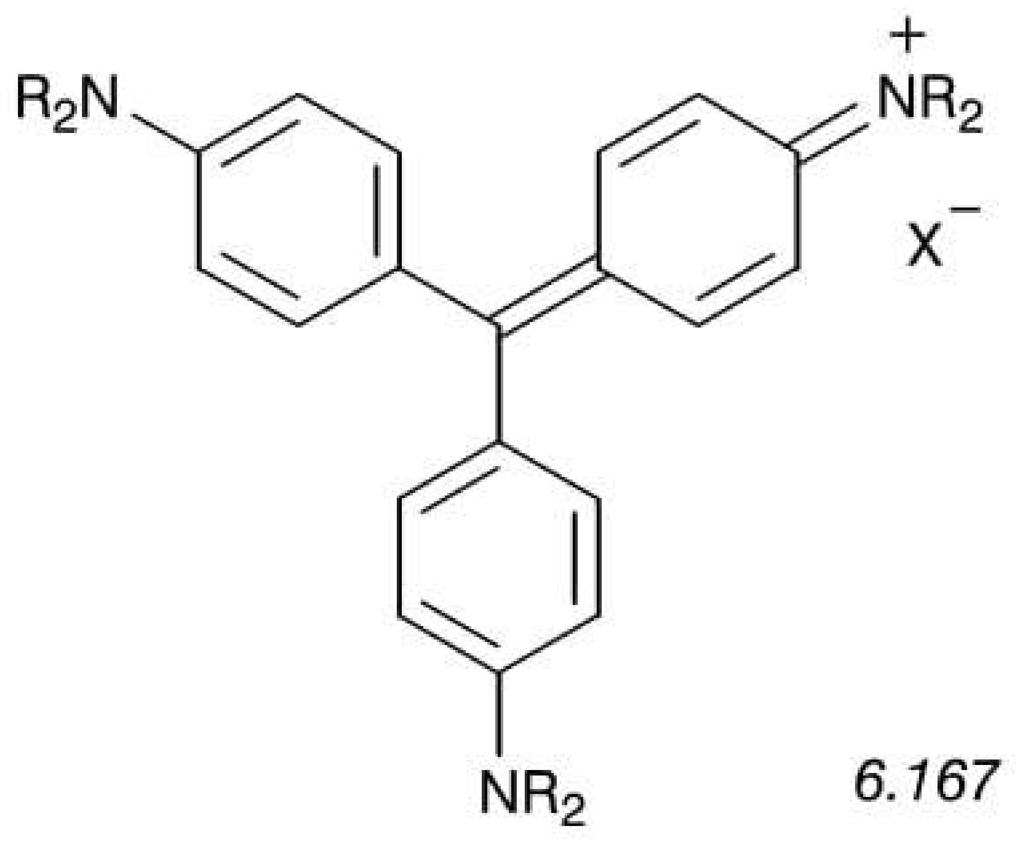
The basic dyes are usually marketed as chlorides, oxalates or zinc chloride double salts; in the case of malachite green (6.162), the last-named derivative has the formula $3[\mathrm{Dye}]\mathrm{Cl}.2\mathrm{ZnCl}_2.2\mathrm{H}_2\mathrm{O}$. Acid dyes of this type are often isolated as the sodium salt.

6.5.2 Acid, basic and mordant dyes

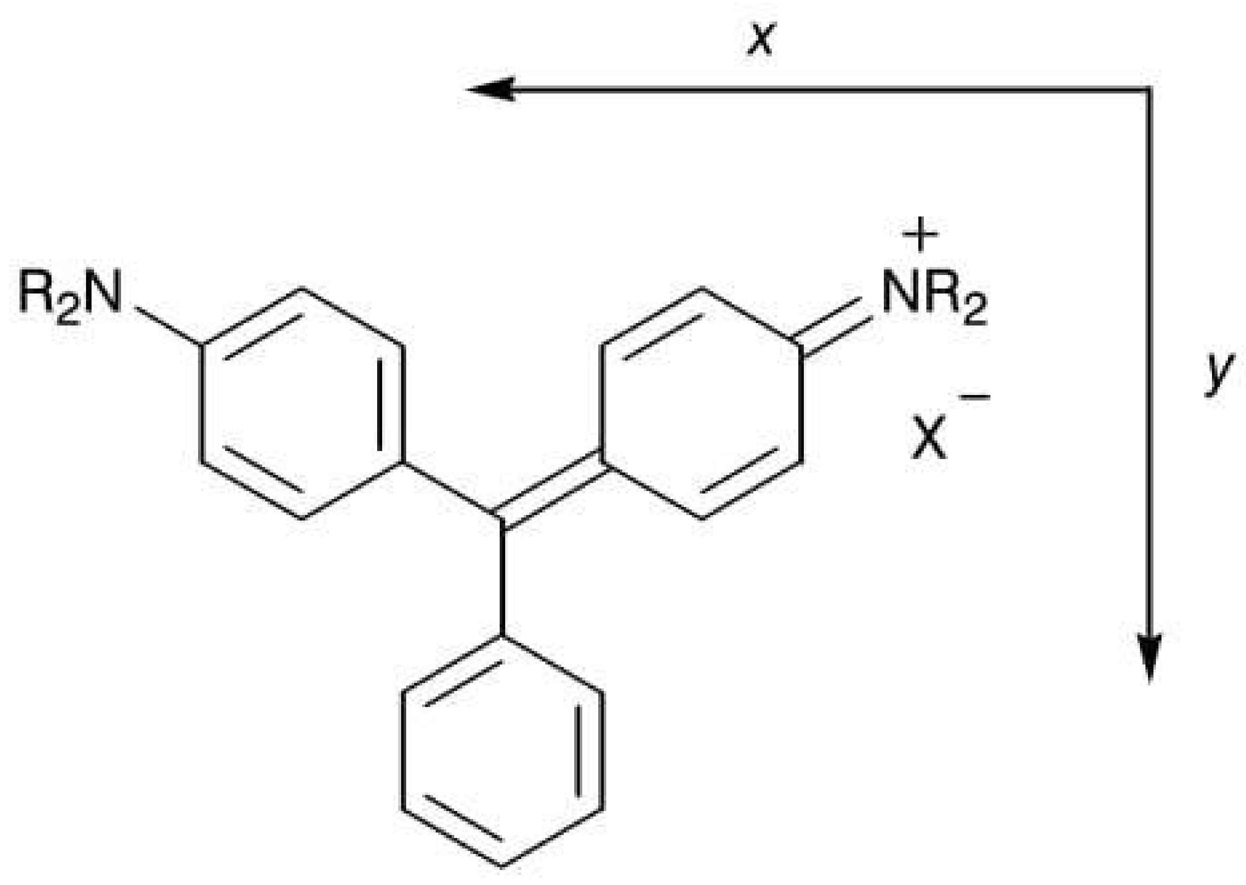
Alkylation of aminotriphenylmethane dyes has a bathochromic effect, which is even more pronounced on arylation, as illustrated in Table 6.5.

Table 6.5 Spectral data for some triphenylmethane dyes in 98% acetic acid

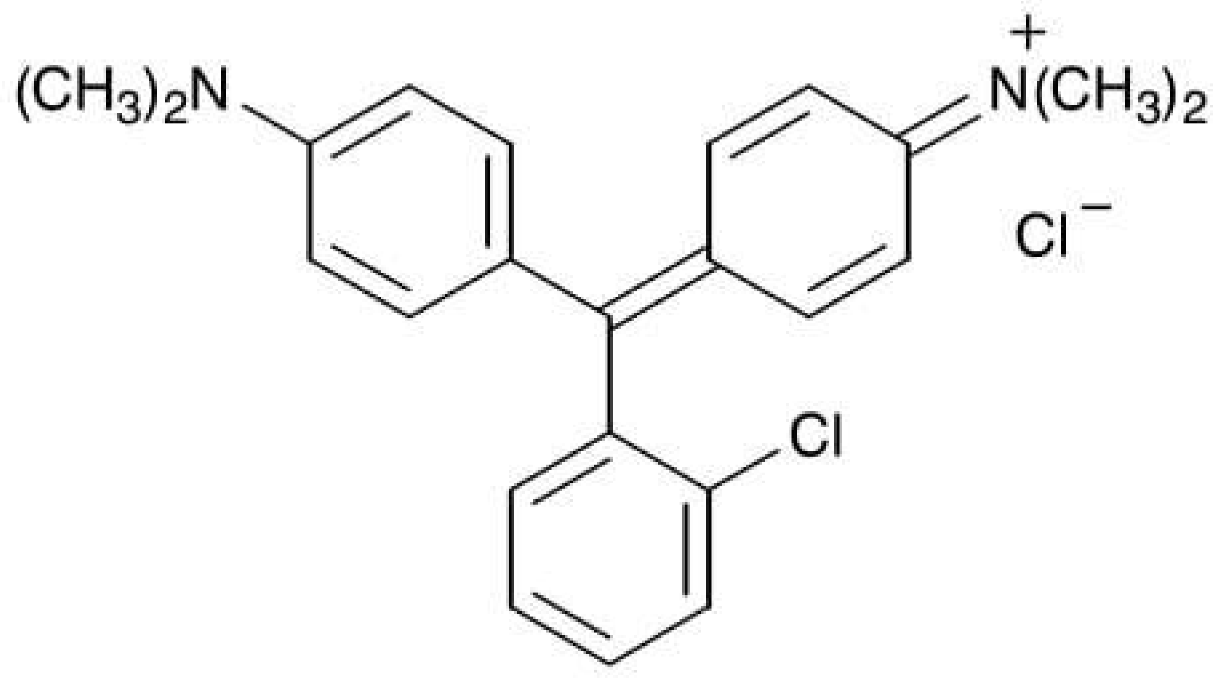
Trivial name	CI Basic	Structure	λ_{max} (nm)
		6.167; R = H	538
Crystal violet	Violet 3	6.167; R = CH_3	589
Ethyl violet	Violet 4	6.167; R = C_2H_5	592.5
		6.168; R = H	570
Malachite green	Green 4	6.168; R = CH_3	621
Brilliant green	Green 1	6.168; R = C_2H_5	629.5



6.167

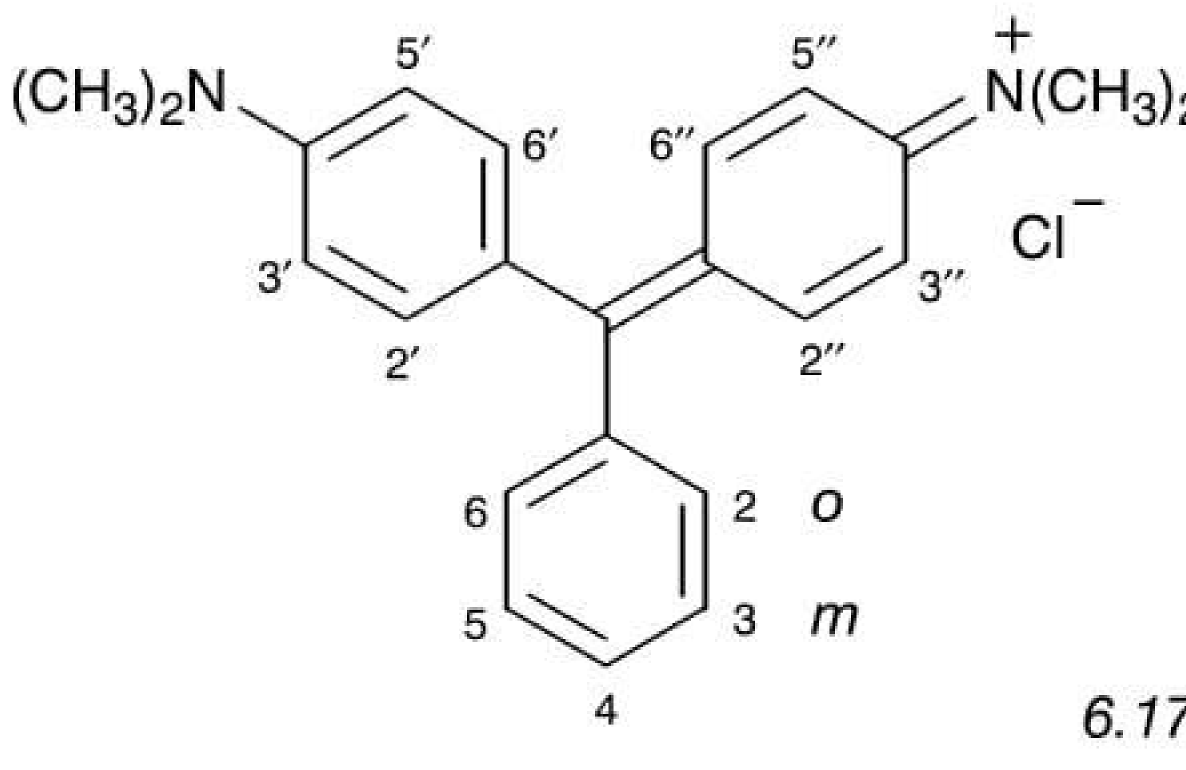


6.168



6.169

CI Basic Blue 1



6.170

CI Basic Green 4

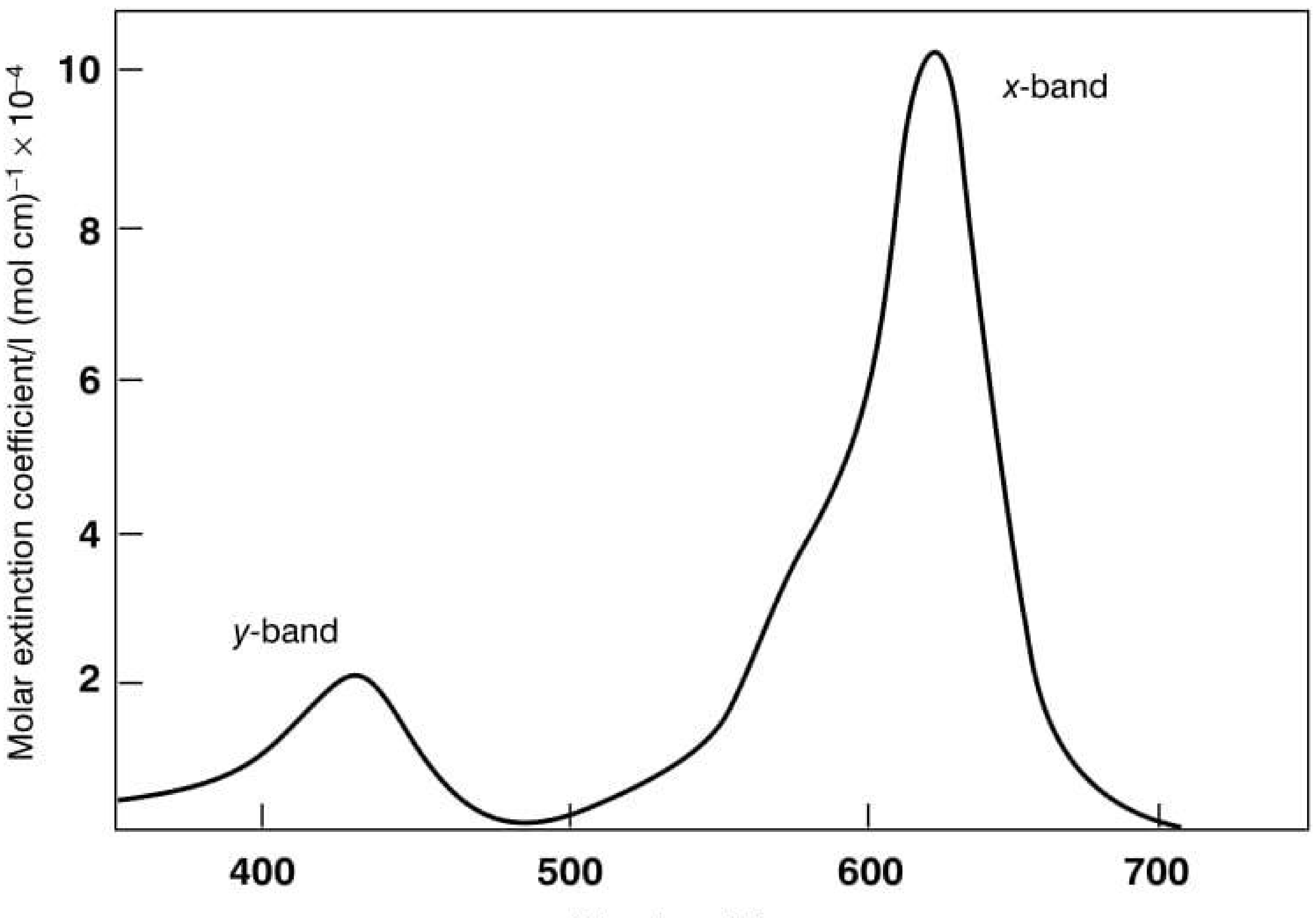


Figure 6.1 Absorption spectrum of malachite green

Unlike Michler's Hydrol Blue (6.153) and crystal violet (6.167; R = CH_3), malachite green (6.168; R = CH_3) shows two absorption bands in the visible region of the electromagnetic spectrum (Figure 6.1). In 98% acetic acid the long-wavelength absorption band (*x*-band) of malachite green, which is associated with polarisation along the *x*-axis, appears at 621 nm ($\varepsilon = 104\,000$) whereas the less significant *y*-band, which is polarised along the *y*-axis, is found at 427.5 nm ($\varepsilon = 20\,000$) [64]; the green colour of the dye arises from these two components. Consequently, the presence of an *ortho* substituent in the phenyl ring of malachite green gives rise to a significant crowding effect, which decreases the importance of the *y*-band by partial deconjugation; at the same time the *x*-band is enhanced. Dyes of this type are therefore blue; for example, the 2-chloro derivative (6.169; CI Basic Blue 1) of malachite green (6.170) displays absorption bands at 635 nm ($\varepsilon = 121\,000$) and 415.5 nm ($\varepsilon = 13\,000$) [64].

As shown by X-ray crystallography, triphenylmethane dyes are unable to adopt a planar conformation and thus the three aromatic rings are twisted out of the molecular plane by approximately 30 degrees. For example, the molecule of pararosaniline perchlorate is shaped like a three-bladed propeller [65]. Steric effects are therefore significant for *o*-substituted analogues of malachite green but not for those with only *m*- or *p*-substitution (6.170). In accordance with theory [66], crowding substituents adjacent to the central carbon atom in triarylmethane dyes give rise to bathochromic shifts of the long-wavelength absorption band.

The *x*-band in malachite green arises from an NBMO$\rightarrow\pi^*$ transition, so that 3- and 4-substituents affect the energy of the excited state only and bring about spectral shifts of the first absorption band which vary linearly with the appropriate Hammett substituent constants. Thus, electron-withdrawing groups cause bathochromic shifts of the *x*-band whereas donor substituents cause hypsochromic shifts (Table 6.6) [64,67]. The *y*-band arises from a $\pi\rightarrow\pi^*$ transition [68] so that substituent effects are less predictable. As the donor strength of the 4-substituent increases, however, the *y*-band moves bathochromically and eventually coalesces with the *x*-band – at 589 nm in the case of crystal violet (6.164), which possesses two NBMOs that are necessarily degenerate [69].

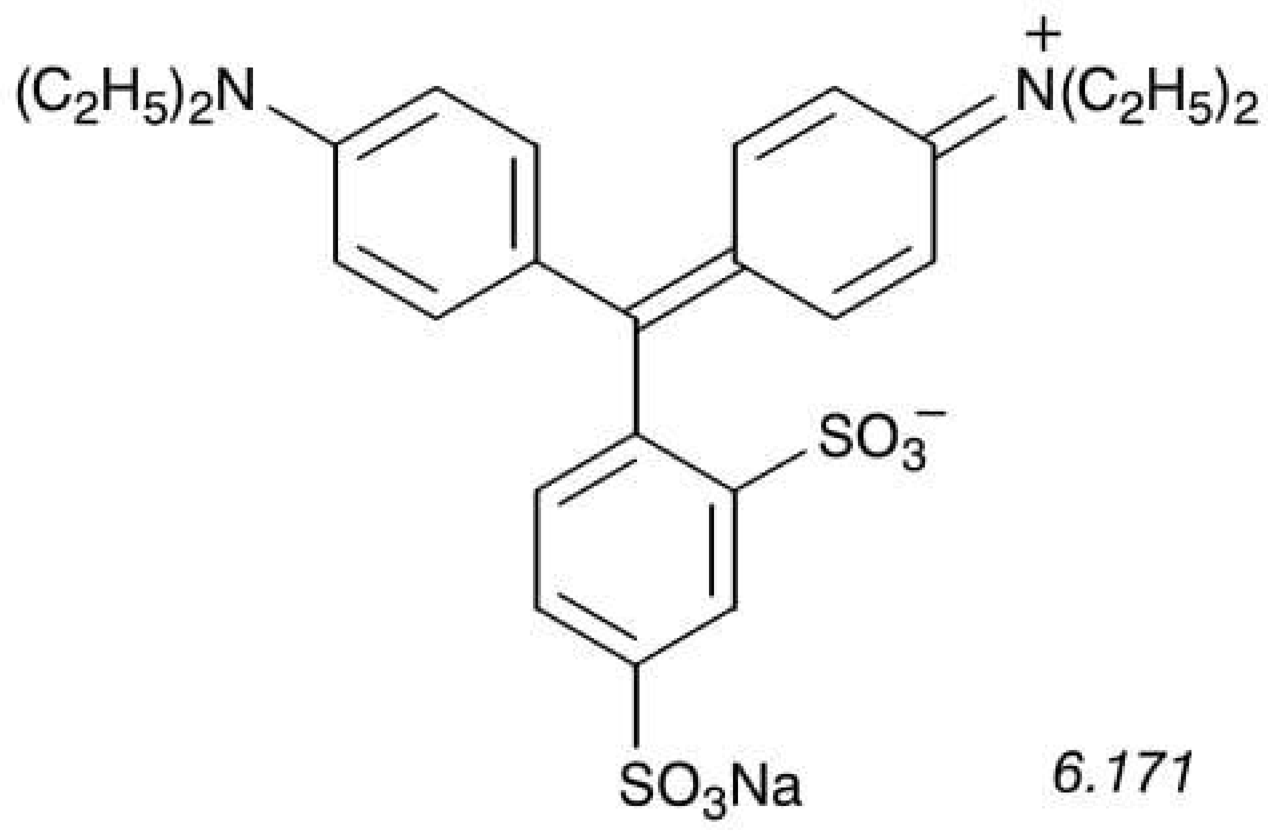
Table 6.6 Spectral data for some derivatives of malachite green

	x-band		*y*-band	
Substituent	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
None	621	104 000	427.5	20 000
3-Cl	630	103 000	426	17 000
4-Cl	627.5	104 000	433	22 000
3-CF_3	634	106 000	424	16 000
4-CF_3	637	104 000	424	15 000
3-CN	637	90 000	426	15 000
4-CN	643	88 000	429	16 000
3-NO_2	637.5	87 000	425	14 000
4-NO_2	645	83 000	425	17 000
3-CH_3	618.5	106 000	433	22 000
4-CH_3	616.5	106 000	437.5	25 000
3-OCH_3	622.5	107 000	435	18 000
4-OCH_3	608	106 000	465	34 000
4-C_6H_5	626	100 000	457	30 000
4-$N(CH_3)_2$	589	117 000	589	117 000

Acid dyes

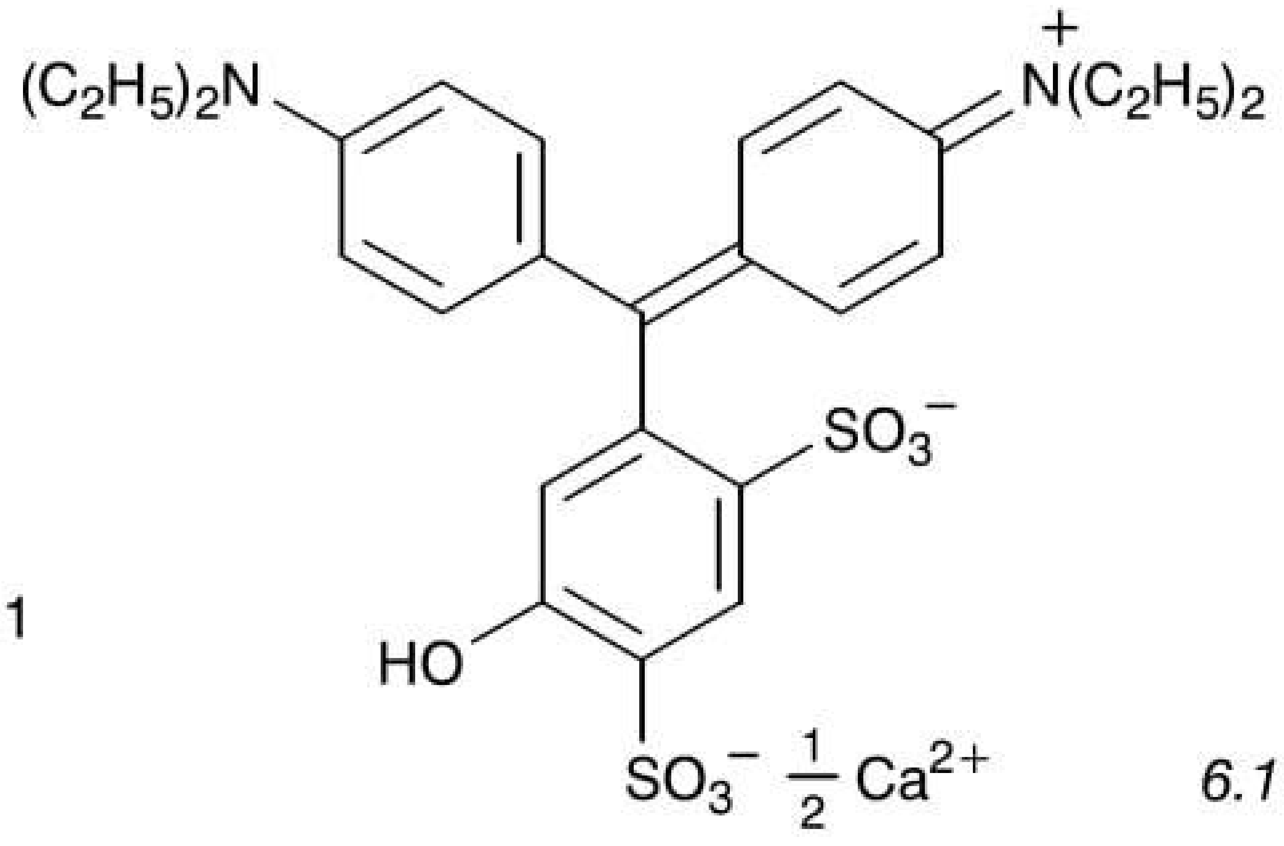
The presence of at least two sulphonic acid groups in the triarylmethane ring system permits the derivatives to be applied as acid dyes. Although sulphonic acid groups are often present in the intermediates used, acid dyes can also be obtained by direct sulphonation of the basic dye itself or at the leuco stage.

Typically, the aldehyde synthesis is used to make the 2,4-disulphonic acid (6.171; CI Acid Blue 1) of Brilliant Green (6.168; R = C_2H_5) from *N,N*-diethylaniline and benzaldehyde-2,4-disulphonic acid. The closely related dye CI Acid Blue 3 (6.172) is obtained by sulphonating the 3-hydroxy derivative of Brilliant Green (CI Basic Green 1) at the leuco base stage. After oxidation the dye is isolated as the calcium salt, which also finds use as a food colorant (CI Food Blue 5). Direct sulphonation of the colour salt is used to prepare CI Acid Blue 93 from diphenylamine blue (6.173; CI Solvent Blue 23). The latter dye is made by phenylation of pararosaniline (6.161) with an excess of aniline in the presence of benzoic acid at about 180 °C. The main product of sulphonation is the trisulphonic acid. CI Acid Green 50 (6.163) has already been mentioned as an example of the hydrol synthesis. The very similar CI Acid Green 16 (6.174) is obtained by condensing Michler's hydrol with naphthalene-2,7-disulphonic acid followed by oxidation.



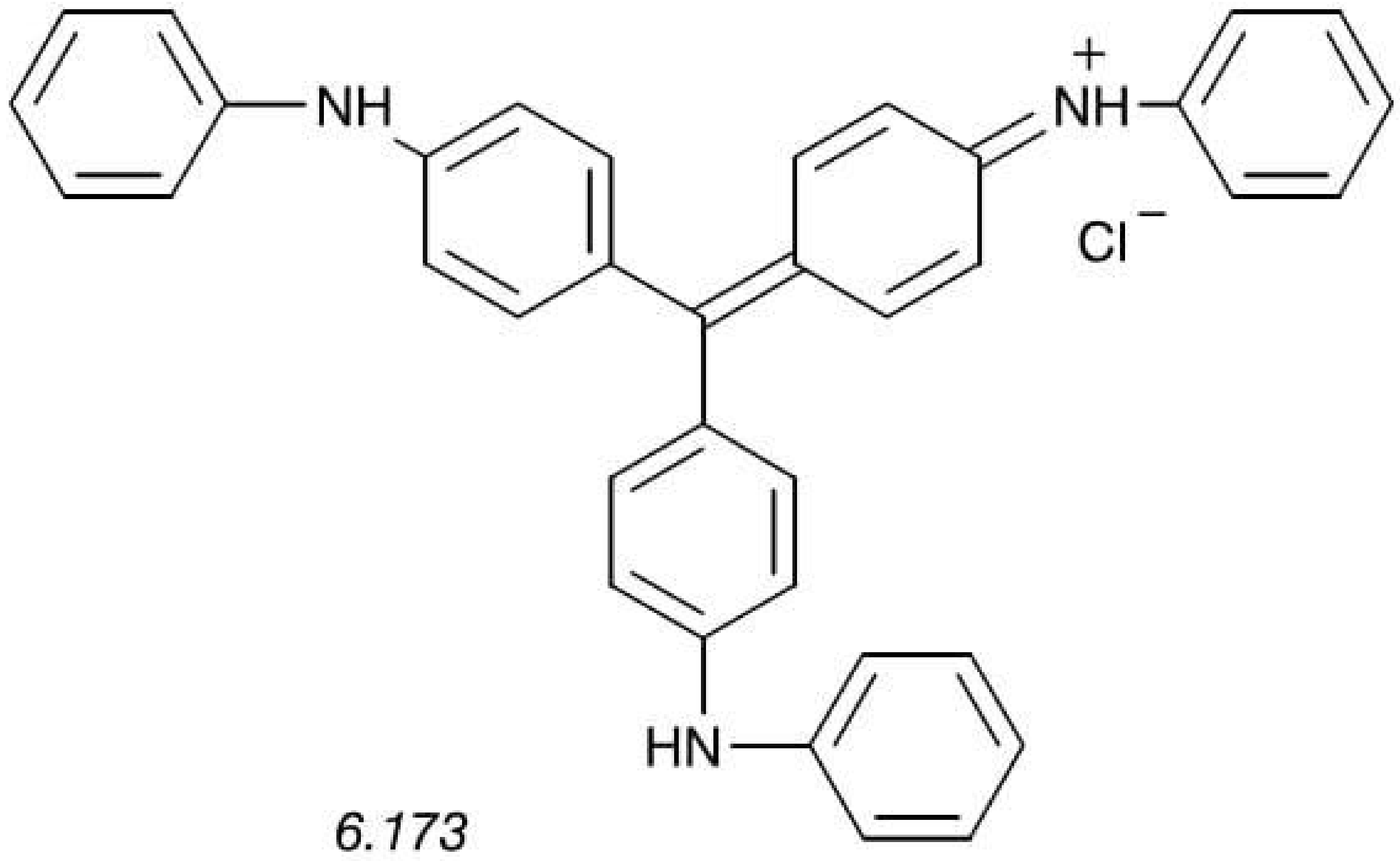
6.171

CI Acid Blue 1



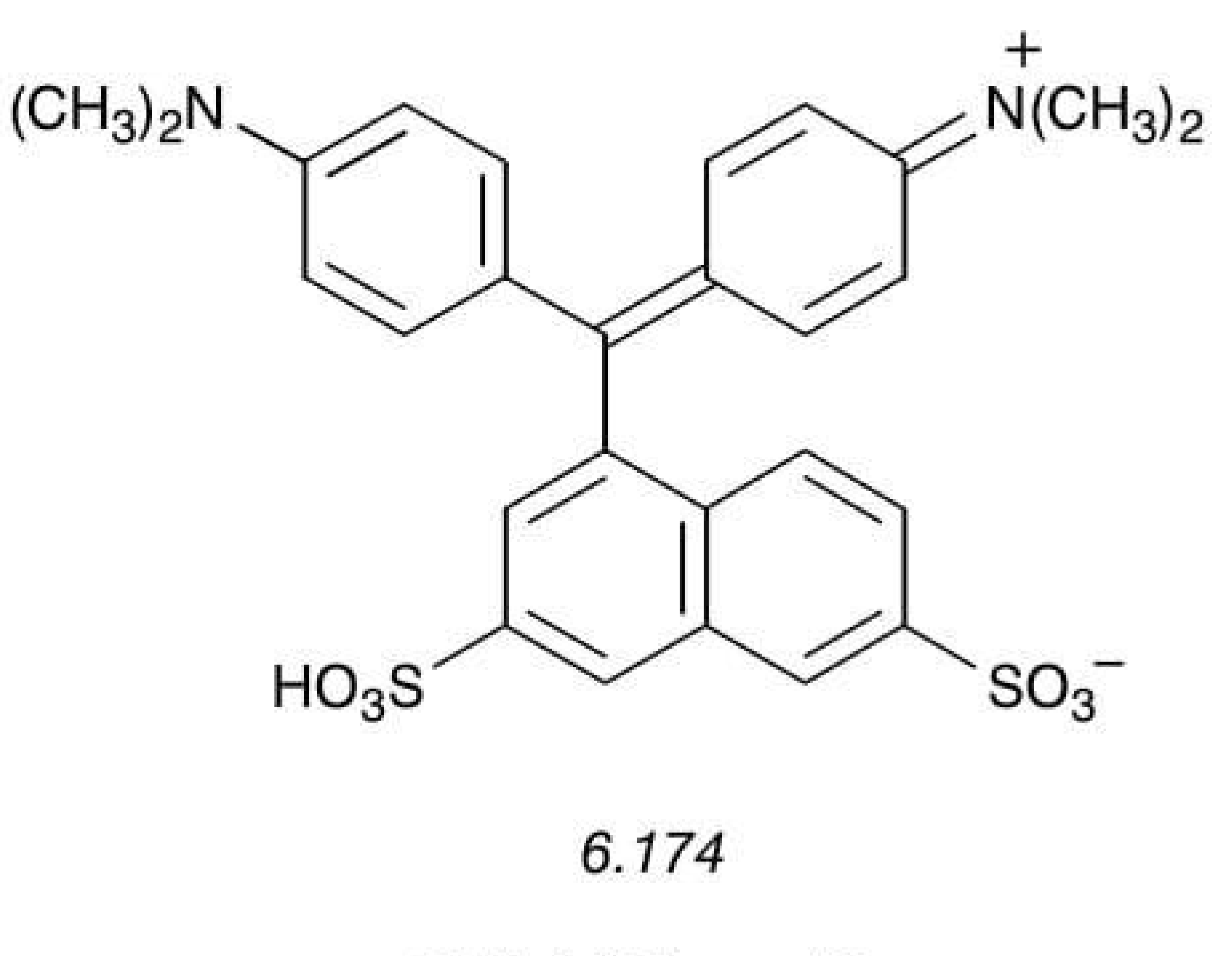
6.172

CI Acid Blue 3



6.173

CI Solvent Blue 23

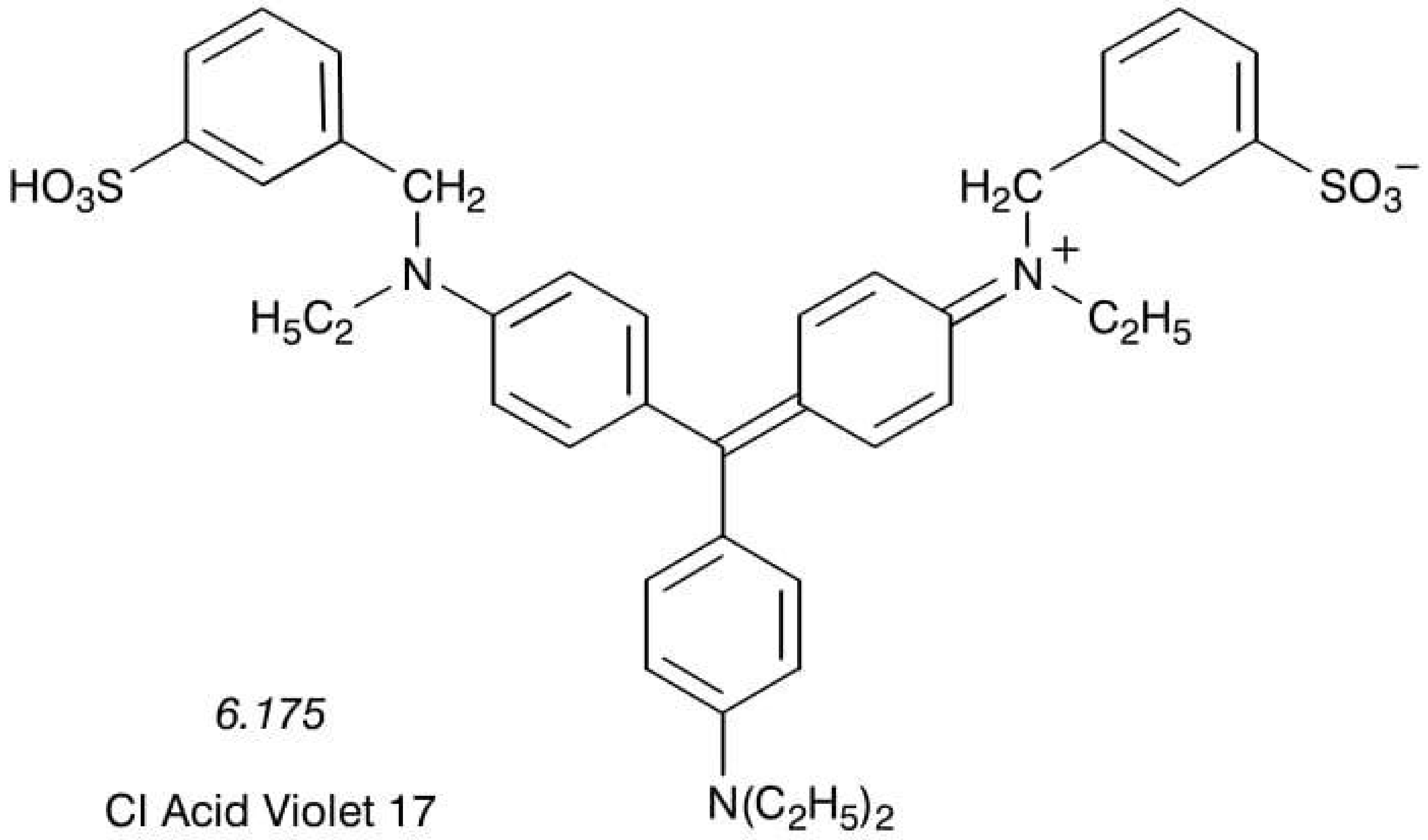


6.174

CI Acid Green 16

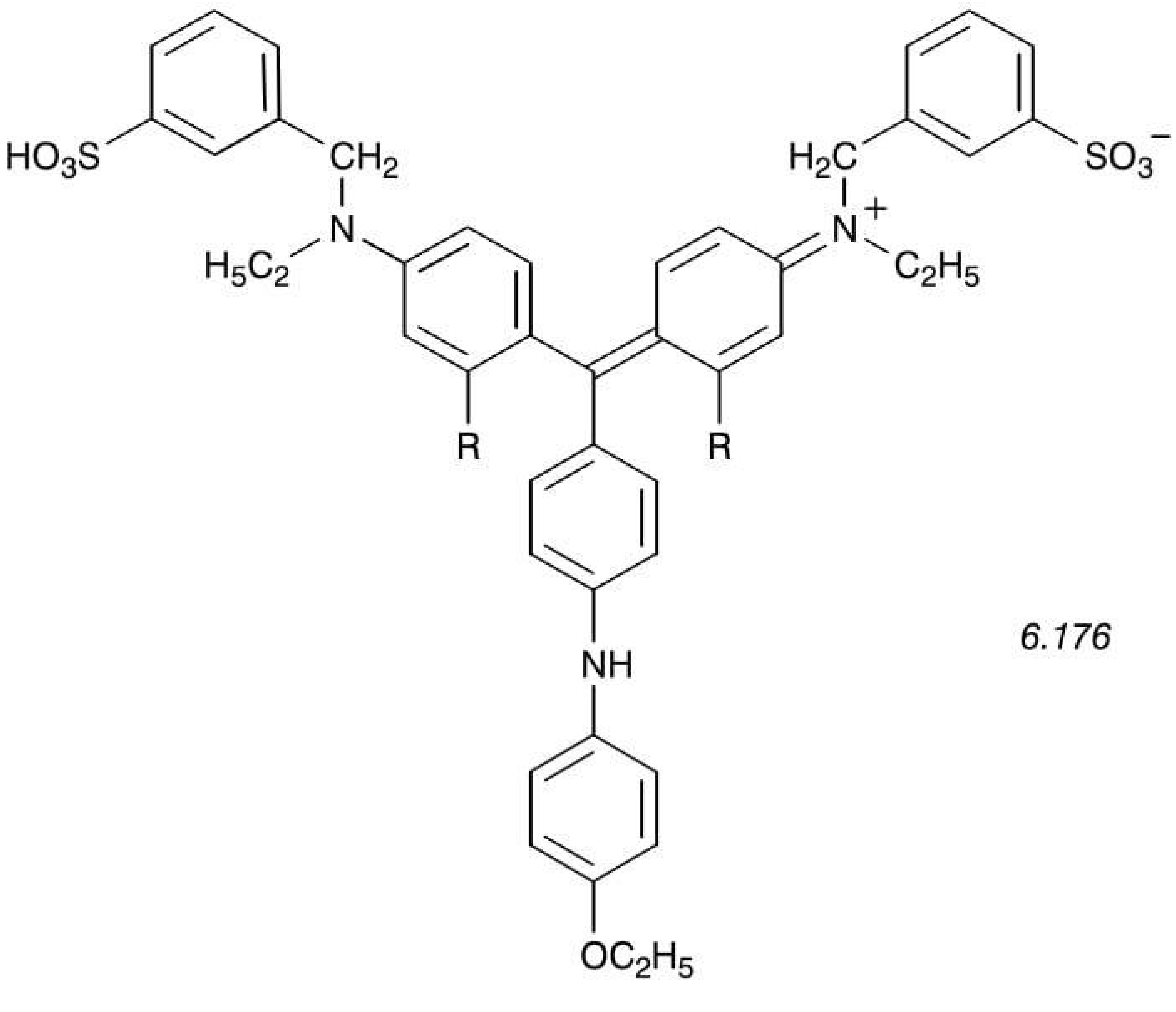
Several acid dyes are derived from *N*-sulphobenzyl-substituted amines. Thus in the production of CI Acid Violet 17 (6.175), *N*-ethyl-*N*-(3-sulphobenzyl)aniline is condensed with formaldehyde to produce the substituted diphenylmethane, which is then oxidised to the hydrol and condensed with *N,N*-diethylaniline. Further oxidation of the leuco base gives the dye. The presence of an *o*-methyl group in the diethylaminophenyl ring gives a bright blue dye (CI Acid Blue 15). Condensation of benzaldehyde-2-sulphonic acid with the same intermediate followed by oxidation of the leuco base gives CI Acid Blue 9, which is used in drop-on-demand ink-jet printing [36]. This dye is also a food colorant (CI Food Blue 2) and the barium salt is used as a pigment (CI Pigment Blue 24). The corresponding 2-chloro derivative is CI Acid Green 9.

The nucleophilic displacement of suitable *para* substituents in analogues of malachite green is used as a means of synthesis of some important acid dyes. For example, CI Acid Blue 83 (6.176; R = H) is made by the aldehyde method, using 4-chlorobenzaldehyde and *N*-ethyl-*N*-(3-sulphobenzyl)aniline. The resulting leuco base is oxidised to the colour salt,



6.175

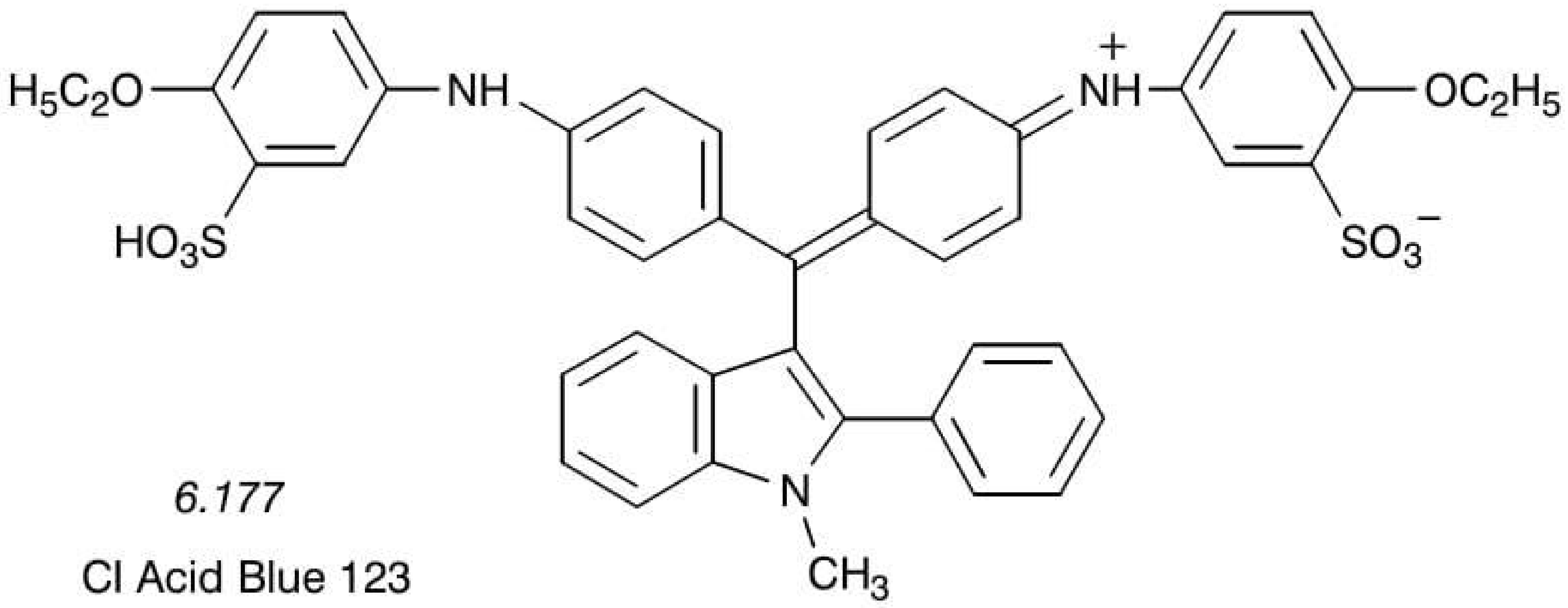
CI Acid Violet 17



6.176

which is then condensed with *p*-phenetidine to give the required product. The sterically hindered dimethyl derivative of this dye, CI Acid Blue 90 (6.176; R = CH_3) is also of interest. It is synthesised by first condensing benzaidehyde with *N*-benzyl-*N*-ethyl-*m*-toluidine to give a leuco base, which is then trisulphonated; after oxidation, the 4-sulphonic acid group is displaced by reaction with *p*-phenetidine.

The incorporation of an indole ring system often leads to an improvement in the light fastness. A suitable example is CI Acid Blue 123 (6.177), which is derived from 4,4′-dichlorobenzophenone. Condensation with 1-methyl-2-phenylindole in the presence of phosphorus oxychloride produces the triarylmethane ring system. Replacement of the chlorine atoms with *p*-phenetidine, followed by sulphonation, gives the dye.



6.177

CI Acid Blue 123

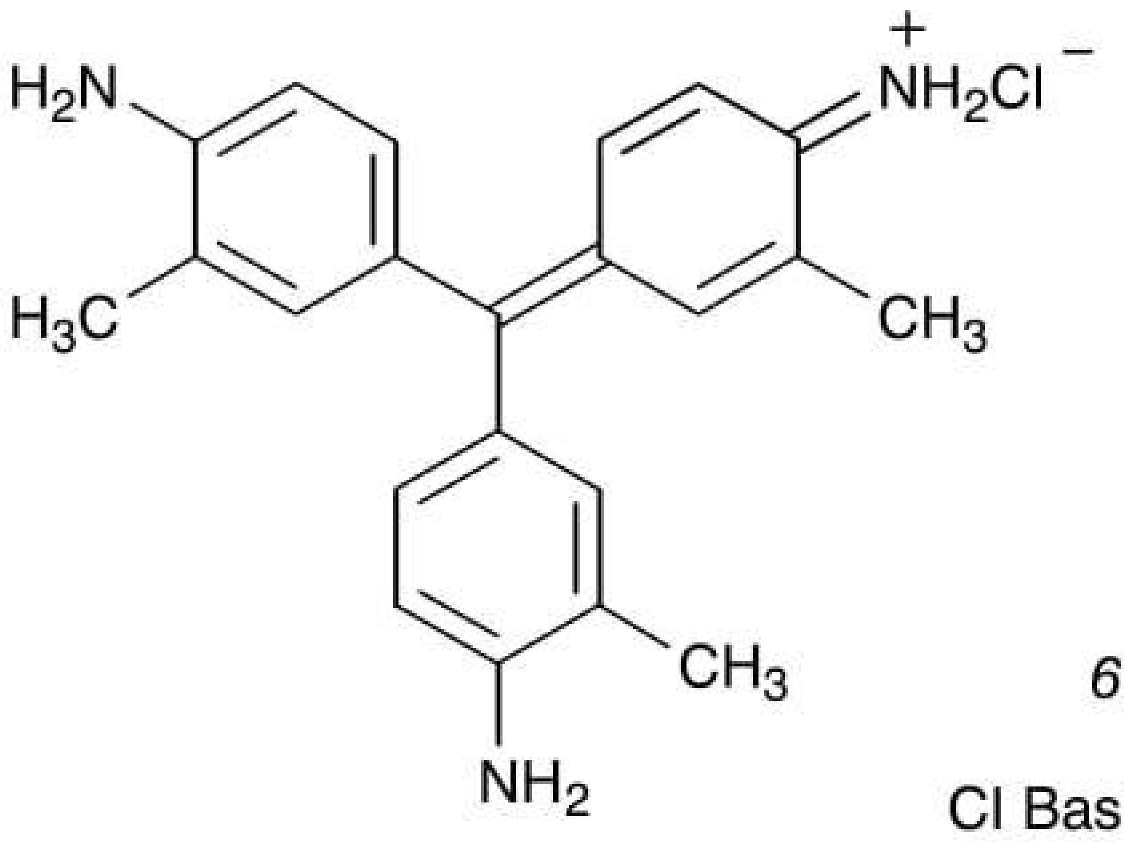
A study of some triphenylmethane acid dyes on model polymer systems has revealed the operation of a complex fading mechanism which probably involves excited triplet-state dye molecules [70].

Basic dyes

Several examples of typical triarylmethane dyes have already been mentioned, in particular, pararosaniline (6.161), malachite green (6.162) its *o*-chloro derivative (6.169), crystal violet (6.164), rosaniline (6.165) and diphenylamine blue (6.173). CI Basic Green 1 (6.168; R = C_2H_5), the ethyl analogue of malachite green, is prepared by the aldehyde route and is isolated as the sulphate. The ethyl analogue of crystal violet is CI Basic Violet 4 (6.167; R = C_2H_5) and is obtained by the ketone route.

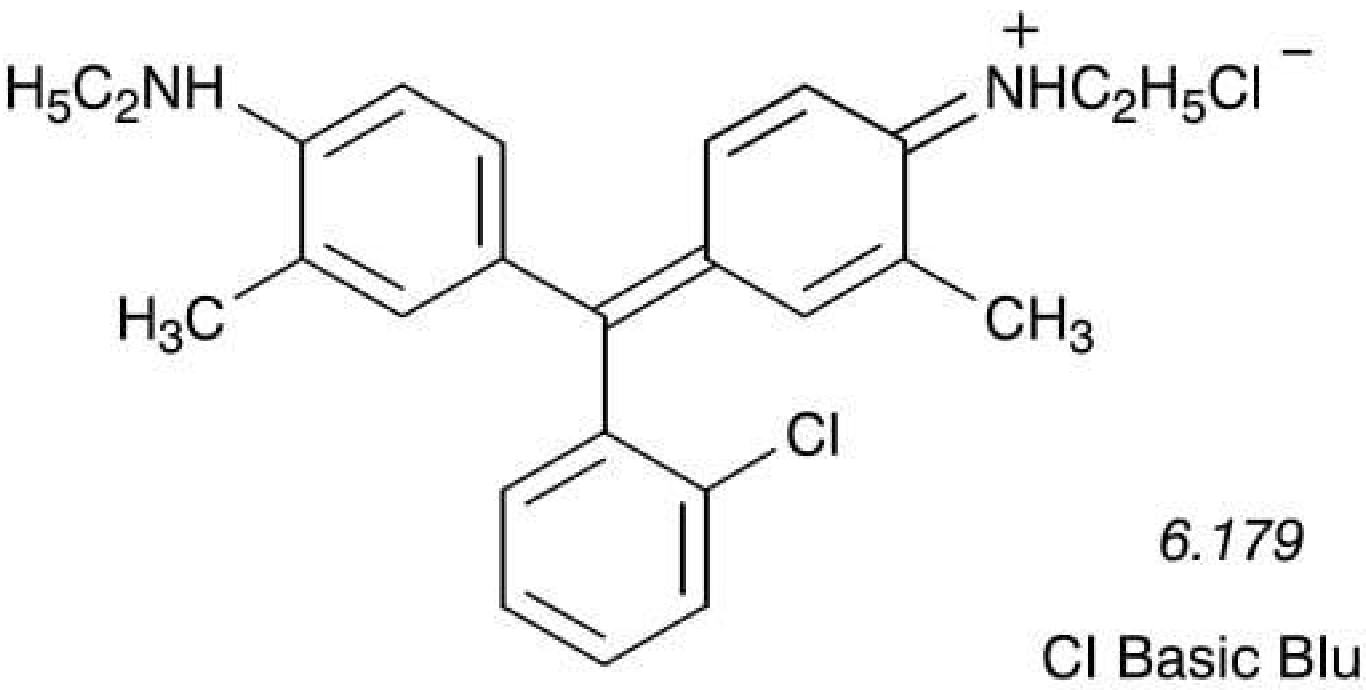
In general, the presence of substituents adjacent to terminal dialkylamino groups leads to partial deconjugation and to complex spectral shifts [71]. Steric effects are minimised, however, in the case of primary and secondary *p*-amino groups. Thus rosaniline (6.165) contains one *o*-toluidine residue and three such groupings are present in new magenta (6.178; CI Basic Violet 2), which is effectively obtained by the hydrol route, involving the reaction of two moles of *o*-toluidine with one of formaldehyde, oxidation to the hydrol, condensation of this intermediate with *o*-toluidine and oxidation of the leuco base. Methyl groups are also sited in two rings of CI Basic Blue 5 (6.179), made by the aldehyde route using 2-chlorobenzaldehyde and *N*-ethyl-*o*-toluidine. The leuco base of the sterically hindered 2′,2″-dimethyl derivative of malachite green (6.170) is used as a charge transport material in electrophotography [36].

Various derivatives of naphthyldiphenylmethane are of value as blue dyes; the naphthyl substituent brings about bathochromic shifts by extending the conjugation and also by a steric effect [72]. The Victoria Blues have been used commercially for many years. Typical examples include CI Basic Blue 26 (6.180), which was discovered in 1883 by Caro and Kern. The dye can be prepared by the ketone route using Michler's ketone (6.155) and 1-phenylaminonaphthalene. A similar condensation between the ethyl analogue of Michler's ketone and 1-ethylaminonaphthalene gives CI Basic Blue 7 (6.181), now classified as toxic by the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) [73].



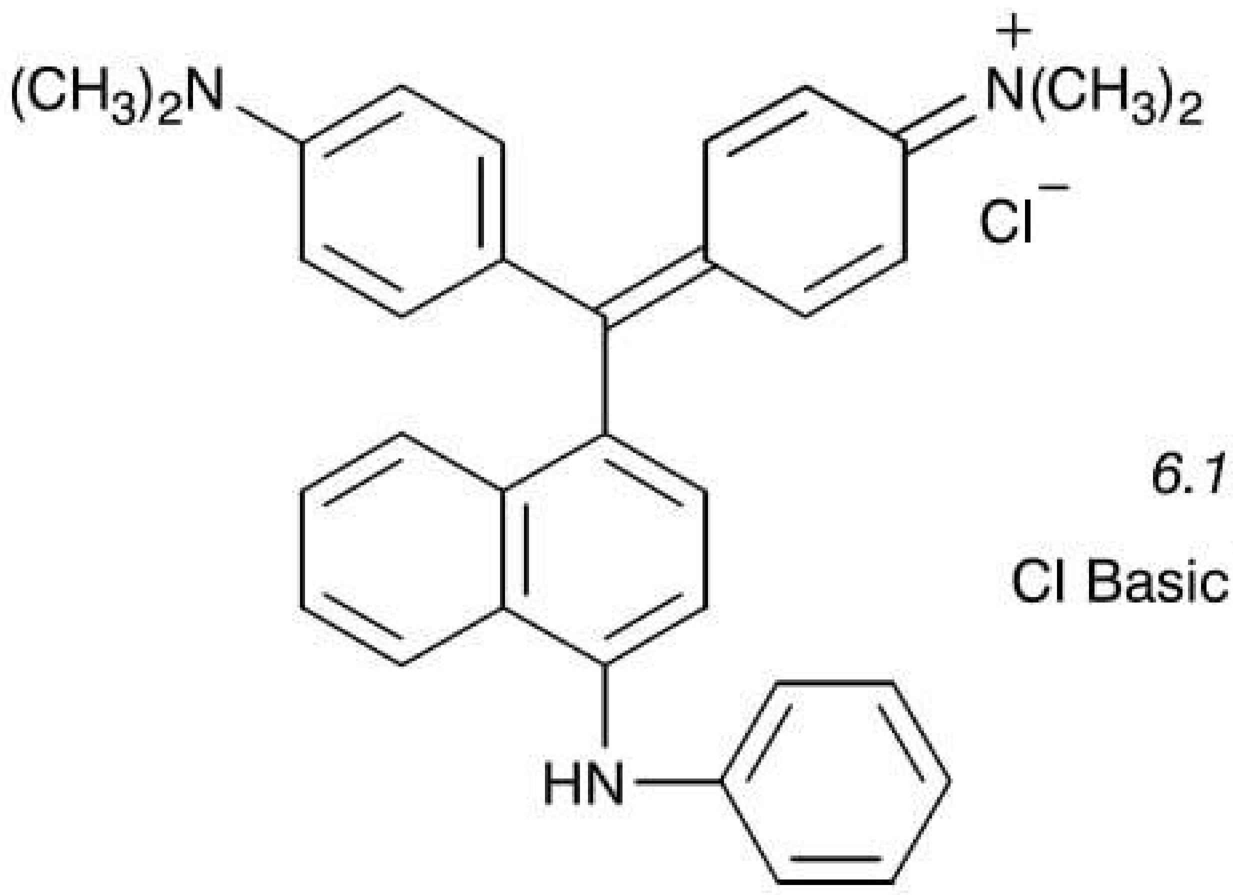
6.178

CI Basic Violet 2



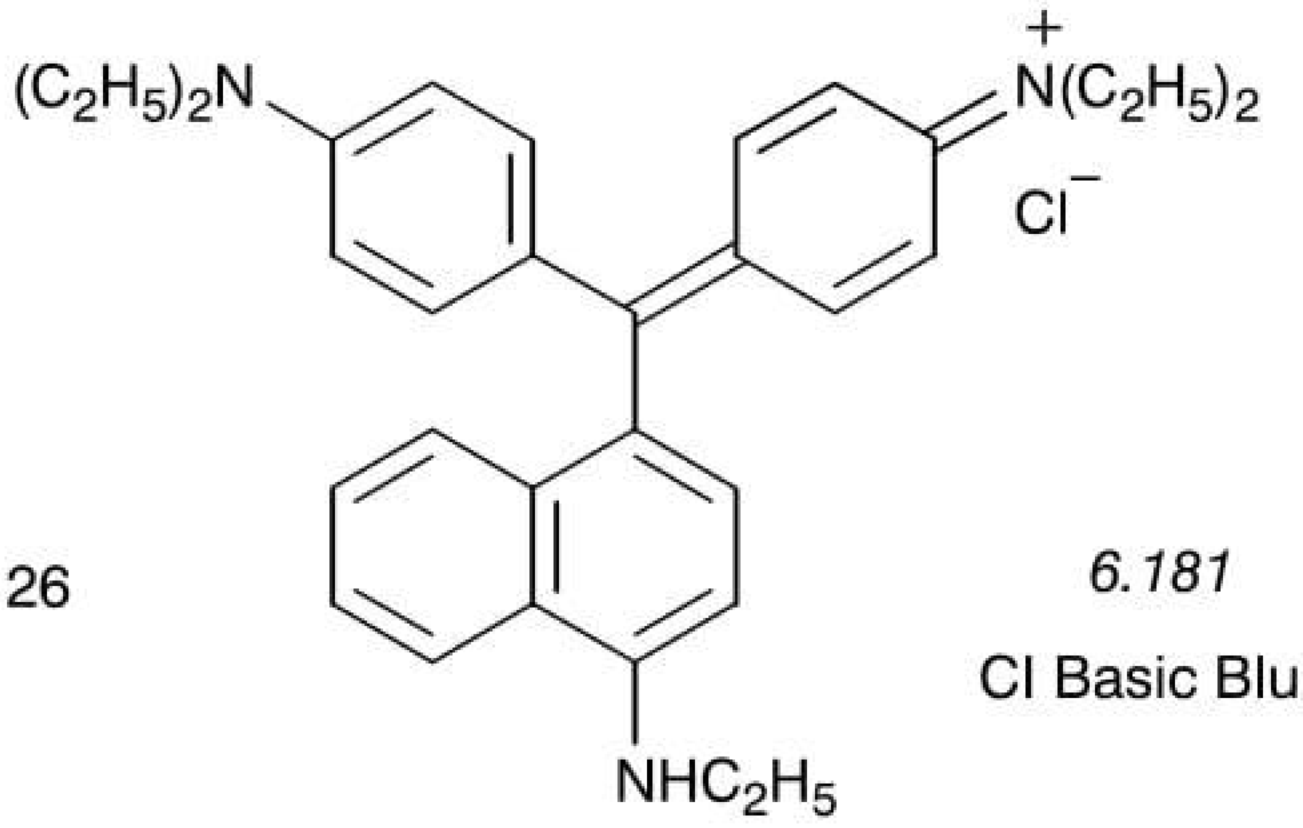
6.179

CI Basic Blue 5



6.180

CI Basic Blue 26

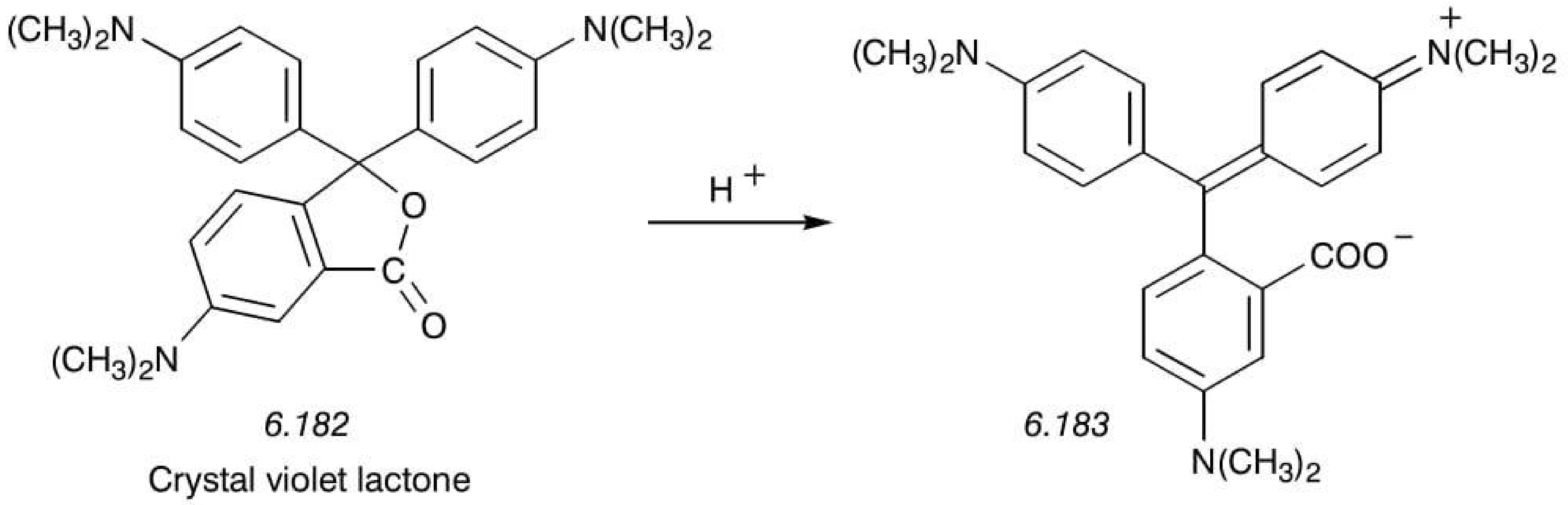


6.181

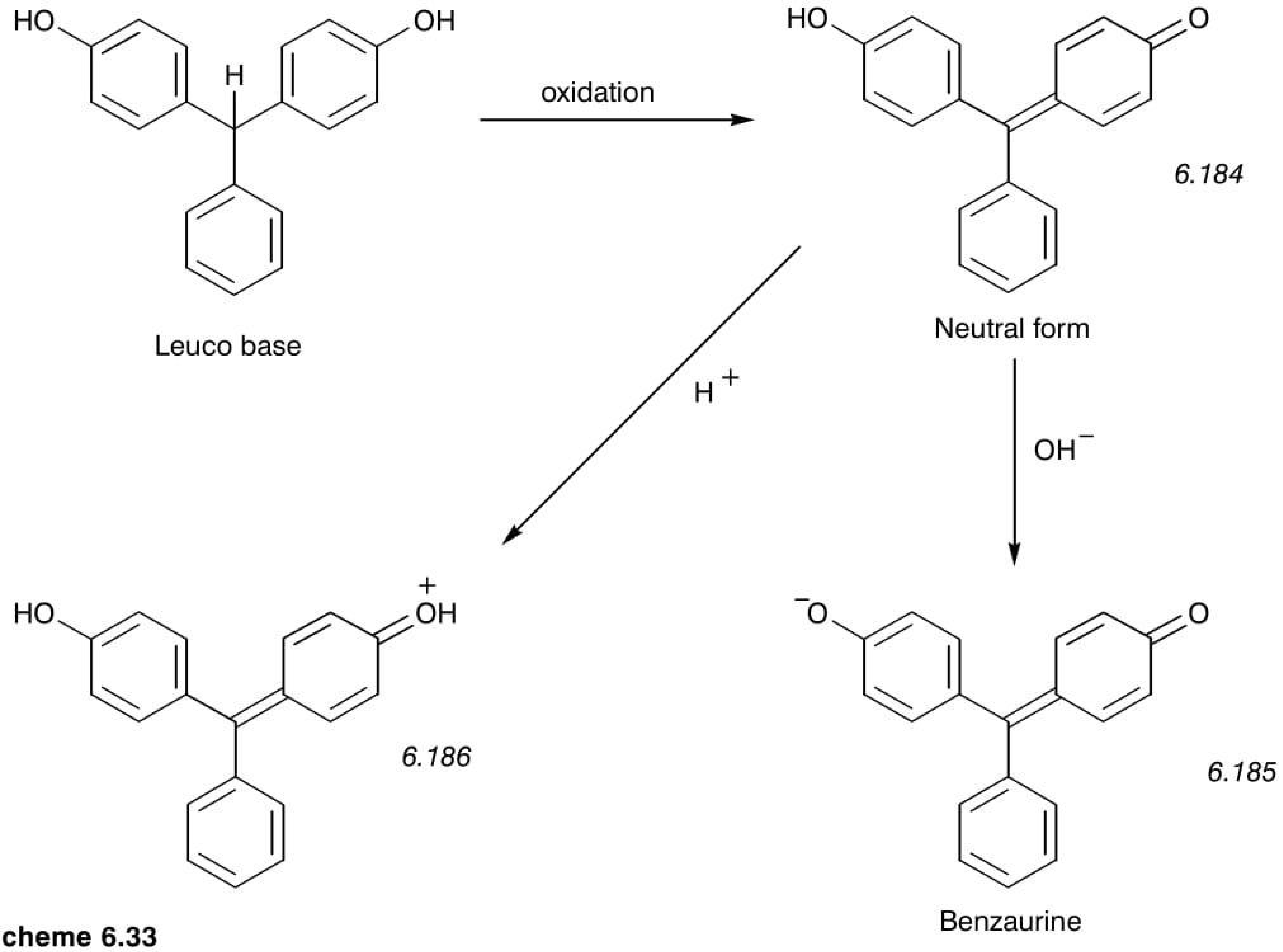
CI Basic Blue 7

The phosphotungstomolybdic acid salts (PTMA lakes) of many basic dyes are used as violet, blue and green pigments [27]. Examples include methyl violet (CI Pigment Violet 3), Victoria Pure Blue BO (CI Pigment Blue 1) and Brilliant Green (CI Pigment Green 1). The copper hexacyanoferrate(II) complex of methyl violet is CI Pigment Violet 27. The free dye bases of various triarylmethane derivatives are used as solvent dyes. Illustrative examples include methyl violet (CI Solvent Violet 8), Victoria Blue B (CI Solvent Blue 4) and malachite green (CI Solvent Green 1).

Certain derivatives of basic triarylmethane dyes are used in pressure-sensitive papers. Carbonless copy papers that make use of the so-called crystal violet lactone (6.182) are of particular importance. The reverse side of the top sheet is coated with microcapsules containing a solution of the colourless lactone (colour former) in a non-polar solvent. The bottom sheet is coated with an acidic clay or an acidic phenolic resin. Application of pressure ruptures the minute capsules and interaction between the released lactone and the lower acidic surface leads to instant dye formation (structure 6.183) at the point of contact (Scheme 6.32). The resulting colour gradually fades; slower-acting colour formers that give rise to longer-lasting images, such as benzoylated leuco methylene blue, are therefore usually



Scheme 6.32

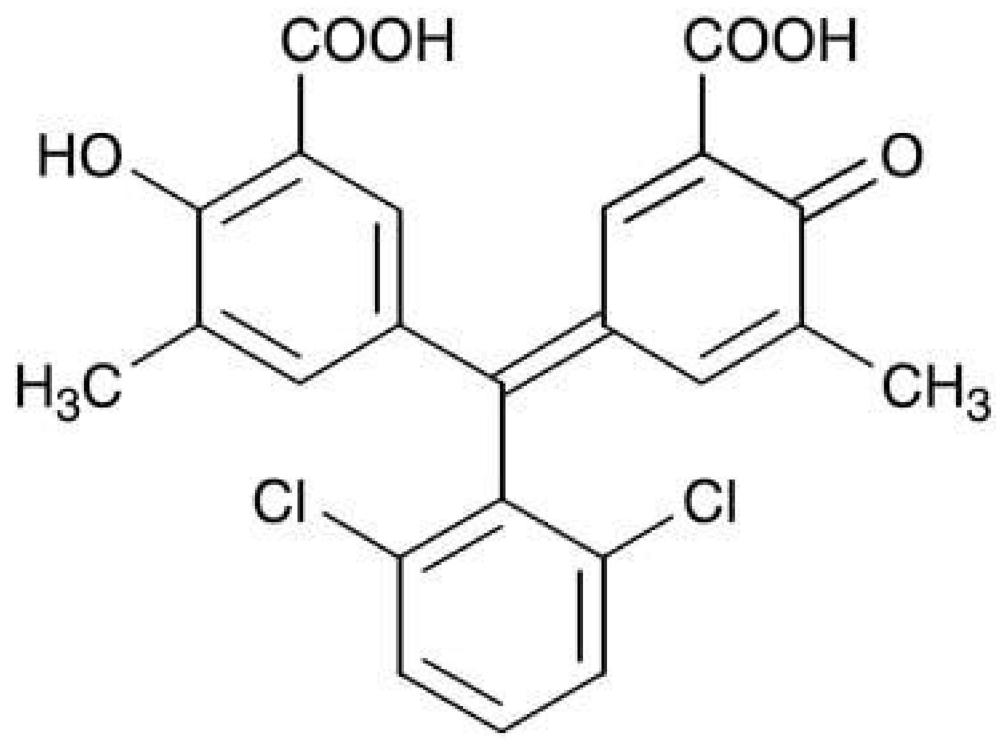


Scheme 6.33

incorporated into the capsules. The synthesis and properties of phthalide-type colour formers have been reviewed [74].

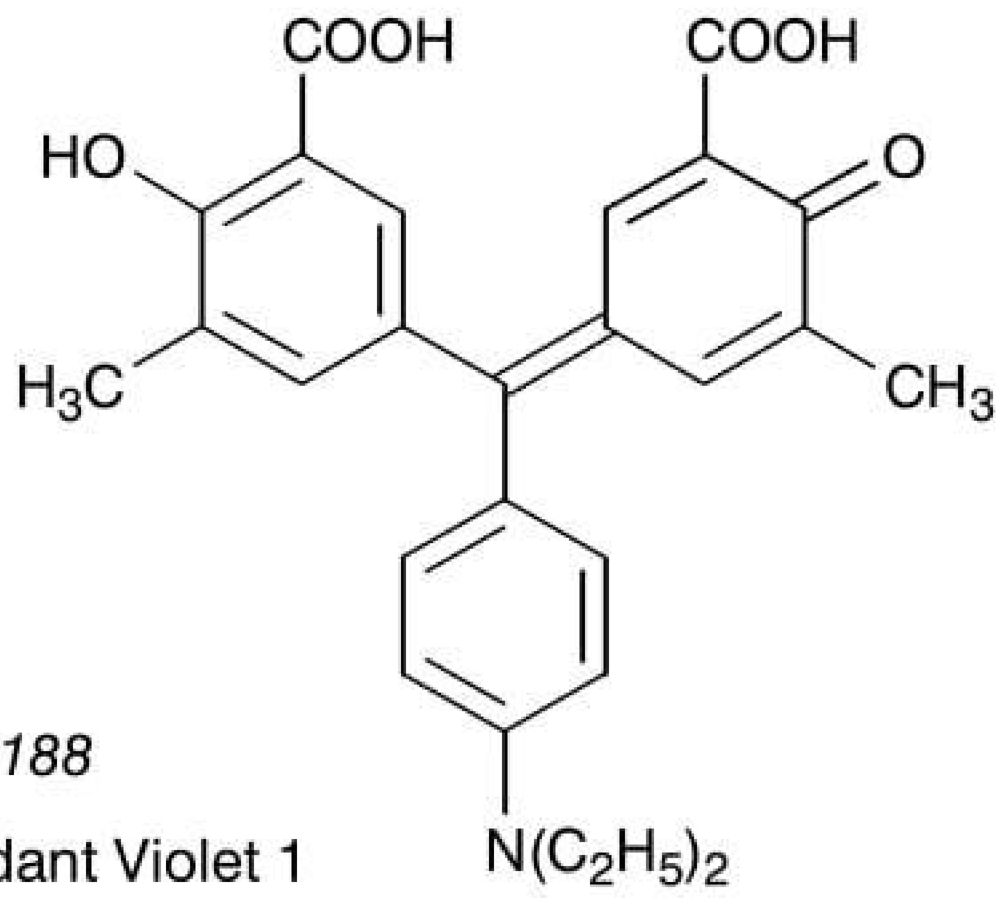
Mordant dyes

Hydroxytriphenylmethane derivatives give rise to anionic charge-resonance systems that are isoconjugate with the corresponding amino-substituted dyes. Thus, for example, the oxonol analogue of malachite green is benzaurine (Scheme 6.33). The quinonoid neutral form (6.184), which is pale yellow, produces a violet anion (6.185) on the addition of alkali; in



6.187

CI Mordant Blue 1



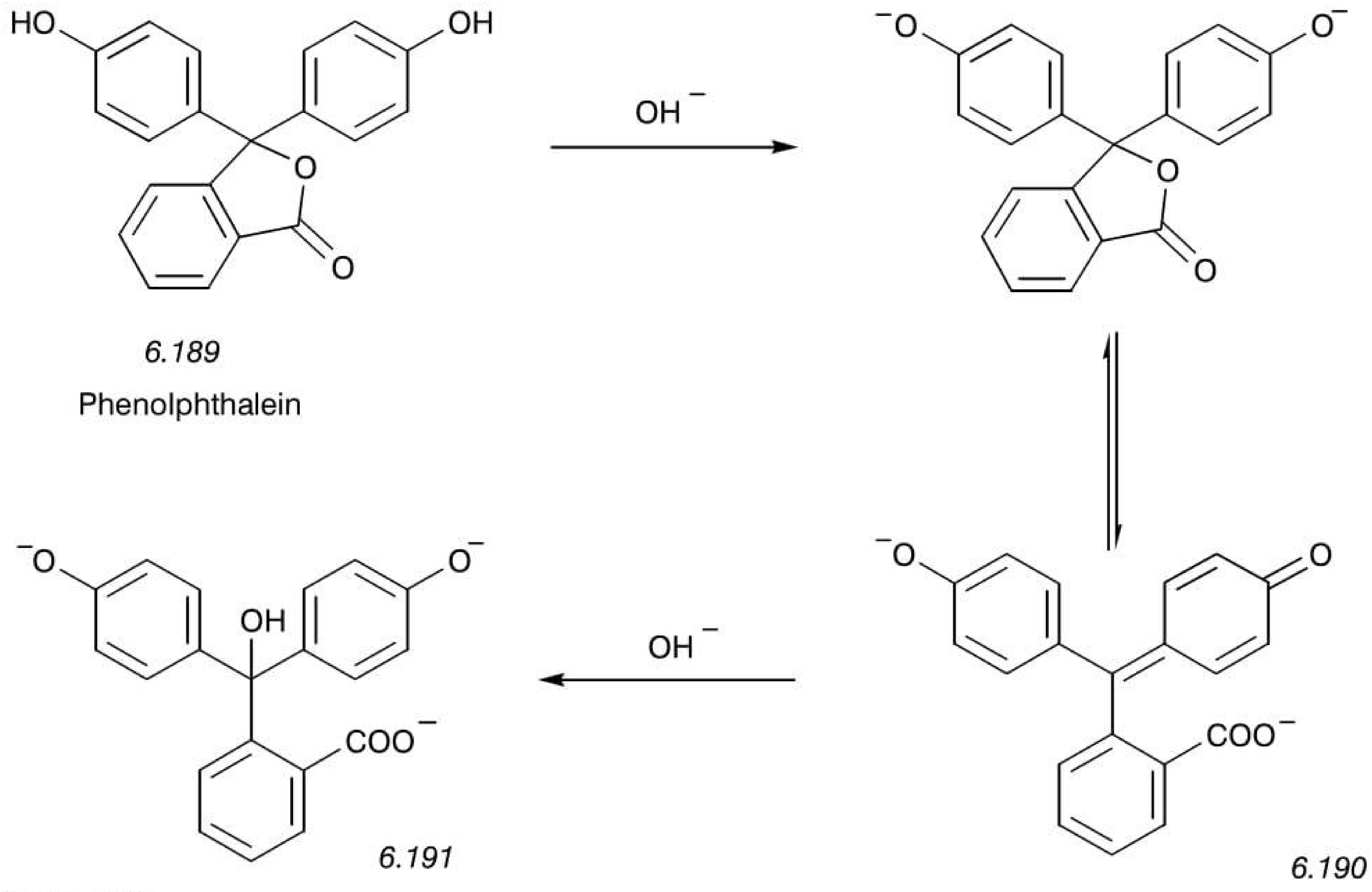
6.188

CI Mordant Violet 1

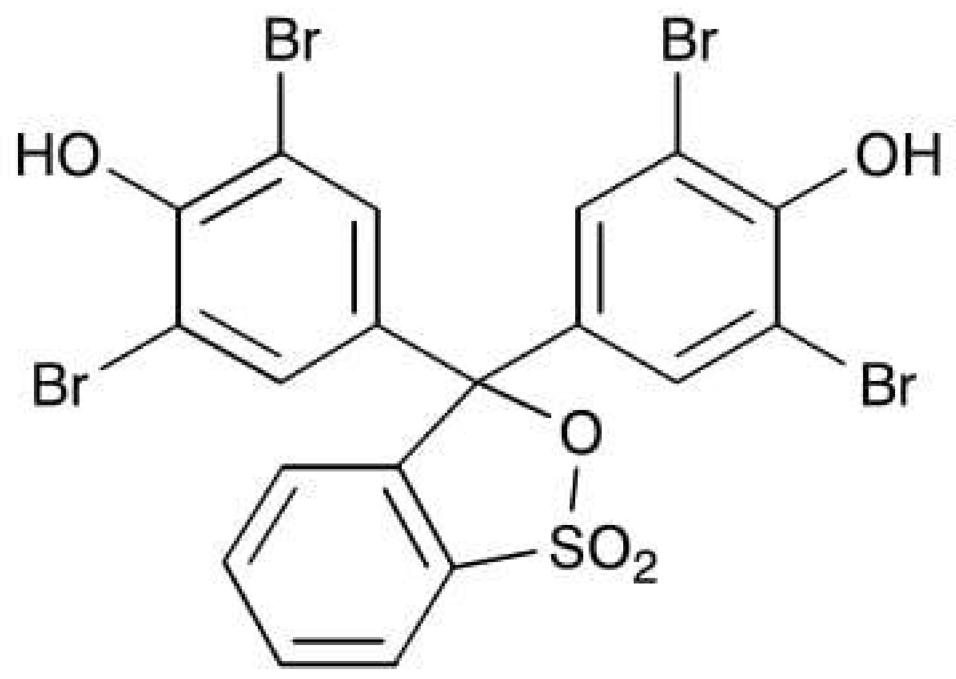
strongly acidic solution the neutral form is protonated to give a cationic charge-resonance system (6.186) which is also violet [75]. The analogous trihydroxytriphenylmethane system is aurine.

Technically important dyes are salicylic acid derivatives that function as chrome mordant dyes for wool. Thus CI Mordant Blue 1 (6.187) is made by the aldehyde synthesis from 2,6-dichlorobenzaldehyde and 2-hydroxy-3-methylbenzoic (*o*-cresotinic) acid in concentrated sulphuric acid. Oxidation of the leuco base is achieved by the addition of sodium nitrite. On wool the product, which is isolated as the sodium salt, is a dull maroon colour, changing to a bright blue on treatment with a chromium salt. Some dyes of this type, such as CI Mordant Violet 1 (6.188), also contain a basic group. This compound is also prepared by the aldehyde route.

The acid–base indicator phenolphthalein is a derivative of benzaurine (Scheme 6.34). Condensation of phthalic anhydride with phenol generates the colourless lactone form

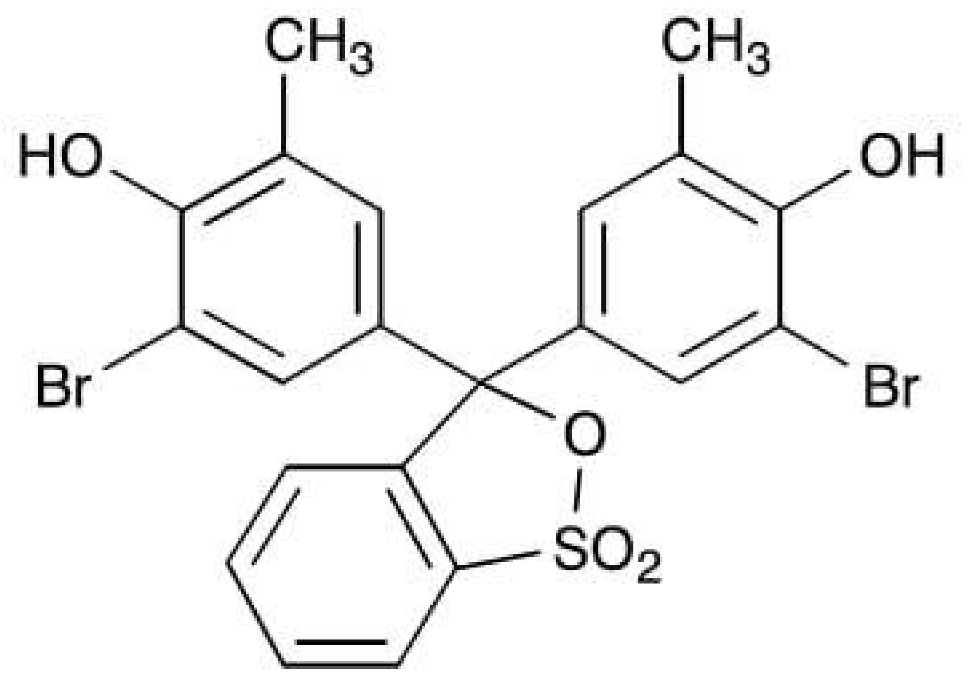


Scheme 6.34



6.192

Bromophenol blue



6.193

Bromocresol purple

(6.189), which ionises in alkaline solution and undergoes ring opening to produce the red dianion (6.190) within the pH range 8.3–10.0. The charge-resonance system is destroyed in an excess of alkali by the formation of the colourless triphenylmethanol derivative (6.191). Several derivatives of phenolphthalein are also used as indicators. The related phenolsulphonephthaleins are particularly versatile as acid-base indicators, covering a wide range of pH. Typical examples include bromophenol blue (6.192) (pH range 3.0–4.6) and bromocresol purple (6.193) (pH range 5.2–6.8).

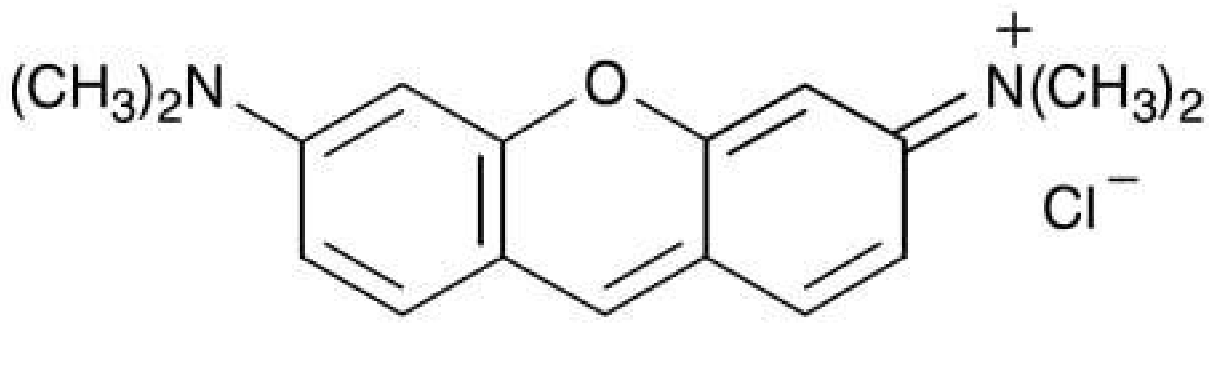
6.5.3 Xanthene dyes

The most important heterocyclic analogues of the di- and triarylmethane dyes are xanthene derivatives containing an oxygen bridge. These dyes produce red, pink and greenish yellow hues that are strongly fluorescent [76]. The oxygen bridge confers greater rigidity on the system, leading to fluorescence and, in accordance with PMO theory [77], the electron donation results in hypsochromic shifts of the long-wavelength absorption band relative to that of the parent dyes.

The xanthene analogue of Michler's Hydrol Blue (6.153) is Pyronine G (6.194), which is used as a red biological stain. Condensation of 3-dimethylaminophenol with formaldehyde followed by dehydration in concentrated sulphuric acid gives the leuco base. Dyes of commercial significance contain three aromatic rings. The bright reddish violet dye Rhodamine B (6.195; CI Basic Violet 10), discovered in 1887 by Cérésole, is a good example. Condensation of 3-diethylaminophenol with phthalic anhydride yields the dye. The free dye base is used as a solvent dye (CI Solvent Red 49) and the phosphotungstomolybdic acid lake finds use as a pigment (CI Pigment Violet 1); the ethyl ester of Rhodamine B is CI Basic Violet 11. A similar reaction between 3-ethylamino-*p*-cresol and phthalic anhydride gives a redder product on esterification (6.196; CI Basic Red 1). The PTMA lake is a valuable pink pigment (CI Pigment Red 81), as is the copper hexacyanoferrate(II) complex (CI Pigment Red 169).

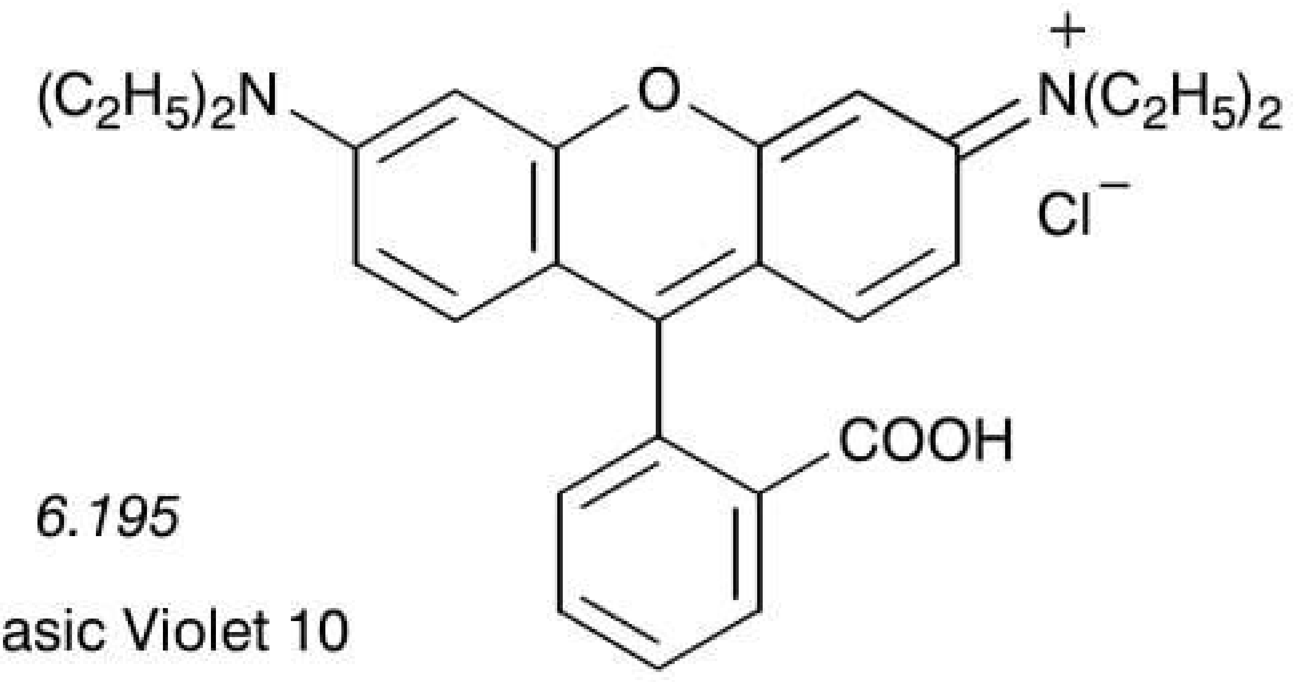
Several xanthene derivatives are applied as acid dyes. For example, condensation of 3-diethylaminophenol with benzaldehyde-2,4-disulphonic acid, followed by cyclisation and oxidation, gives Acid Rhodamine B (6.197; CI Acid Red 52). This dye is used in drop-on-demand ink-jet printing [36].

Fluorescein (6.198; X = H; CI Acid Yellow 73) is the xanthene analogue of phenolphthalein (6.190) and gives rise to an anionic charge-resonance system. This was the



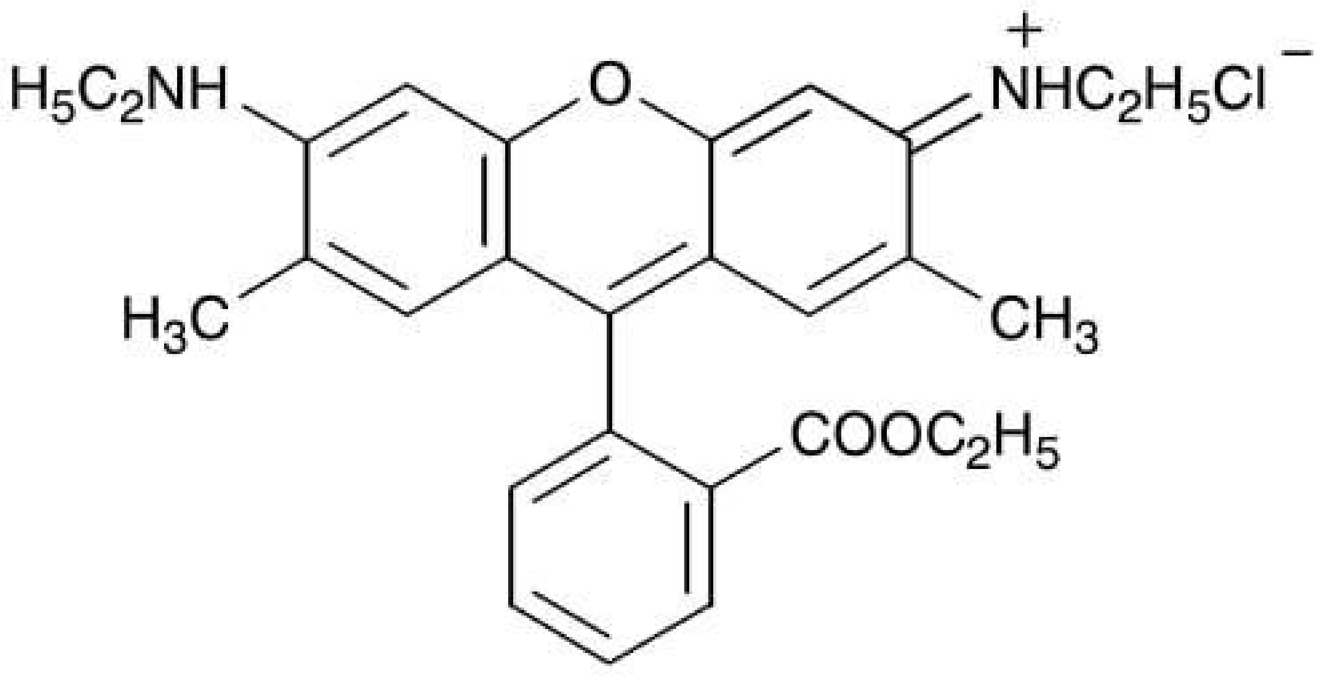
6.194

Pyronine G



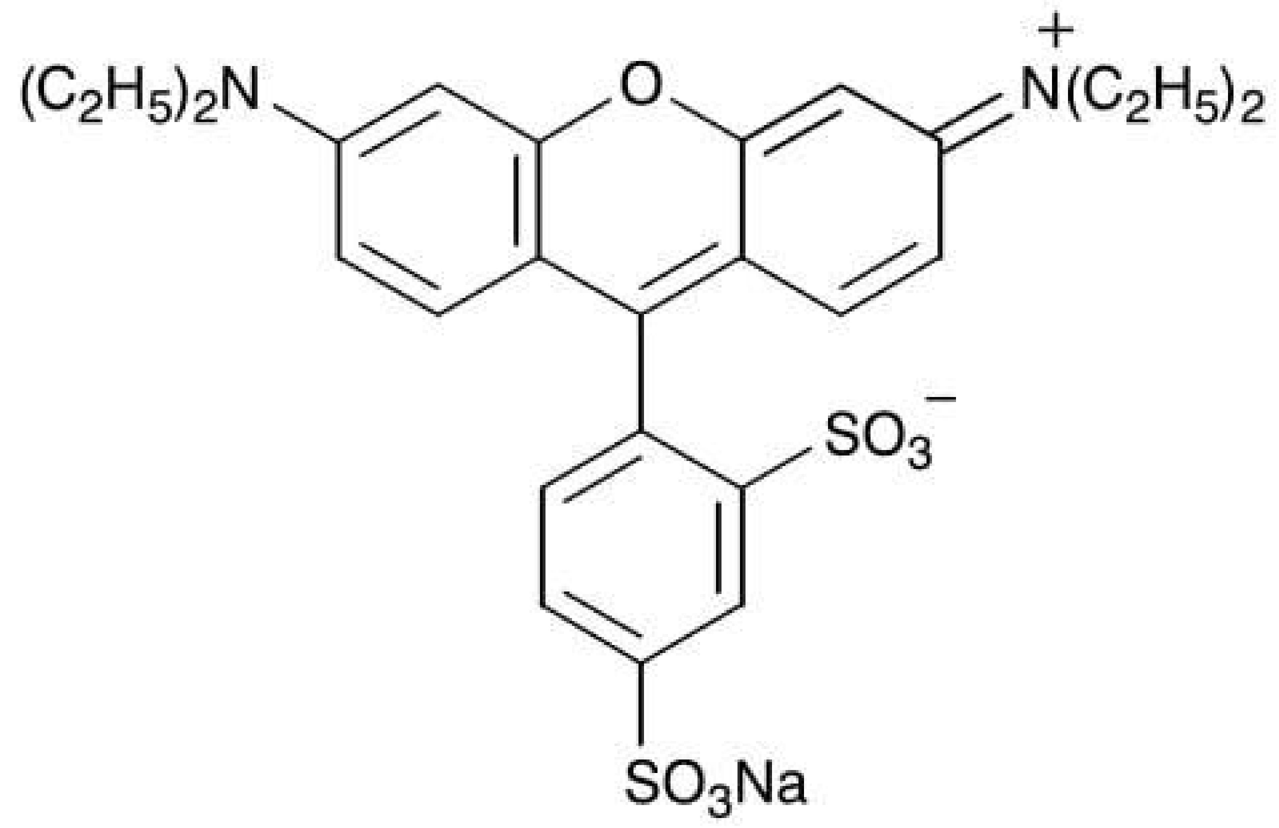
6.195

CI Basic Violet 10



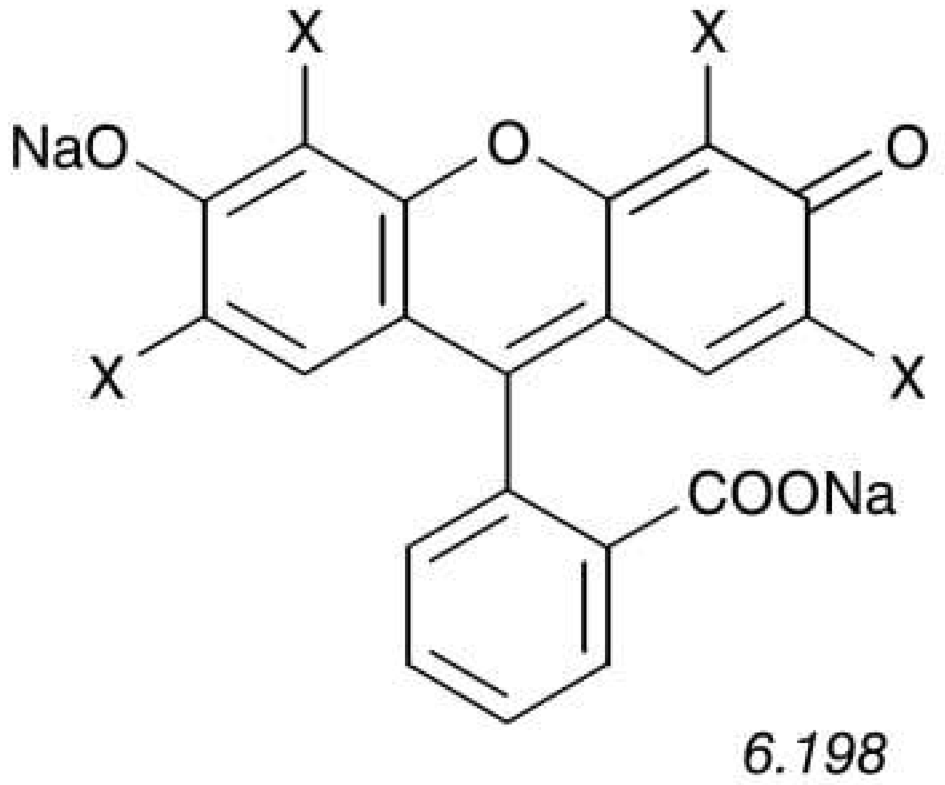
6.196

CI Basic Red 1

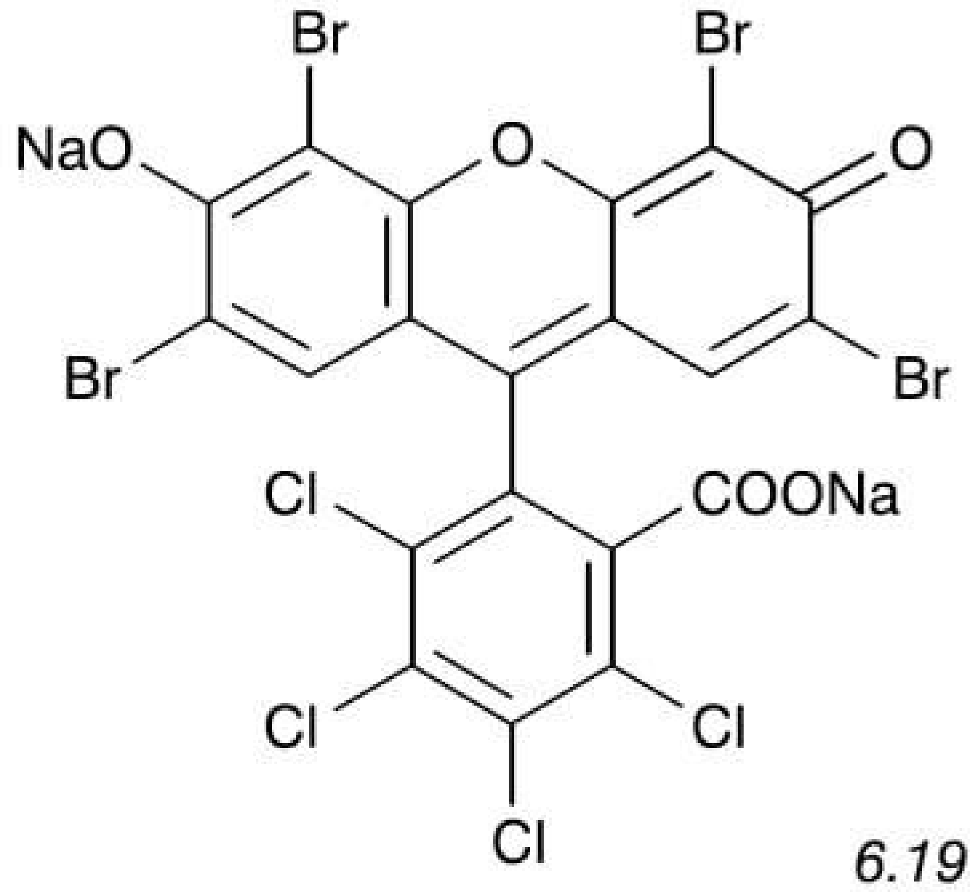


6.197

CI Acid Red 52



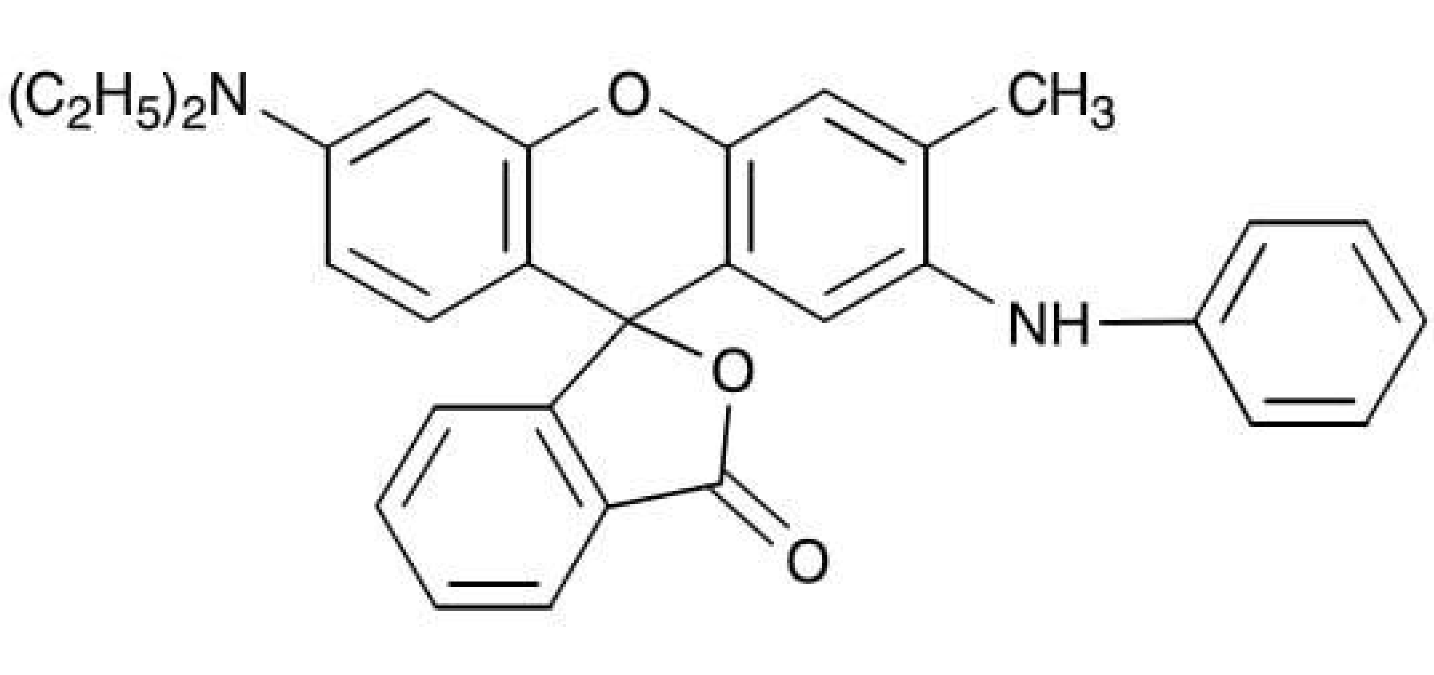
6.198



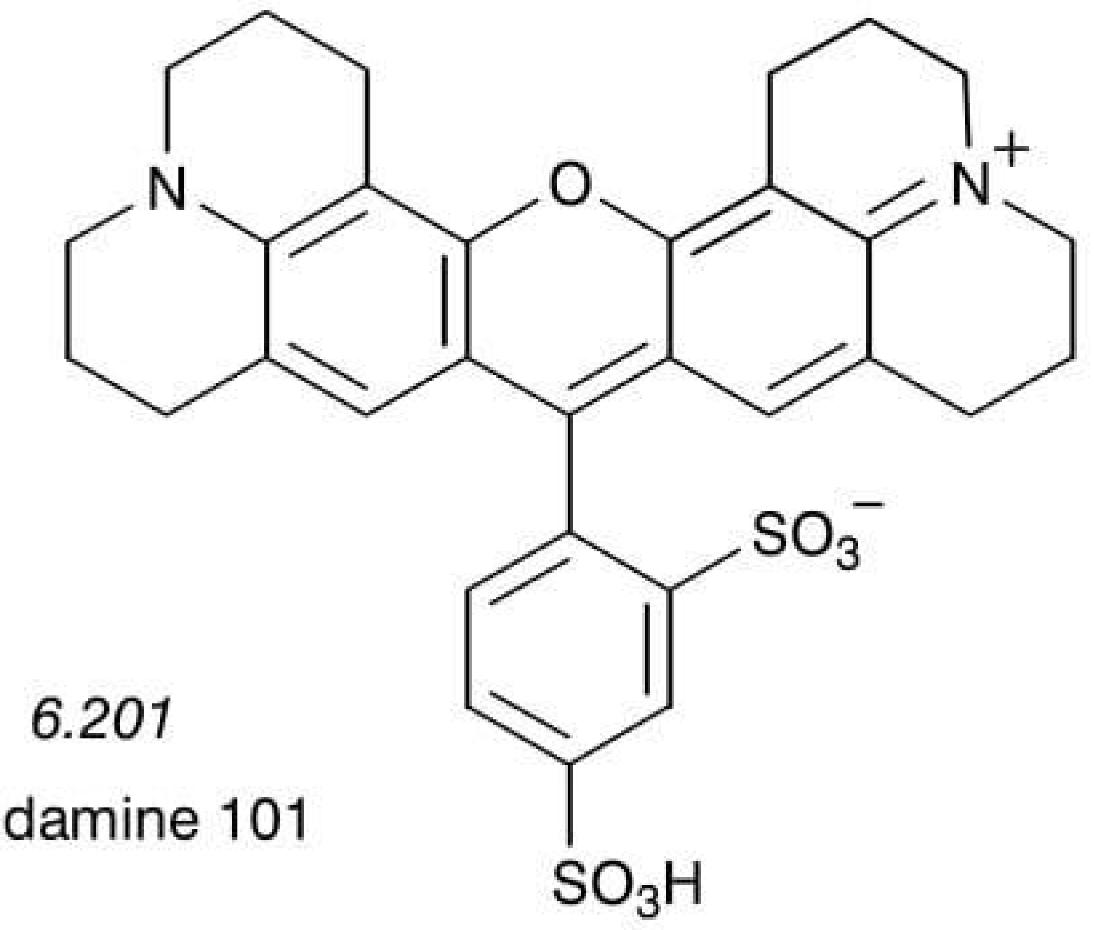
6.199

CI Acid Red 192

first xanthene dye, originally made in 1871 by von Baeyer from phthalic anhydride and resorcinol. This dye has a strong green fluorescence in solution even at very great dilution and is widely used as a marker. Various halogenated derivatives are of interest, especially the bright red tetrabromo compound eosine (6.198; X = Br; CI Acid Red 87), and the equivalent tetraiodo compound erythrosine (6.198; X = I; CI Acid Red 51). Eosine is widely used for colouring paper, inks and crayons; CI Pigment Red 90:1 is the aluminium salt. Purified erythrosine is a permitted food colorant (CI Food Red 14); the aluminium salt is also used for this purpose (CI Food Red 14:1) and as a pigment (CI Pigment Red 172). Condensation of tetrachlorophthalic anhydride with resorcinol, followed by tetrabromination of the product, gives the bright pink Phloxine B (6.199; CI Acid Red 92); the free acid is used as a solvent dye (CI Solvent Red 48) and the aluminium salt is a pigment (CI Pigment Red 174).

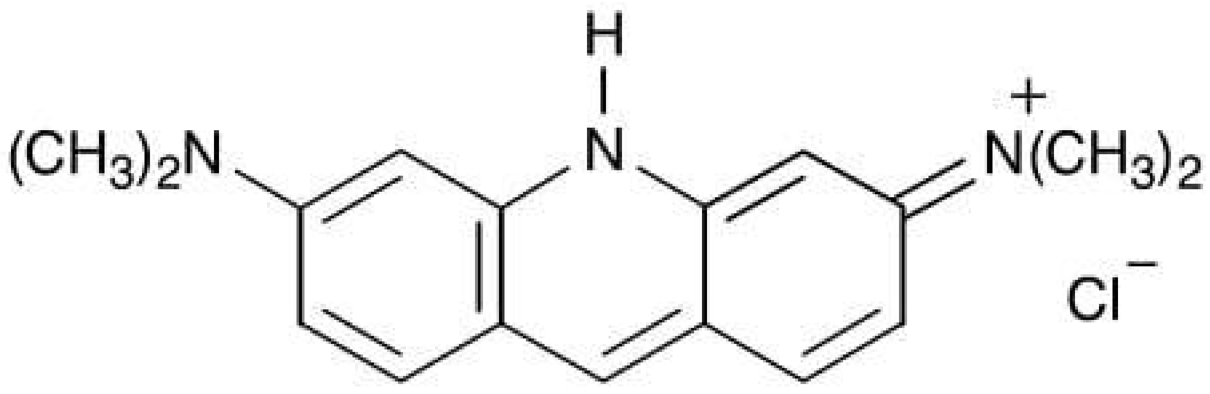


6.200



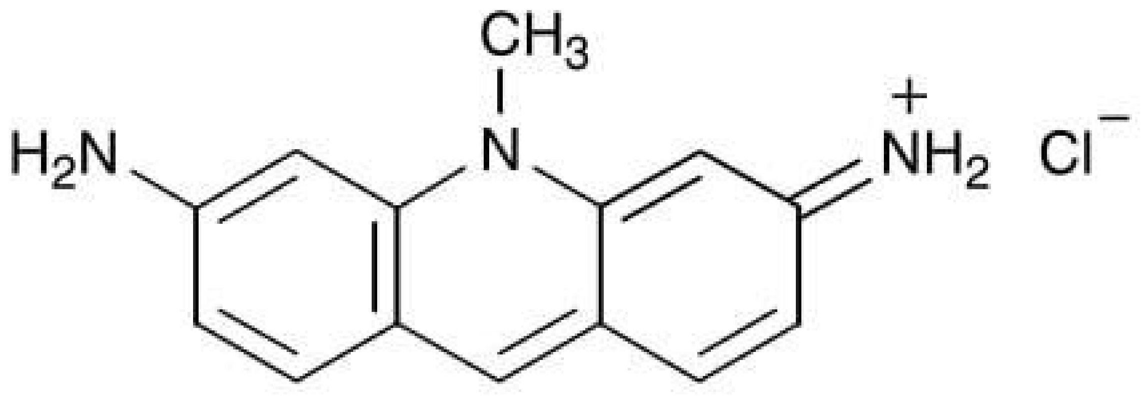
6.201

Rhodamine 101



6.202

CI Basic Orange 14



6.203

Acriflavine

Xanthene dyes are used as colour formers. These so-called fluorans usually contain amino groups sited *para* and *meta* to the central carbon atom. Such a substitution pattern gives rise to broad absorption bands and leads to almost black colour production; the lactone 6.200 is a typical example. This xanthene derivative finds use in direct thermal printing [36]. The chemistry of fluoran leuco dyes has been reviewed [78].

Various xanthene derivatives, including fluorescein, are also used as laser dyes to cover the spectral region from 500 to 700 nm. A modern example is the julolidine-based dye Rhodamine 101 (6.201), which absorbs at 576 nm and lases at 648 nm [79].

6.5.4 Acridine dyes

The presence of a nitrogen bridge in di- and tri-arylmethane dyes gives rise to the less significant acridine dyes; the parent heterocyclic ring system is so-called because of its irritant action in the nose and throat. The acridine analogue of Michler's Hydrol Blue is acridine orange (6.202; CI Basic Orange 14). This dye is made by nitration of 4,4′-bis(dimethylamino)diphenylmethane (6.156), reduction of the resulting dinitro derivative and oxidation of the cyclised diamino intermediate.

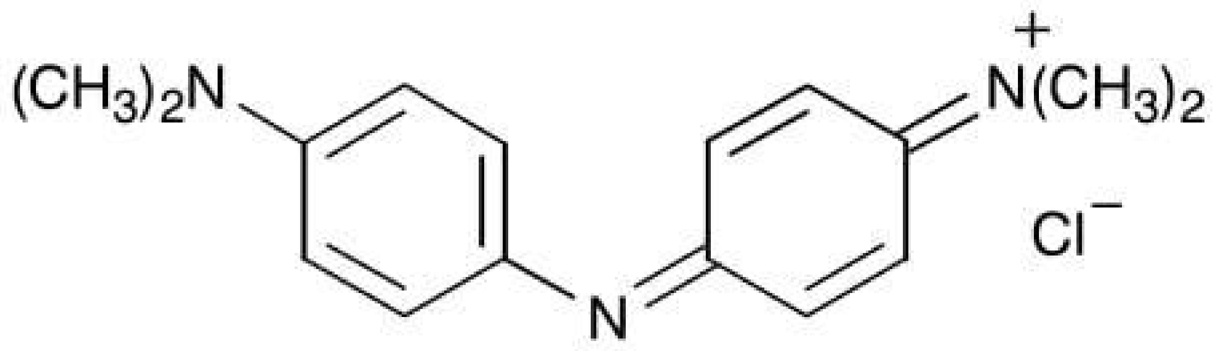
The antiseptic acriflavine (6.203) is obtained by condensation of *m*-phenylenediamine with glycerol and oxalic acid, followed by methylation of the product.

The triphenylmethane acridine analogue chrysaniline (6.166) has already been mentioned as a by-product in the synthesis of magenta.

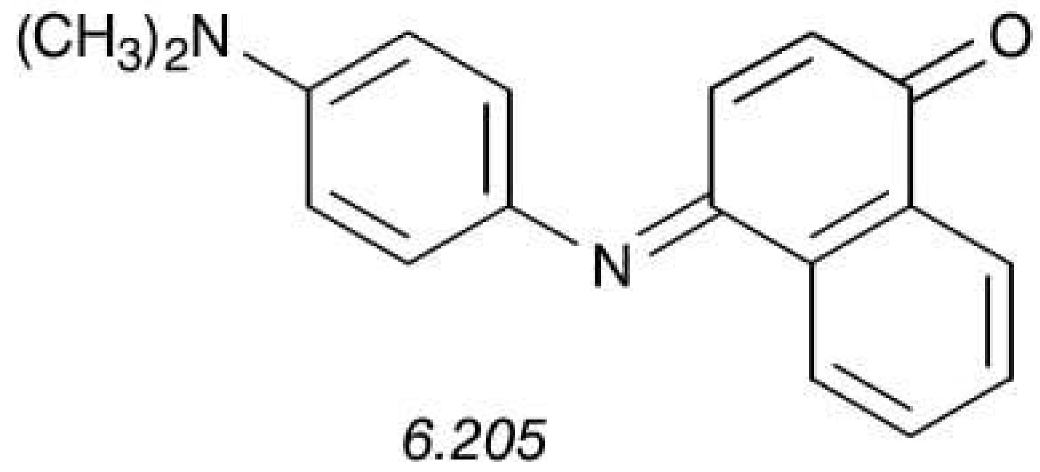
6.6 MISCELLANEOUS COLORANTS

6.6.1 Azines, oxazines and thiazines

Heterocyclic analogues of diarylmethane dyes in which the central carbon atom has been replaced by nitrogen are of some importance. Such a replacement leads to significant bathochromic shifts of the long-wavelength absorption band in accordance with PMO theory [77]. Thus Bindschedler's Green (6.204), the aza analogue of Michler's Hydrol Blue, absorbs at 725 nm. This indamine dye is only of historical interest but a related indoaniline derivative is used as a solvent dye (6.205; CI Solvent Blue 22). Of more importance are the azines, oxazines and thiazines which contain a heteroatom bridge.



6.204
Bindschedler's Green

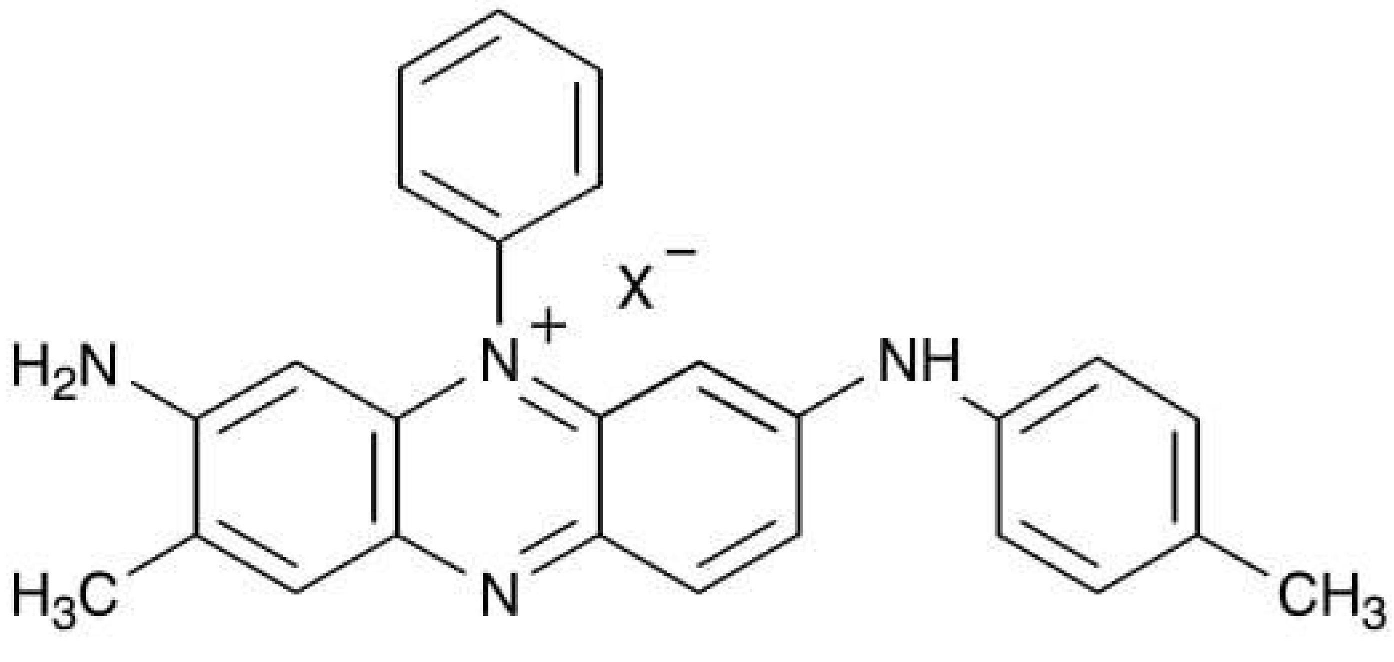


6.205
CI Solvent Blue 22

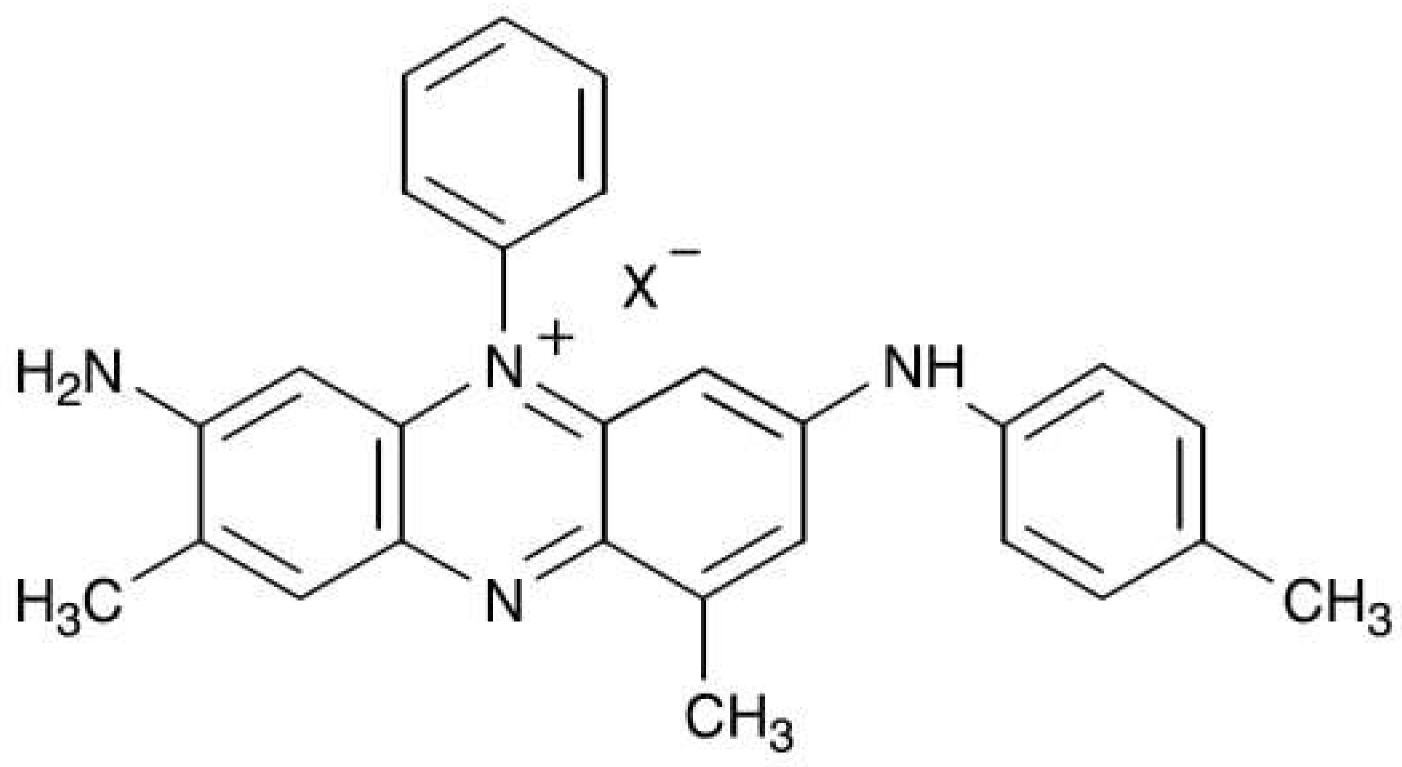
Azine dyes

The first synthetic dye, mauveine, belongs to this group. The previously accepted structure for Perkin's dye (CI 50245) has been shown to be incorrect [80]. Chromatography of an authentic sample of mauveine yielded two major components (6.206 and 6.207) which were subjected to spectroscopic analysis. Few dyes of this type remain of industrial significance, an exception being Safranine T (6.208; CI Basic Red 2), discovered in 1859 by Greville Williams. The oxidative sequence leading to the formation of Safranine T (Scheme 6.35) was only elucidated in recent times [81]. The 1:1 mixture of *o*-toluidine and 2-methyl-1,4-diaminobenzene required for the first oxidative step can be obtained by reductive cleavage of the monoazo dye formed by coupling diazotised *o*-toluidine with *o*-toluidine. Further oxidation of the intermediate diphenylamine derivative gives an electrophilic quinonediimine (indamine), which then reacts with aniline. Oxidative cyclisation produces a dihydroazine that yields the dye in a final oxidative step.

Aniline black (CI Oxidation Base 1) is a complex polymeric phenazine that can be produced on cotton fabric by impregnation with aniline hydrochloride and suitable inorganic oxidants, such as sodium chlorate, ammonium vanadate and copper hexacyanoferrate(II). Aniline black is also made directly for use as a pigment (CI Pigment Black 1).



6.206



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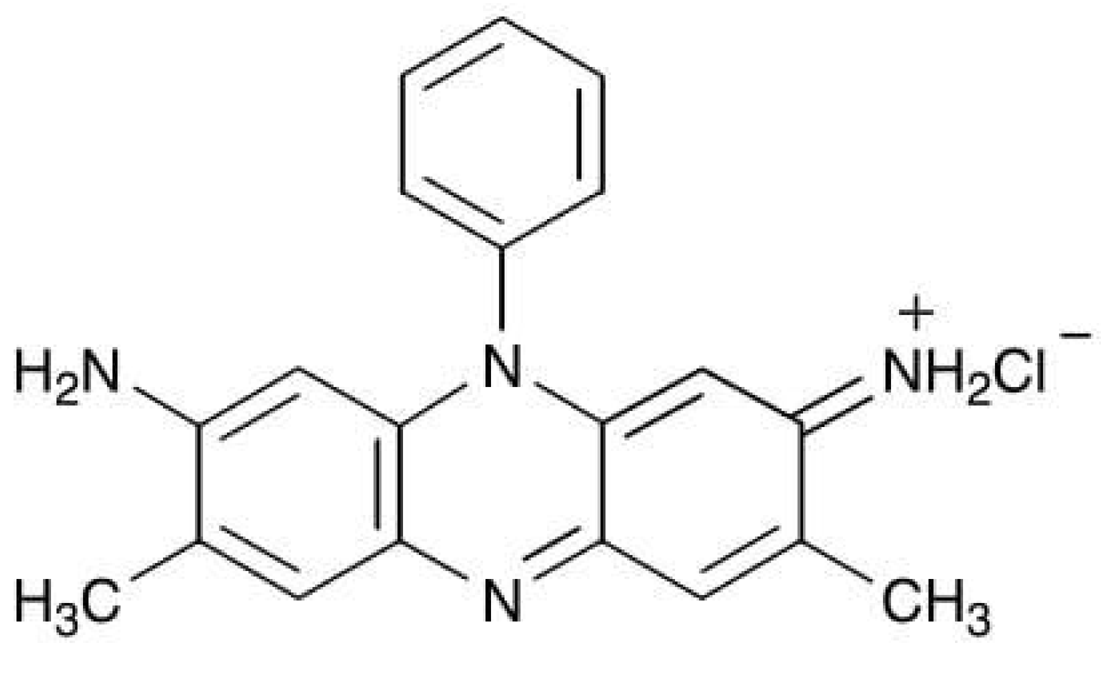

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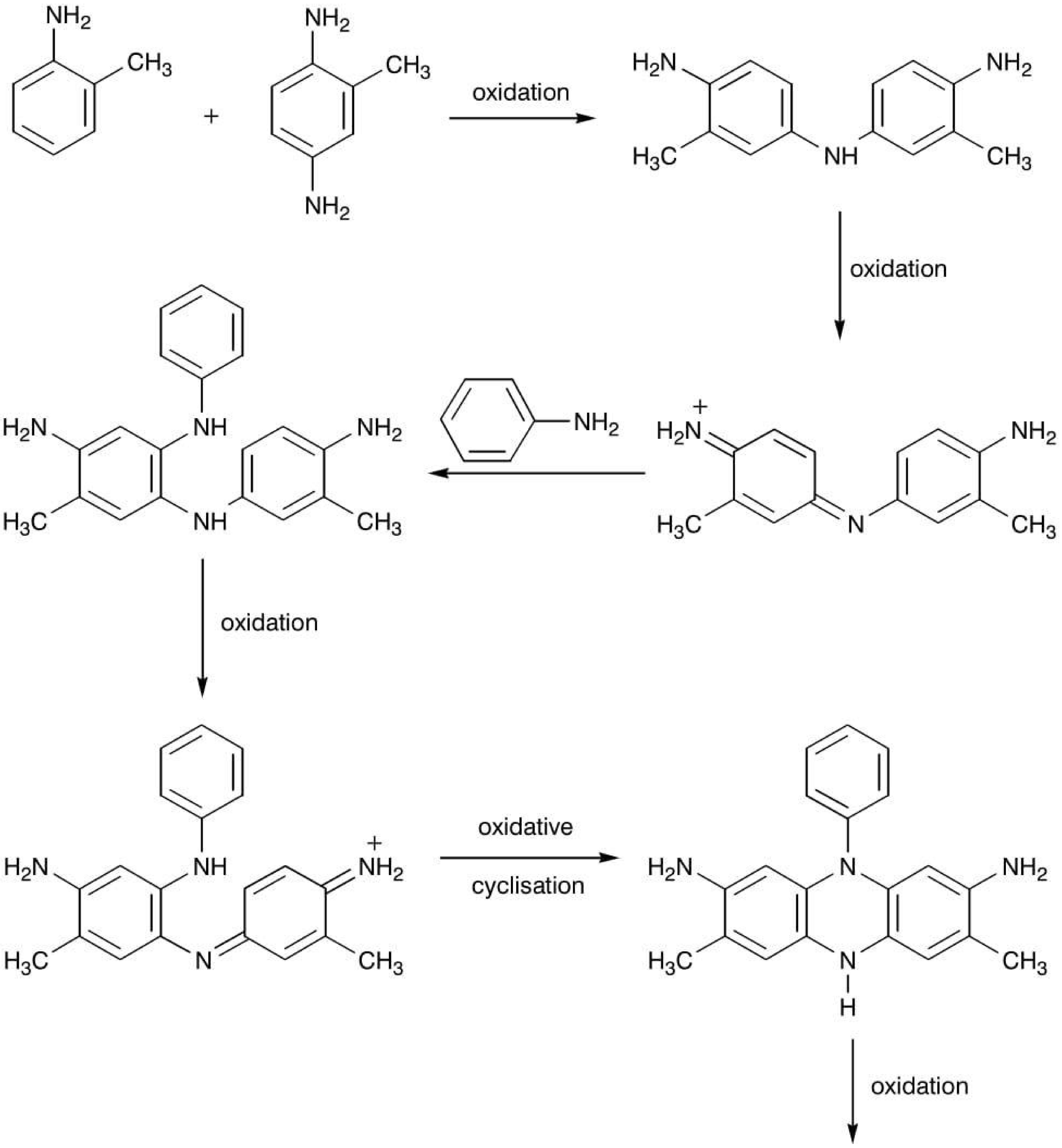


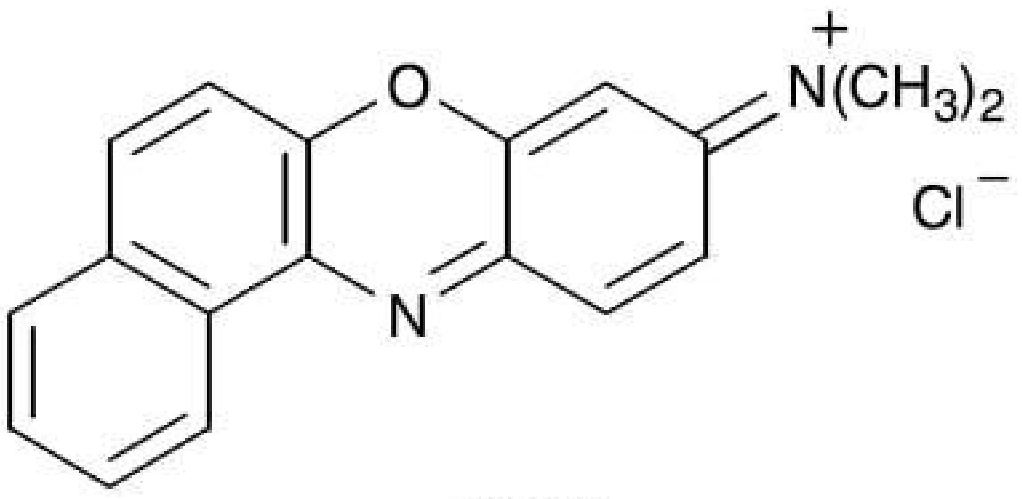
6.208
CI Basic Red 2

Scheme 6.35

Oxazine dyes

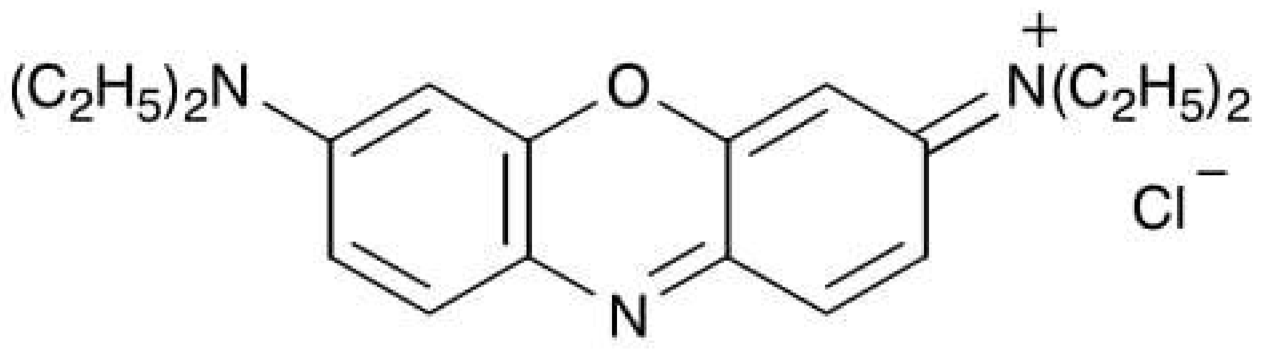
Bindschedler's Green (6.204) can be made by condensing *p*-nitroso-*N,N*-dimethylaniline with *N,N*-dimethylaniline. A similar condensation with 2-naphthol gives Meldola's Blue (6.209; CI Basic Blue 6), the first oxazine dye, discovered in 1879. The symmetrical CI Basic Blue 3 (6.210) is of more commercial significance. It is synthesised by nitrosation of *N,N*-diethyl-*m*-anisidine followed by condensation with *N,N*-diethyl-*m*-aminophenol, and is used for dyeing acrylic fibres. This dye is now classified by ETAD as toxic [73].

The dioxazine ring system is the source of some valuable violet pigments, such as CI Pigment Violet 23 (6.211). This colorant is obtained by condensing 3-amino-9-ethylcarbazole with chloranil. Sulphonation of the pigment gives the dye CI Direct Blue 108. Triphenodioxazines have recently been the source of some blue reactive dyes [24]. Examples are known of symmetrical bifunctional structures (6.212; NHRNH = alkylenediamine, Z = haloheterocyclic system) and unsymmetrical monofunctional types such as 6.213 [37].



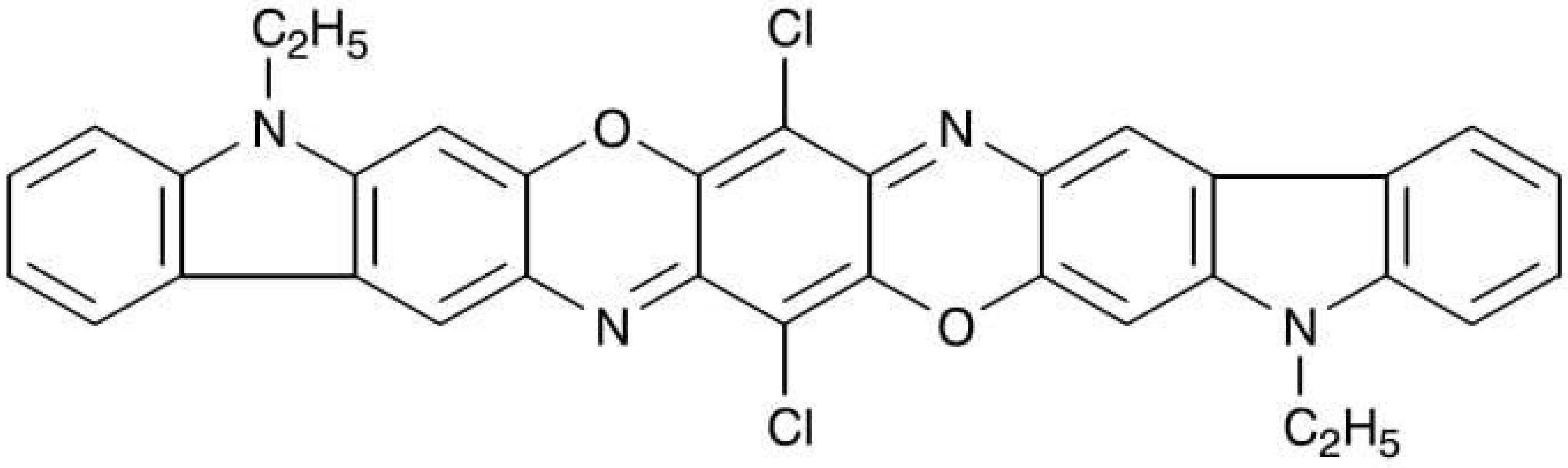
6.209

CI Basic Blue 6



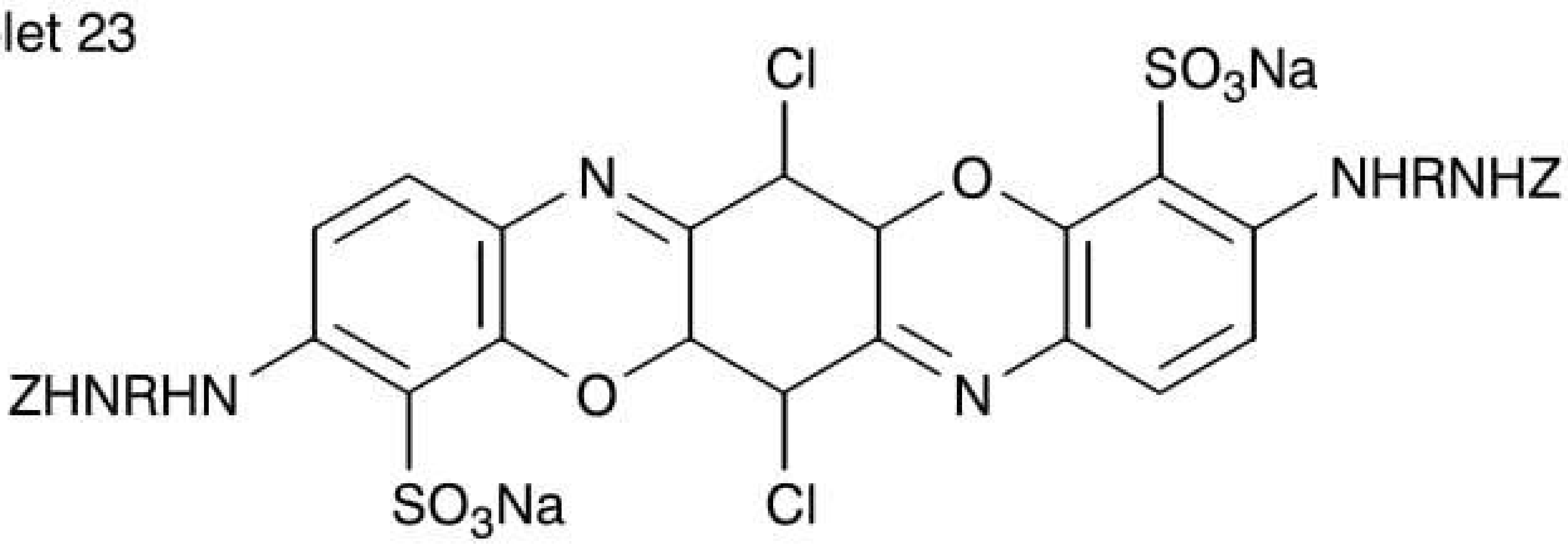
6.210

CI Basic Blue 3

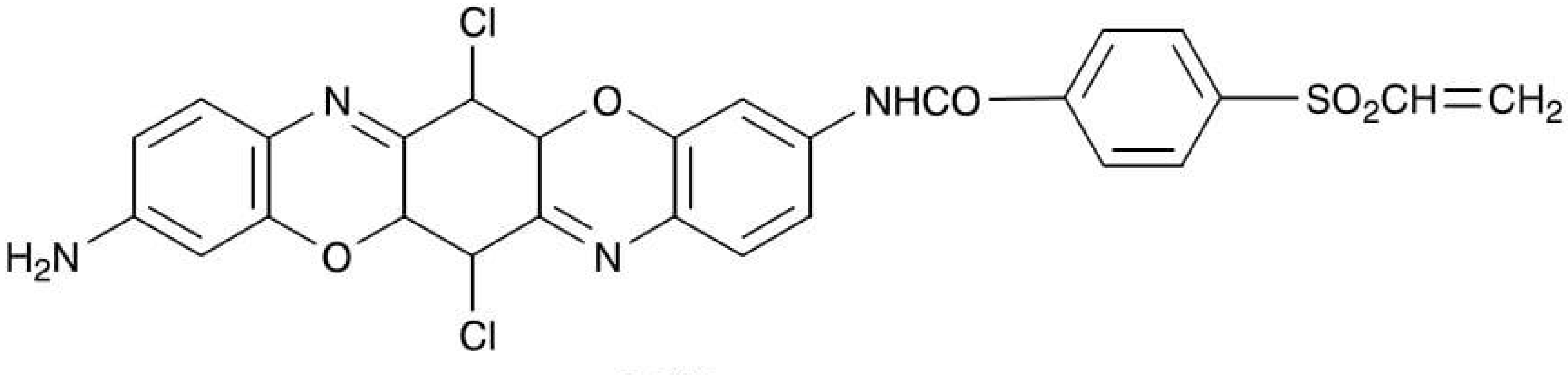


6.211

CI Pigment Violet 23



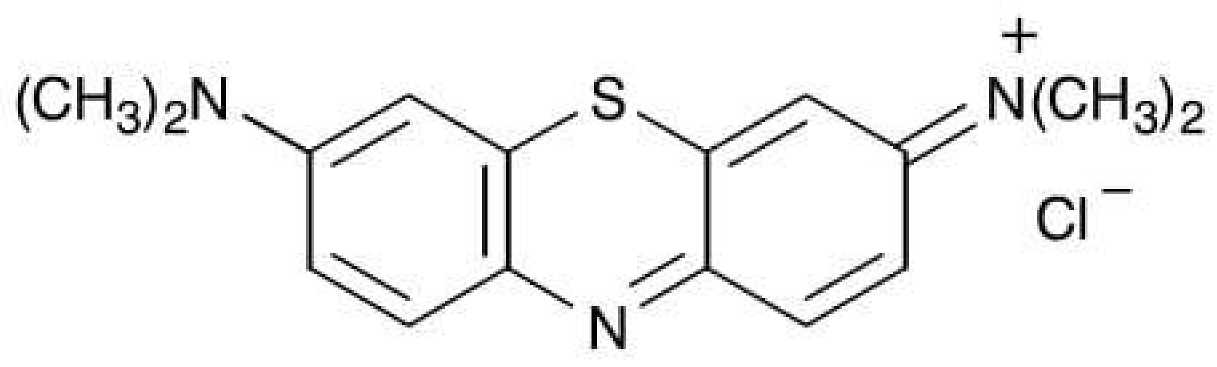
6.212



6.213

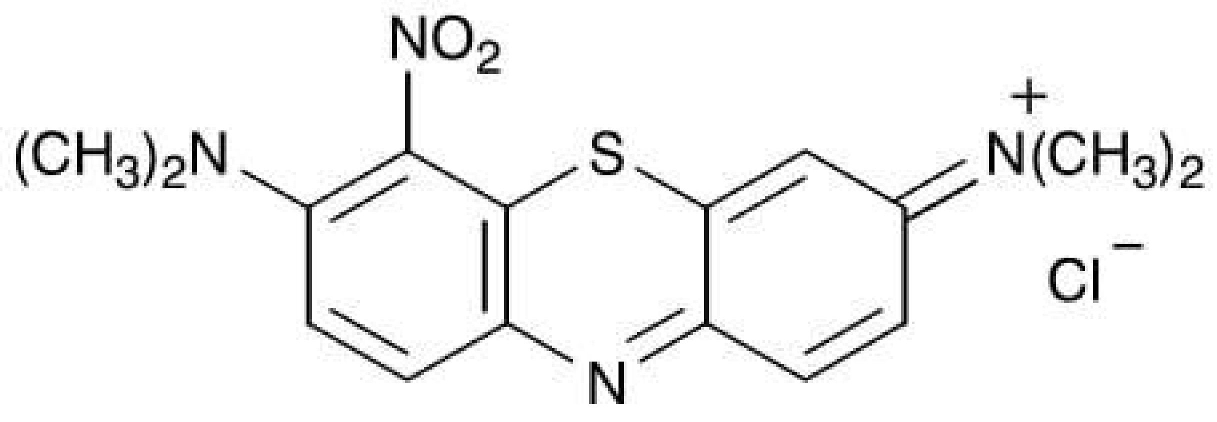
Thiazine dyes

The most important thiazine dye is methylene blue (6.214; CI Basic Blue 9), which is also widely used as a biological stain and as a redox indicator. Its synthesis (Scheme 6.36) involves the oxidative thiosulphonation of *p*-amino-*N,N*-dimethylaniline. Condensation of the product with *N,N*-dimethylaniline then gives an intermediate indamine that subsequently undergoes oxidative ring closure. Nitration of methylene blue produces methylene green (6.215; CI Basic Green 5), which shows better light fastness on acrylic fibres. The *N*-benzoyl derivative of leuco methylene blue is used as a colour former in carbonless copy papers (section 6.5.2).



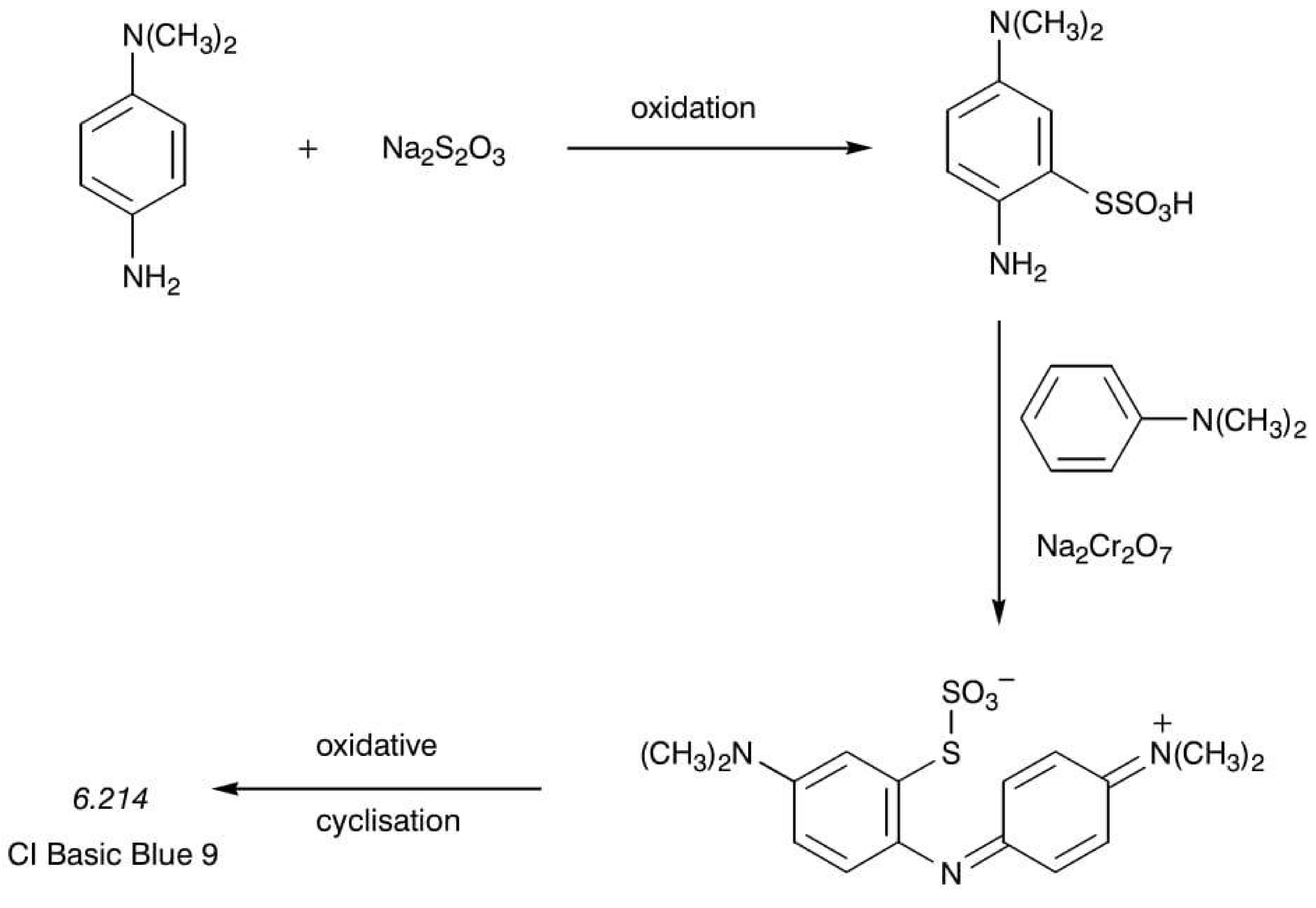
6.214

CI Basic Blue 9



6.215

CI Basic Green 5



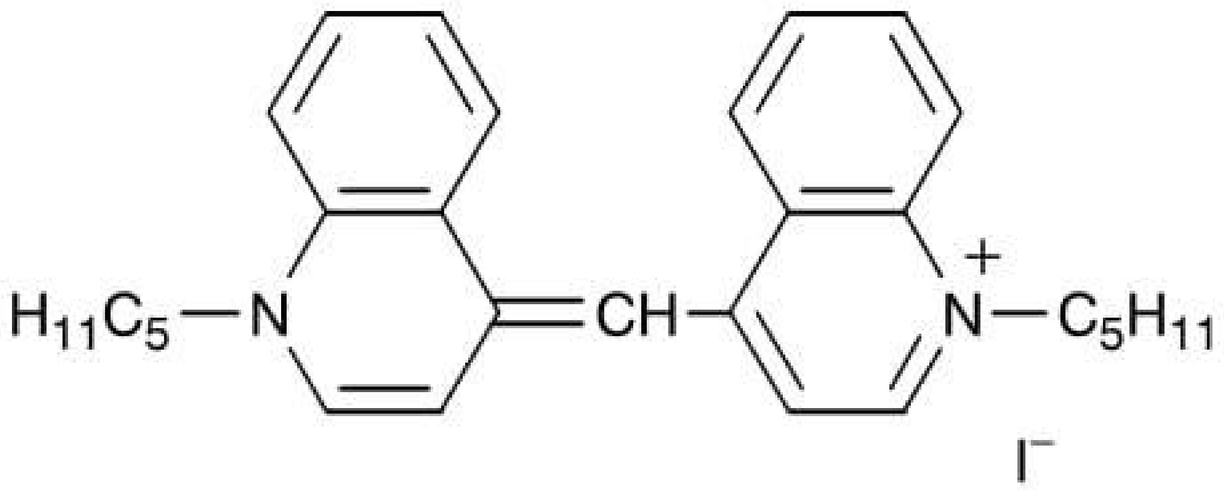
Scheme 6.36

6.6.2 Polymethine dyes

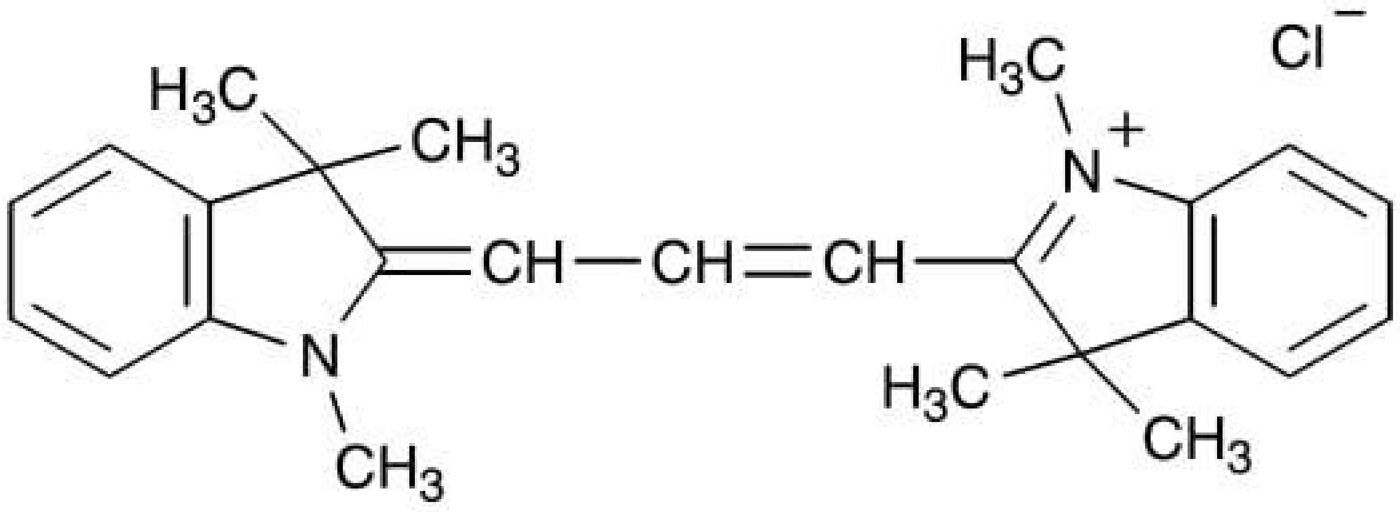
Cyanine dyes fall within the more general category of polymethine dyes, in which a chain of methine groups is terminated with a donor group and an acceptor group respectively [82].

The first cyanine dye was made in 1856 by Greville Williams. Thus the blue charge-resonance system 6.216 was produced when oxidative coupling took place between *N*-

pentylquinolinium iodide and the corresponding 4-methyl derivative. Dyes of this kind were later found to have colour-sensitising properties in photographic films and hundreds of related compounds have been synthesised, making use of a great variety of heterocyclic terminal groups [83]. Long-chain cyanines absorb beyond the visible region and are useful as infrared sensitisers in photography. Few cyanine colorants have found use as textile dyes, however, owing to inferior fastness properties. Astra Phloxine (6.217; CI Basic Red 12) is an example of a carbocyanine (trimethine) dye derived from 1,3,3-trimethylindoline. This product is now classified by ETAD as toxic [73]. Structurally unsymmetrical dyes of this type are exemplified by CI Basic Orange 21 (6.218), which is obtained by condensing Fischer's aldehyde (6.219) with 2-methylindole. The use of polymethine cyanine dyes in photography and dye lasers has been reviewed [84].

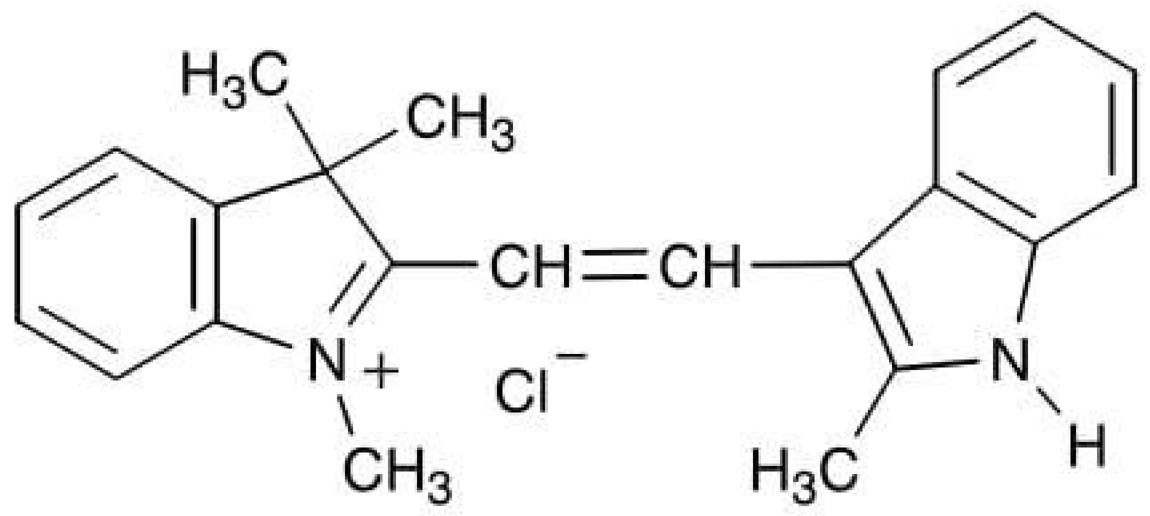


6.216



6.217

CI Basic Red 12

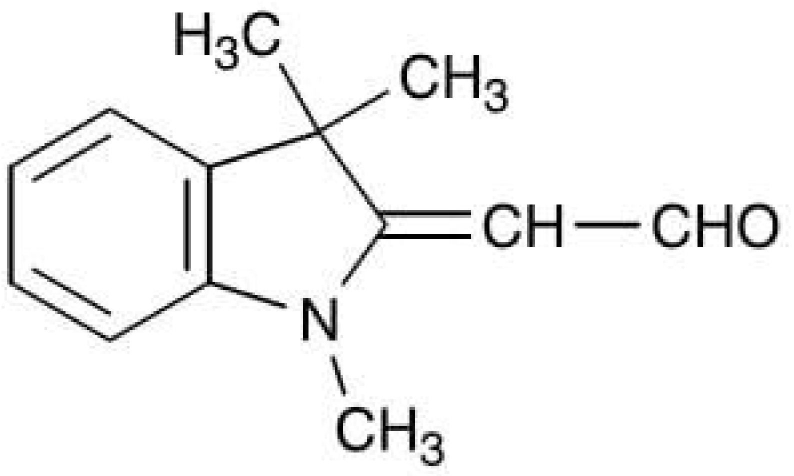


6.218

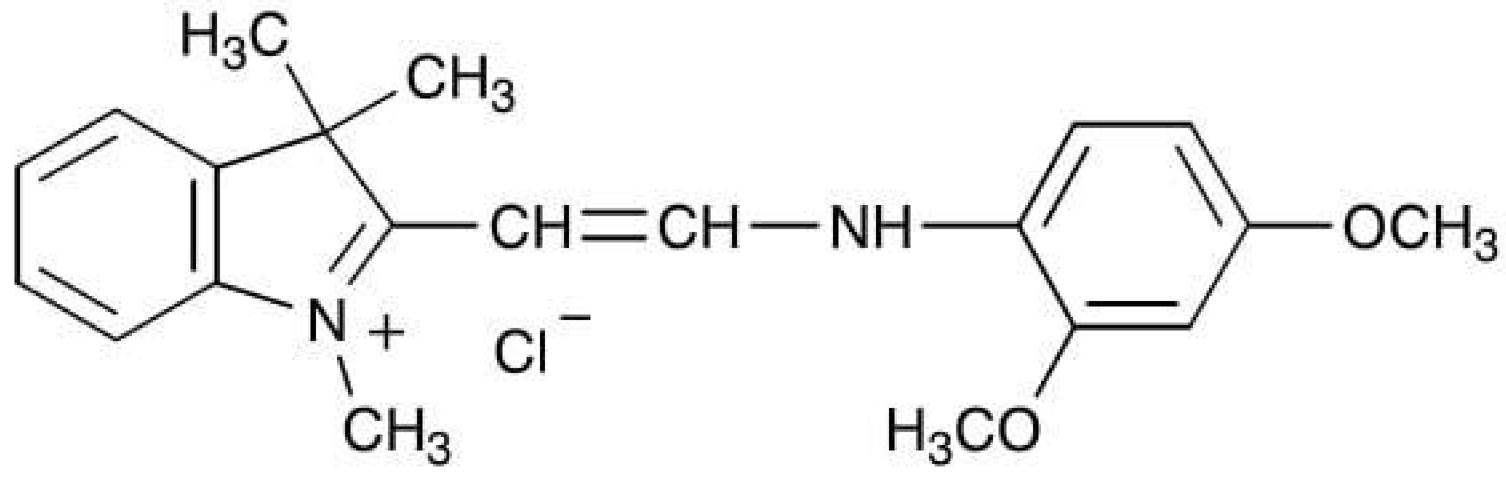
CI Basic Orange 21

6.219

Fischer's aldehyde

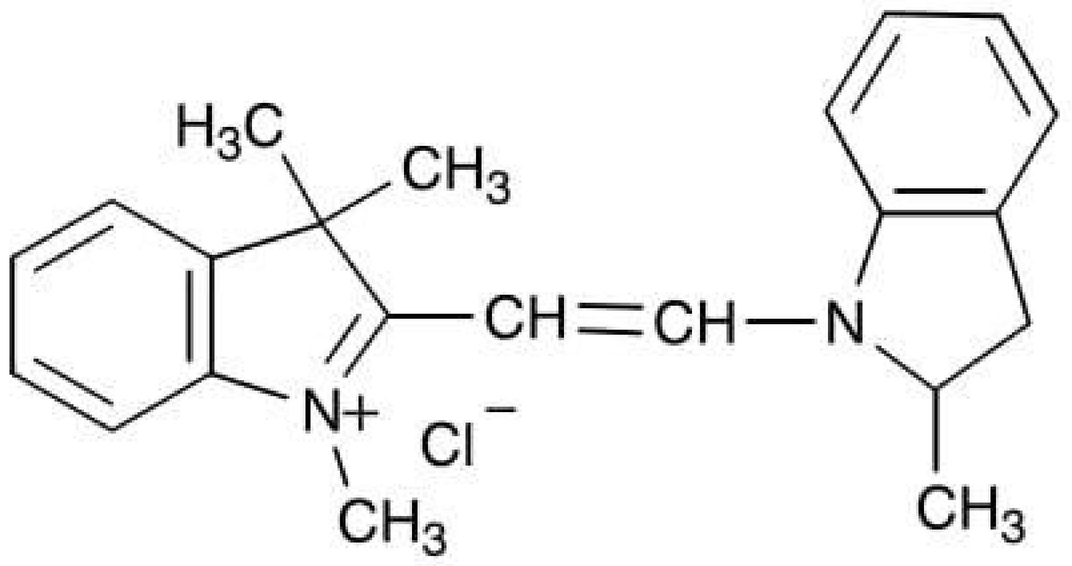


Of some importance as textile dyes are aza analogues of polymethine (cyanine) dyes. Azacarbocyanines result when Fischer's aldehyde is heated with primary aromatic amines. Thus CI Basic Yellow 11 (6.220) is obtained when Fischer's aldehyde is condensed with 2,4-dimethoxyaniline. The equivalent reaction with 2-methylindoline gives CI Basic Yellow 21 (6.221), which has superior light fastness but has been classified by ETAD as toxic [73]. The tinctorially strong golden yellow diazacarbocyanine dye CI Basic Yellow 28 (6.222) is prepared by coupling diazotised *p*-anisidine with Fischer's base (6.223), followed by quaternisation with dimethyl sulphate. Some triazacarbocyanine dyes are also used commercially.



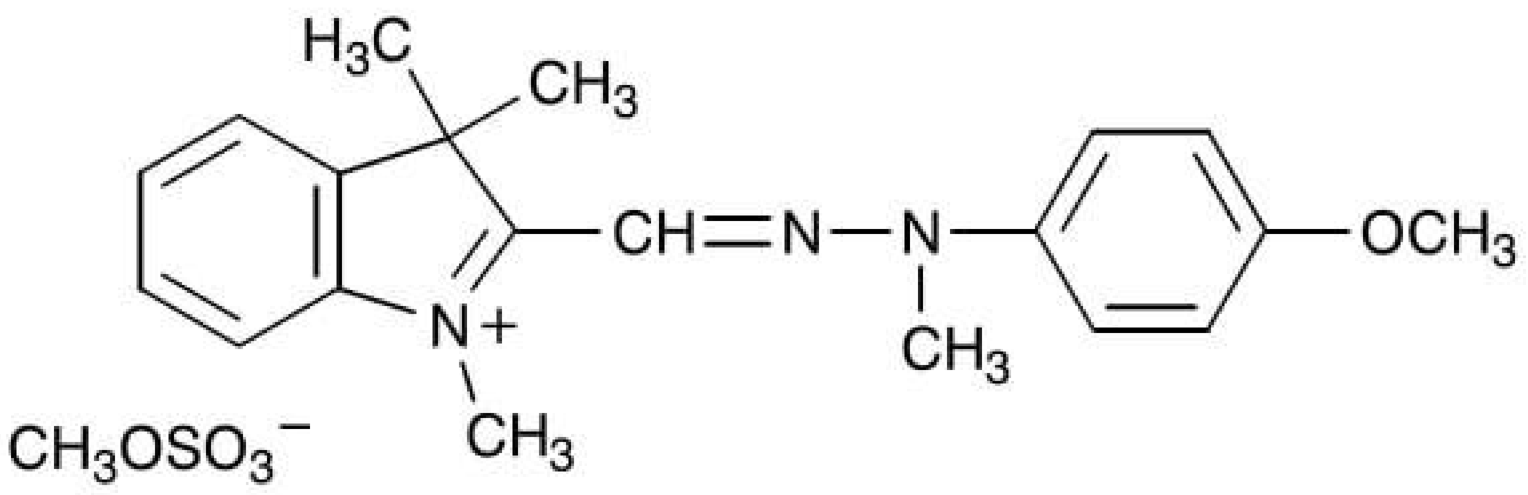
6.220

CI Basic Yellow 11



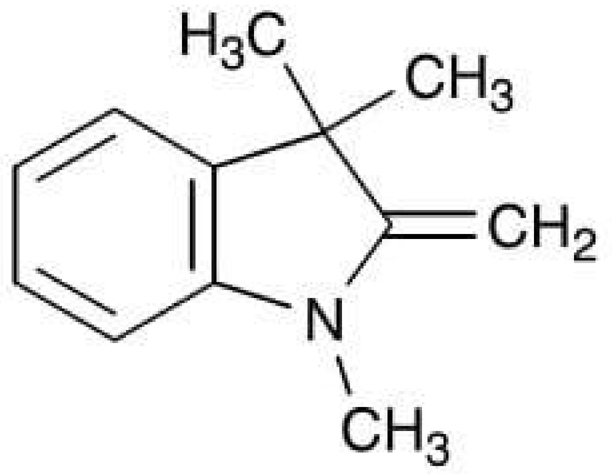
6.221

CI Basic Yellow 21



6.222

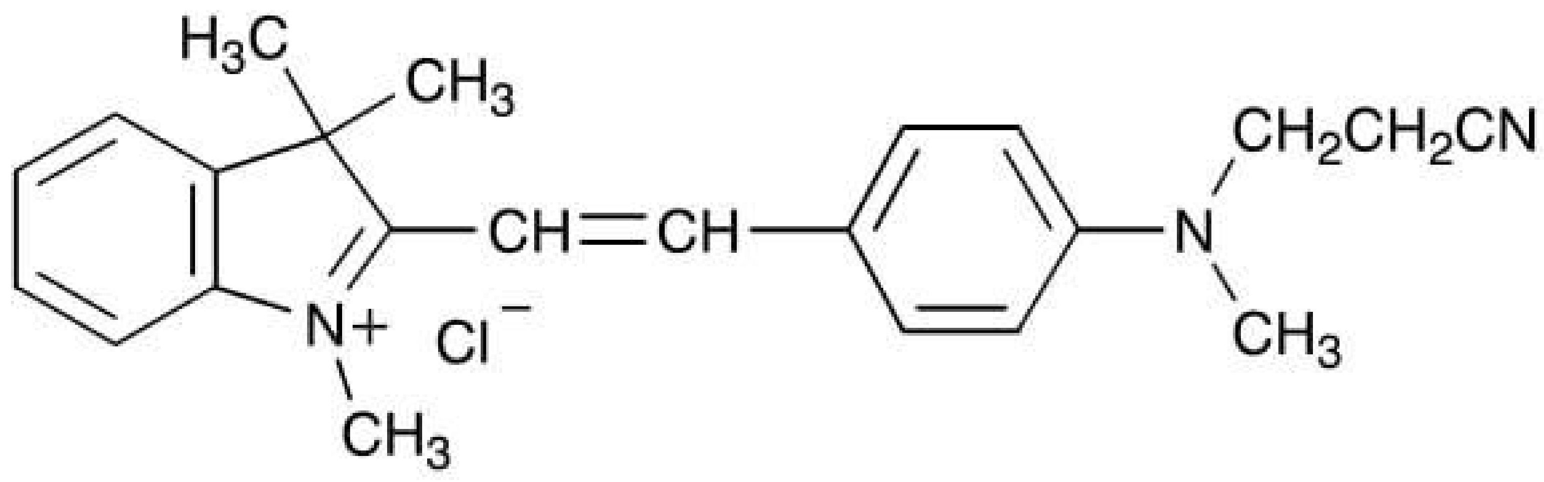
CI Basic Yellow 28



6.223

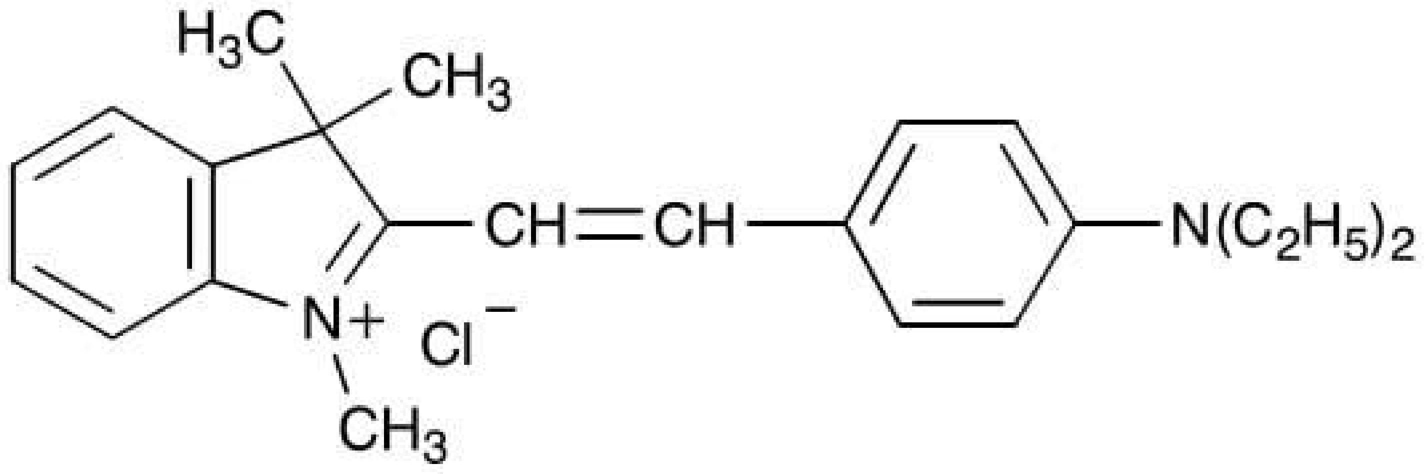
Fischer's base

Hemicyanine (styryl) dyes are readily obtained by heating Fischer's base with an appropriate aldehyde. Typical products include CI Basic Red 14 (6.224) and CI Basic Violet 16 (6.225). The latter dye has been classified by ETAD as toxic [73].



6.224

CI Basic Red 14

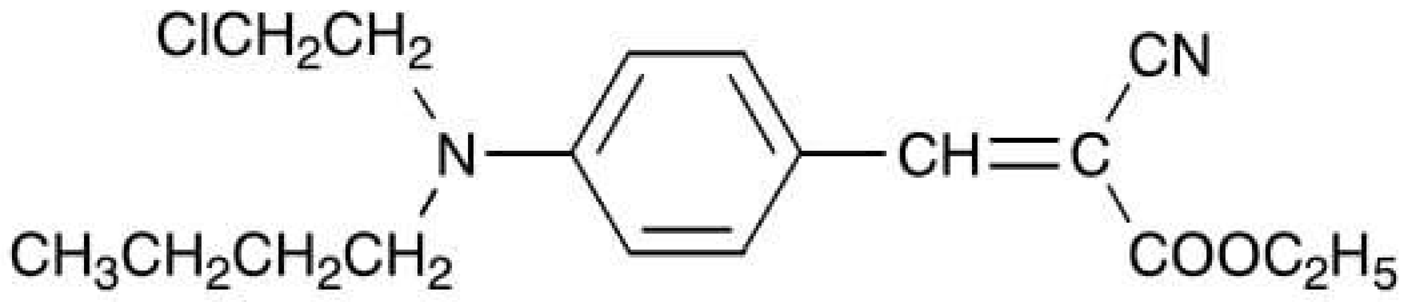


6.225

CI Basic Violet 16

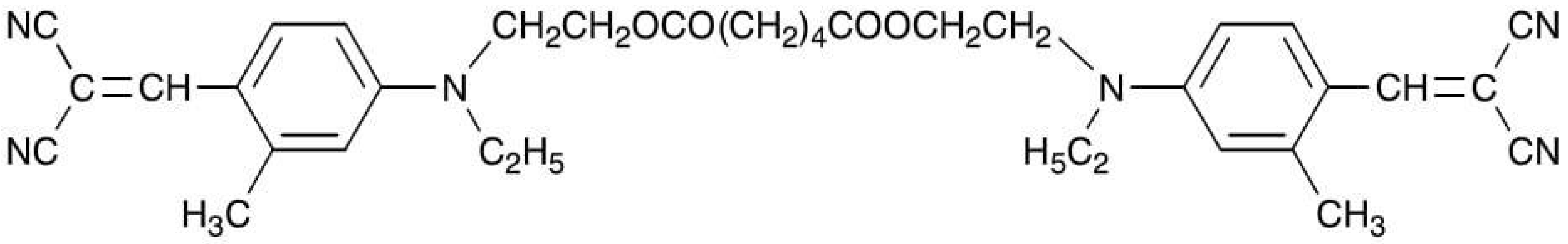
Cationic monoazo dyes can be classified as diazahemicyanines; examples of such dyes are considered in section 4.10.

Uncharged styryl (methine) disperse dyes were originally introduced to provide greenish yellow colours on cellulose acetate fibres. One such dye still in use is CI Disperse Yellow 31 (6.226), which is made by condensing 4-(*N*-butyl-*N*-chloroethylamino)benzaldehyde with ethyl cyanoacetate. Suitable compounds for polyester usually contain the electron-accepting dicyanovinyl group, introduced with the aid of malononitrile. An increased molecular size leads to improved fastness to sublimation, as in the case of CI Disperse Yellow 99 (6.227). A novel polymethine-type structure of great interest is present in CI Disperse Blue 354 (6.228), which is claimed to be the most brilliant blue disperse dye currently available [85].



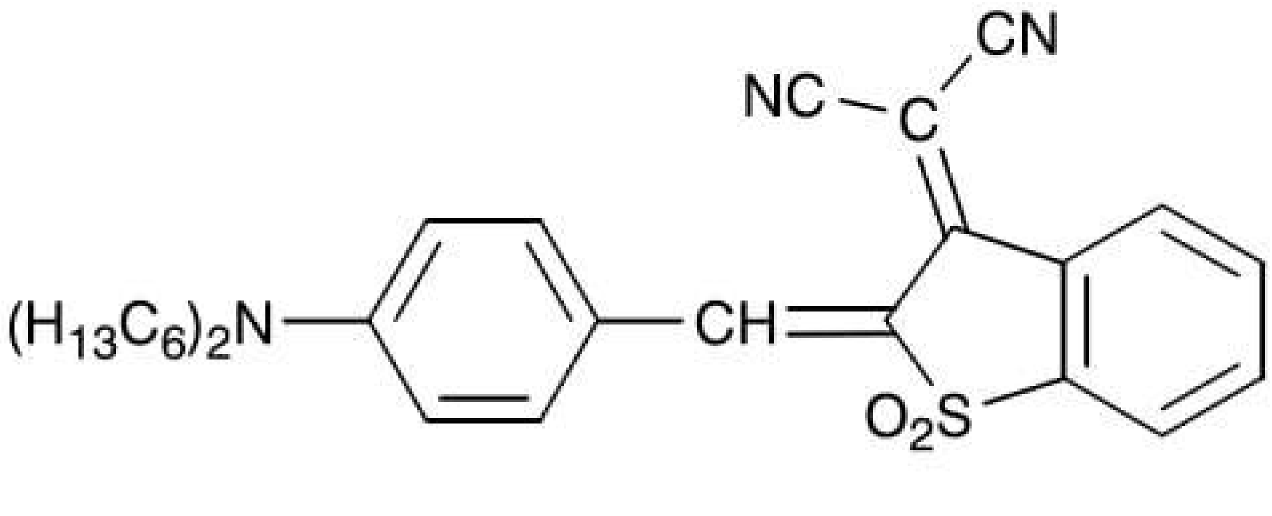
6.226

CI Disperse Yellow 31



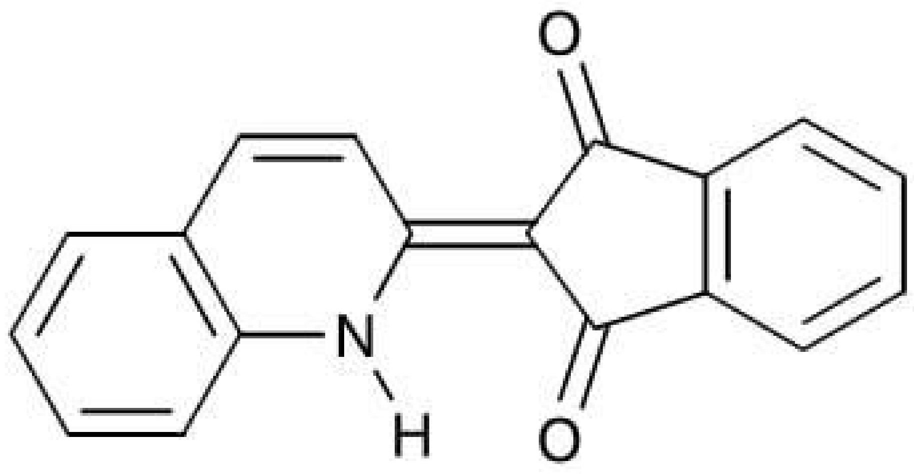
6.227

CI Disperse Yellow 99



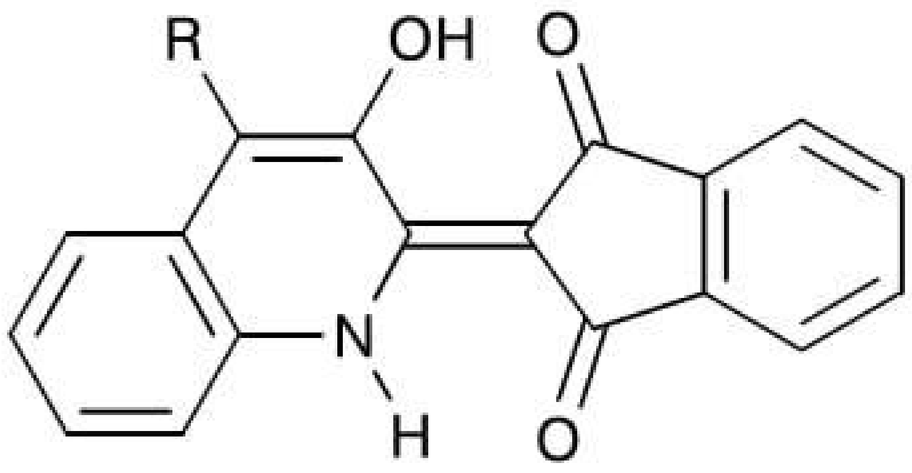
6.228

CI Disperse Blue 354



6.229

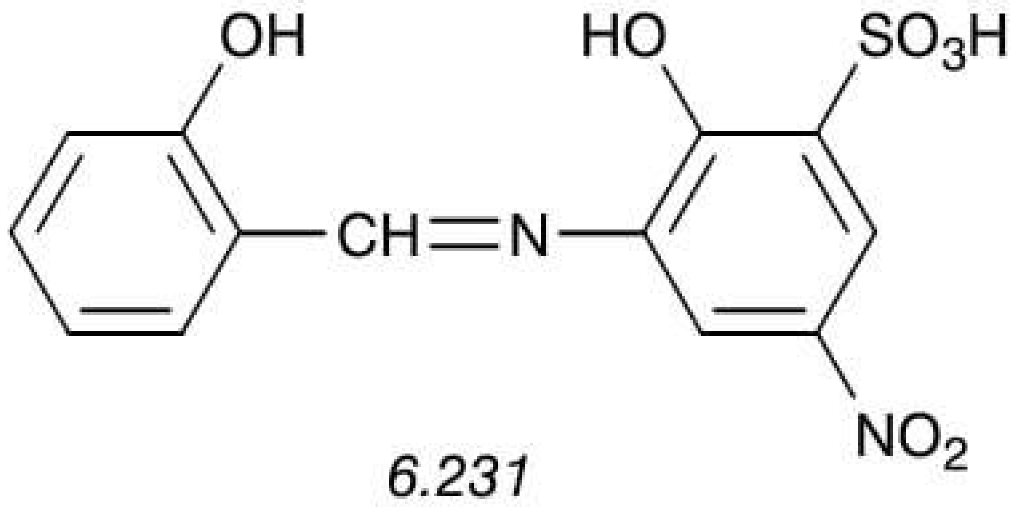
Quinophthalone



6.230

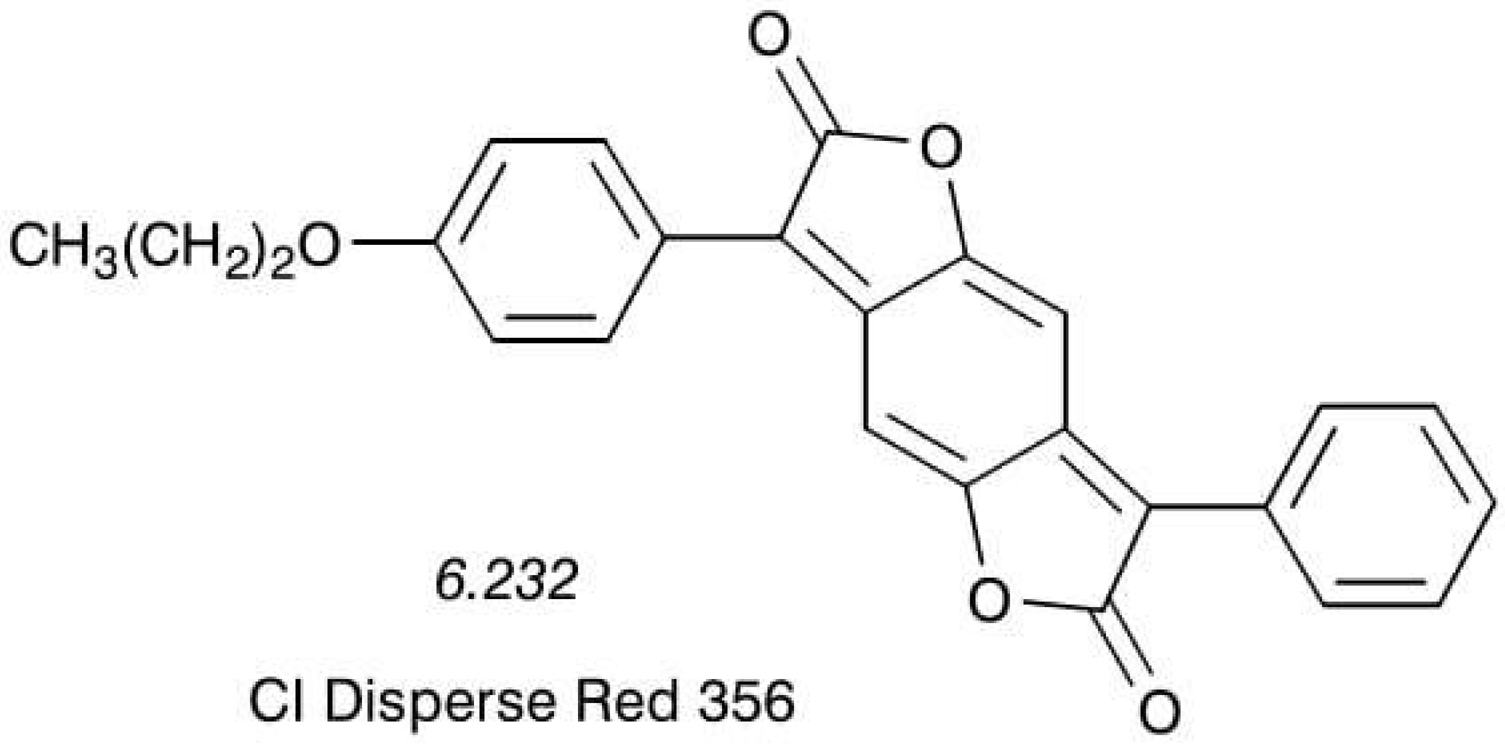
Quinophthalone (6.229) and its derivatives [86] also fall into the methine category, although they appear in the *Colour Index* under quinoline colouring matters. The parent compound was discovered in 1882 by Jacobsen, who condensed 2-methylquinoline (quinaldine) with phthalic anhydride. The product, quinoline yellow, is used as a solvent dye (CI Solvent Yellow 33). The light fastness is improved by the presence of a hydroxy group in the quinoline ring system. Derivatives of this type provide greenish yellow disperse dyes for polyester. The moderate sublimation fastness of CI Disperse Yellow 54 (6.230; R = H) is improved by the introduction of an adjacent bromine atom in CI Disperse Yellow 64 (6.230; R = Br).

The chromium complexes of some azomethine derivatives are used as solvent dyes. CI Solvent Yellow 32 (6.231) is an example, obtained by condensing one mole of salicylaldehyde with the appropriate amine, followed by treatment with one equivalent of chromium.



6.231

CI Solvent Yellow 32



6.232

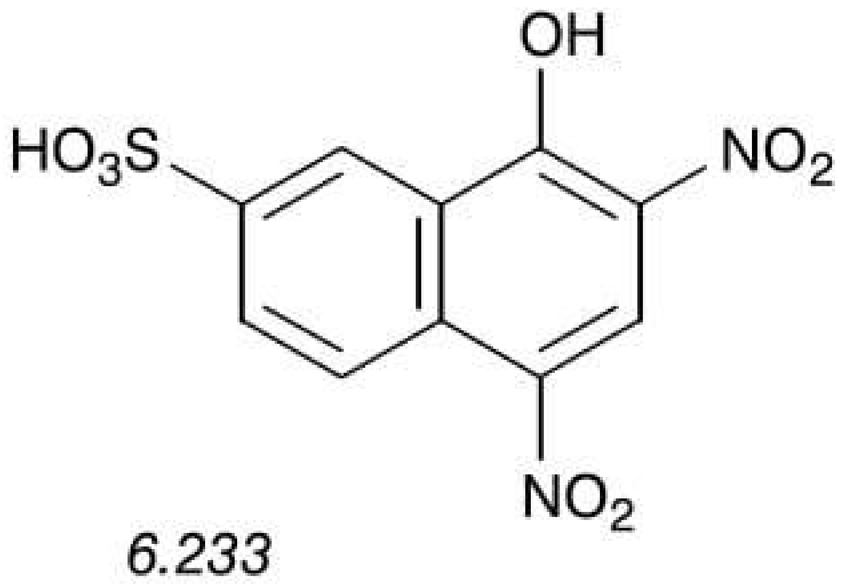
CI Disperse Red 356

A new cross-conjugated methine-type chromogen was introduced in 1984. The dye CI Disperse Red 356 (6.232) exemplifies this system, which contains two α,ω-donor-acceptor dienone segments. The development of such benzodifuranone disperse dyes has been described [87].

6.6.3 Nitro and nitroso dyes

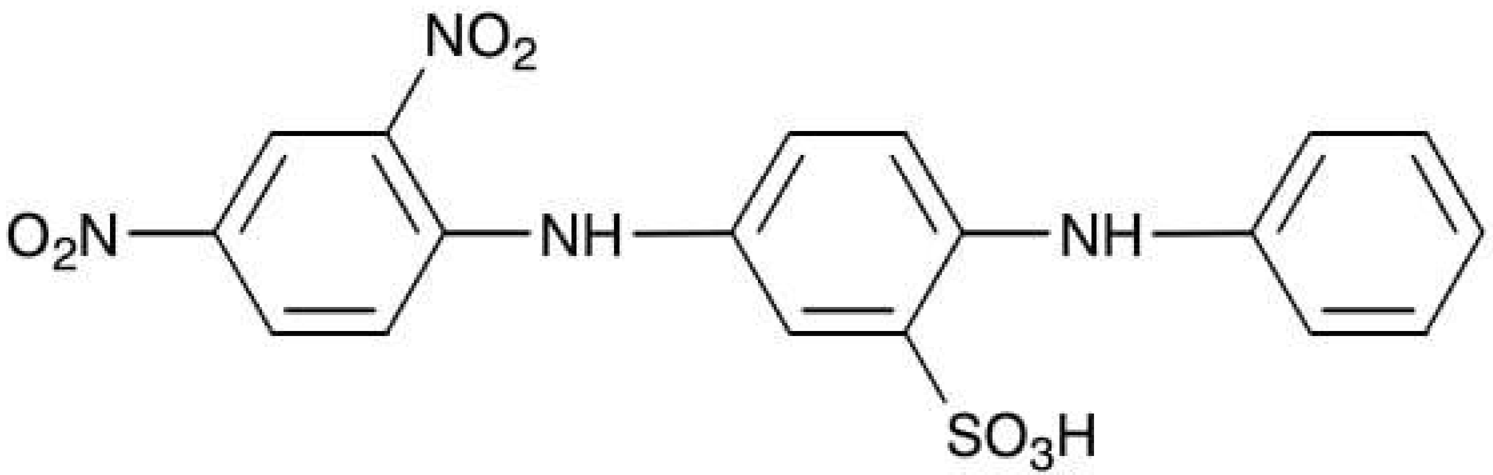
Yellow to brown compounds are obtained when one or more nitro groups are conjugated with electron-donor substituents such as hydroxy or, of more importance, amino groups. Such dyes are relatively cheap. Picric acid, 2,4,6-trinitrophenol, can be regarded as the oldest synthetic dye; it was produced in 1771 by Woulfe by treating indigo with nitric acid.

The hydroxy-nitro dye Naphthol Yellow S (6.233; CI Acid Yellow 1) was discovered in 1879 by Caro and is still manufactured. It is produced by sulphonation of 1-naphthol to give 1-naphthol-2,4,7-trisulphonic acid, followed by replacement of the 2- and 4-sulpho groups in nitric acid medium. Nucleophilic substitution of 1-chloro-2,4-dinitrobenzene with 4-aminodiphenylamine-2-sulphonic acid gives CI Acid Orange 3 (6.234).



6.233

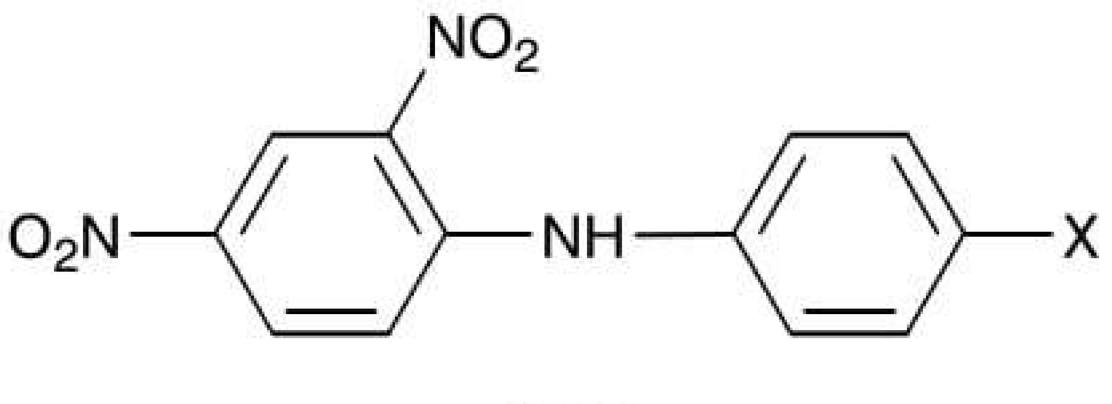
CI Acid Yellow 1



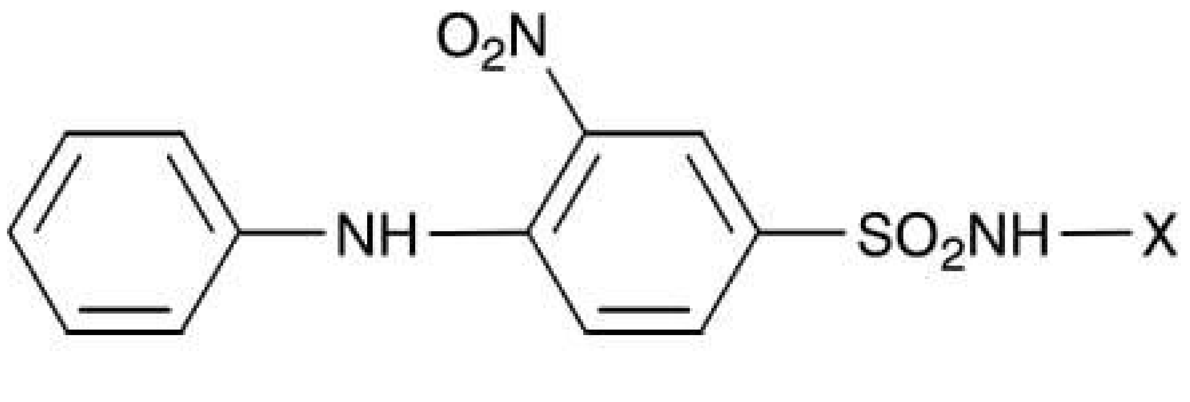
6.234

CI Acid Orange 3

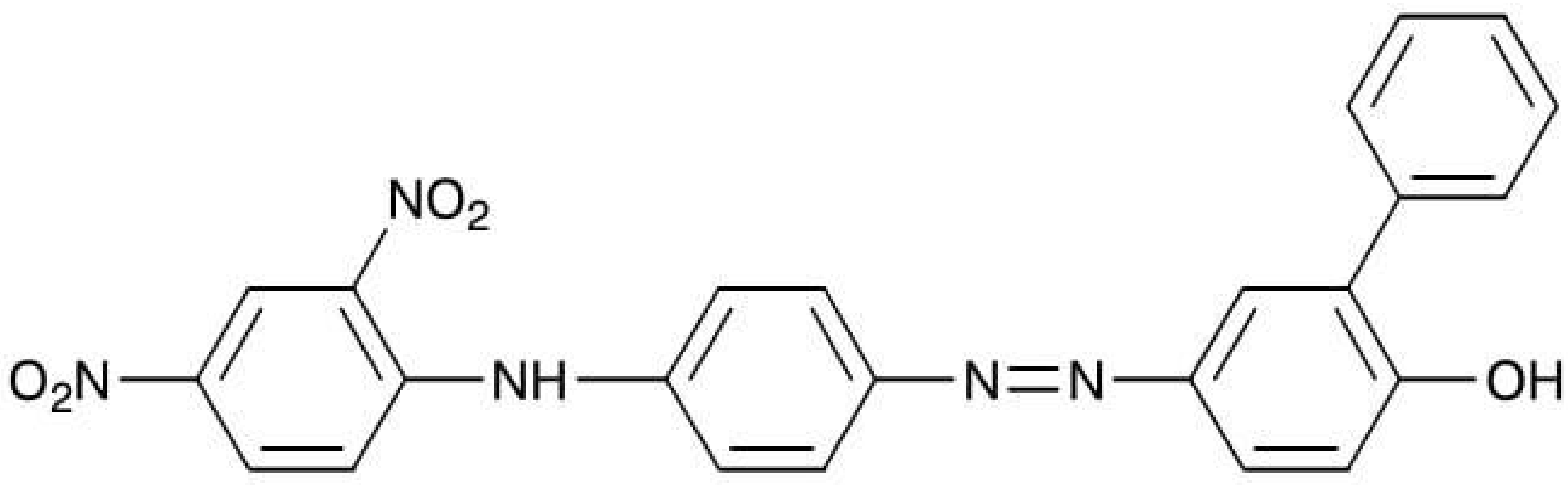
Of particular importance are disperse dyes based on *o*-nitrodiphenylamine. The light fastness of such compounds is better than that of their *p*-substituted isomers, owing to intramolecular hydrogen bonding. The *o*-nitro derivatives are more bathochromic than the *p*-nitro analogues but the latter possess greater tinctorial strength. Dyes such as CI Disperse Yellow 1 (6.235; X = OH) and CI Disperse Yellow 9 (6.235; X = NH_2) are examples of typical products used on cellulose acetate. Such dyes generally have lower substantivity for polyester, but this can be improved by minor structural changes. Thus CI Disperse Yellow 42 (6.236; X = C_6H_5) has higher substantivity for polyester than has the parent dye CI Disperse Yellow 33 (6.236; X = H) [21]. The inclusion of a photostabiliser grouping in the terminal phenyl ring of CI Disperse Yellow 42 (6.236; X = C_6H_5) leads to improved light fastness [88]. The incorporation of an azo group into the diphenylamine system improves sublimation fastness and colour strength; for example, CI Disperse Yellow 9 (6.235; X = NH_2) is the source of CI Disperse Yellow 70 (6.237).



6.235

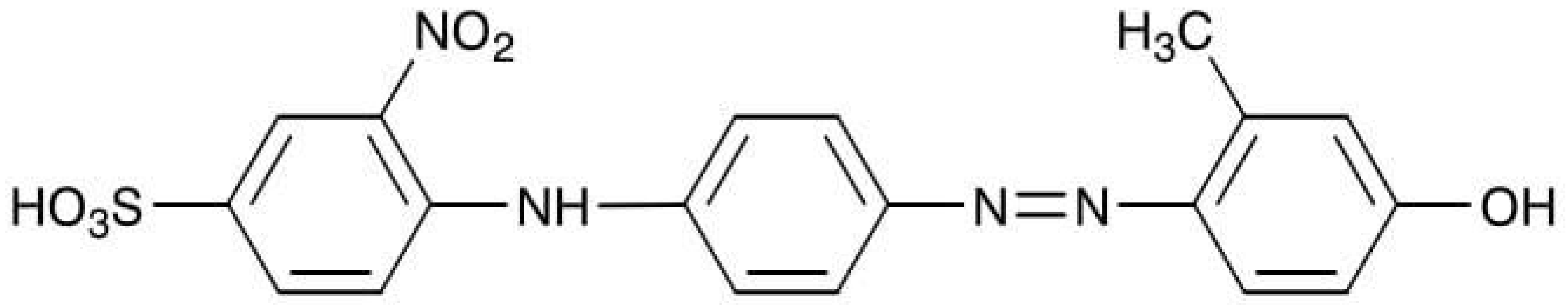


6.236



6.237

CI Disperse Yellow 70

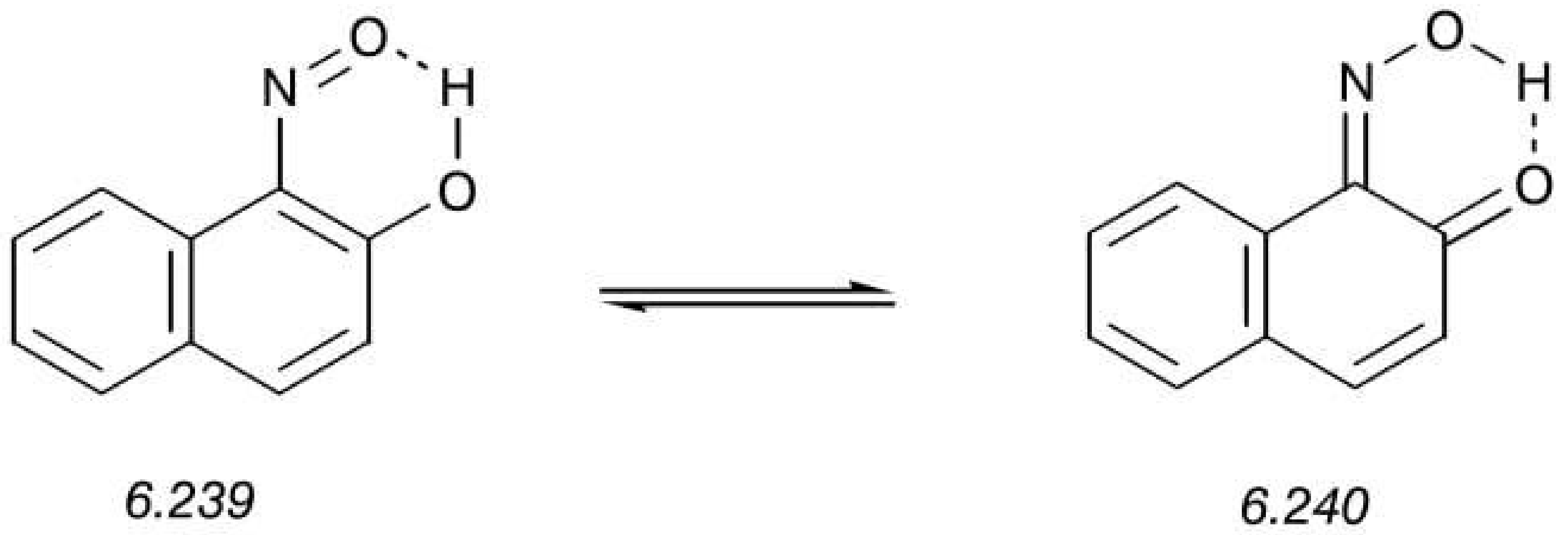


6.238

CI Acid Yellow 199

The introduction of sulphonic acid groups into dyes of this kind provides acid dyes suitable for nylon, such as CI Acid Yellow 199 (6.238).

The so-called nitroso dyes are metal complexes of 1-nitroso-2-naphthol. In the parent system a tautomeric equilibrium (Scheme 6.37) exists between hydroxynitroso (6.239) and quinoneoxime (6.240) forms. Only the green iron(II) complexes, which have good light fastness, have been exploited commercially. The unsubstituted iron(II) complex is CI Pigment Green 8. The corresponding 6-sulphonic acid complex, Naphthol Green B (CI Acid Green 1), was discovered in 1885 by Hoffmann.



6.239

6.240

Scheme 6.37

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