CHAPTER 3

Dye structure and application properties

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3.1 DYE CHARACTERISTICS AND CHEMICAL STRUCTURE

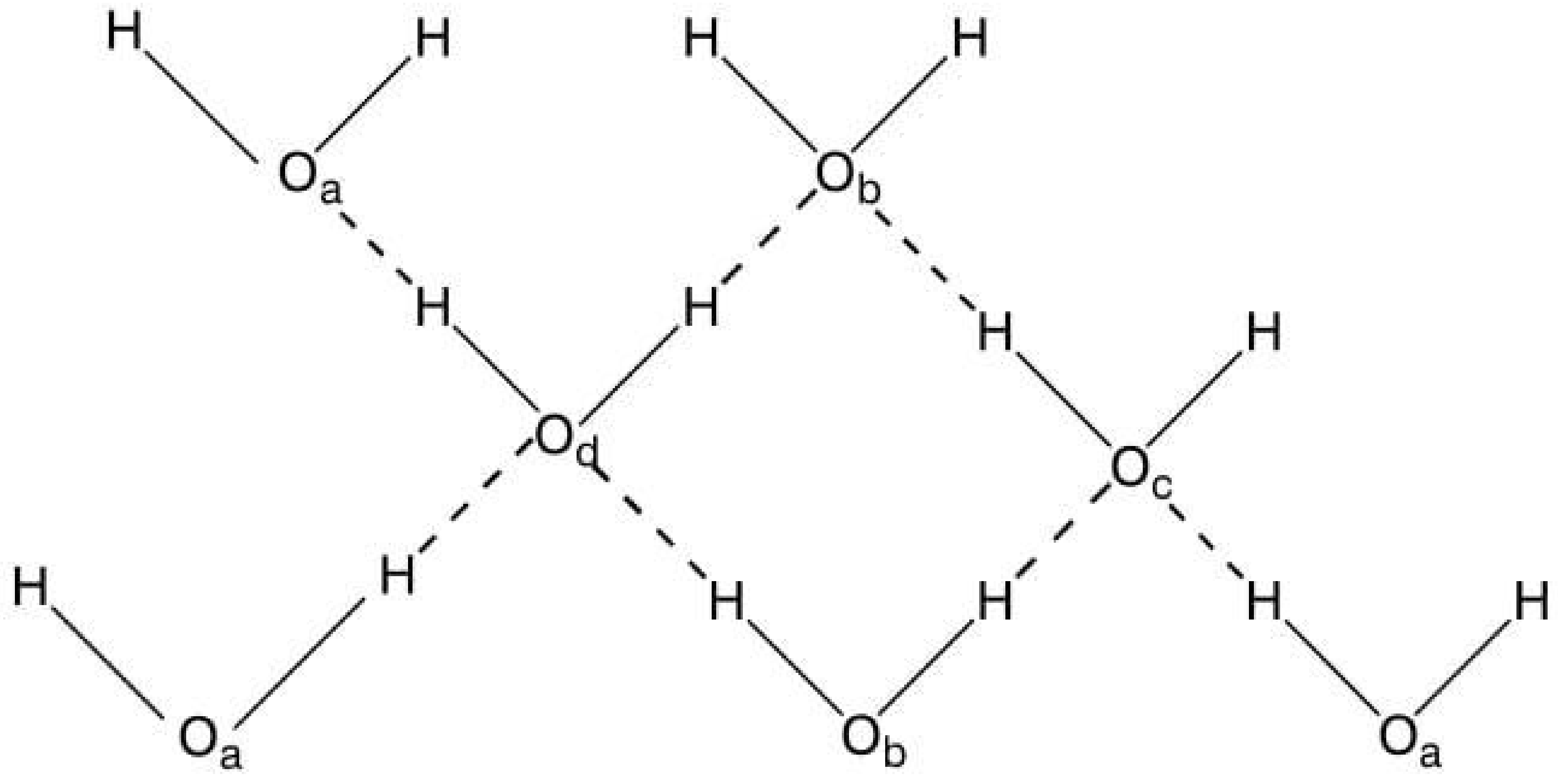
Virtually all commercial textile dyeing and printing processes take place by the application of a solution or a dispersion of the dyes to the textile material followed by some type of fixation process. The dye solution or dispersion is almost always in an aqueous medium. A major objective of the fixation step is normally to ensure that the coloured textile exhibits satisfactory fastness to subsequent treatment in aqueous wash liquors. In view of the overriding importance of water as a transfer medium in dyeing and printing it seems reasonable to begin with a discussion of the properties of dyes in solution and in dispersion.

3.1.1 The solubility of dyes in water

In a pure ice crystal each oxygen atom is surrounded by four hydrogen atoms located in a tetrahedral configuration. Two of them are covalently bonded to the oxygen atom, conveniently forming an angle of 120 degrees. Hydrogen atoms from two other molecules are thus positioned equidistantly on opposite sides of the plane of this H–O–H structure. In steam, on the other hand, each molecule is freely and rapidly in motion, frequently colliding with other molecules but not capable of forming any type of bond with them at such elevated temperatures. The association between water molecules in the liquid state represents an intermediate condition. Molecular motion is slower than in steam and water is much denser. The formation, motion, collision and re-formation of clusters of two or more molecules is a characteristic feature of the liquid state.

A hydrogen atom normally consists of a positively charged nucleus (a proton) and a much smaller orbiting electron. The proton is thus virtually unscreened, permitting the two electronegative oxygen atoms in neighbouring water molecules to approach one another more closely than they could in the absence of the intervening hydrogen atom. This reduction in the force of repulsion between the two electronegative atoms is known as a hydrogen bond [1].

This idealised two-dimensional representation of a seven-molecule cluster (3.1) illustrates that some molecules are more firmly held than others. In reality, of course, each cluster is three-dimensional in shape and the individual molecules adopt a more random orientation than indicated here. As the temperature of the liquid increases and the cluster becomes more mobile, the loose network of hydrogen bonds (indicated by dashed lines) holding the molecules together is weakened. In a collision the cluster is more likely to lose one or more fringe members (a) depending on a single hydrogen bond than those held in place by two (b), three (c) or four (d) links. The average cluster size thus decreases as the temperature rises. A higher proportion of free molecules is formed as the boiling point is approached, heralding the incipient evaporation as steam.



3.1

The dissolution of an inert nonpolar solute molecule in water has been described in terms of the 'iceberg' concept, by which transient local clusters of water molecules are stabilised by cohesive association around the nonpolar molecule. The enveloping cluster surrounding the latter contains a higher proportion of multilinked members (b–d) than are present in the freely mobile clusters typical of pure water. Hydrophobic interaction between nonpolar solute molecules arises directly from this 'iceberg' effect. Pairs of such stabilised cohesive clusters tend to merge and redistribute, forming a larger and more stable sheath around two or more solute molecules. These molecules then behave as if a binding force exists between them, described as hydrophobic interaction [2]. An analogous process within a clustering aqueous sheath favours preferential interaction between the hydrophobic segments of dissolved solute ions in concentrated solutions of dyes or surfactants. A dissolved ionic solute always has a more stable cluster of water molecules around the hydrophobic portion of the ion. This asymmetrical distribution favours coalescence of solute molecules in concentrated solution to form a dye aggregate or surfactant micelle. Once formed, however, such an associated moiety is further stabilised by the inner sheath of charged ionic groupings oriented outwards towards the aqueous clusters.

Many anionic dyes (section 1.6) depend on their sulphonic acid groups for their solubility in water. Dye sulphonic acids have pK values within the range of pH 1–2 and are fully ionised under dyeing conditions as either the free acid or the sodium salt. The mutual electrostatic repulsion between dye sulphonate anions ensures their uniform separation and distribution in dilute aqueous solution. At higher concentrations, however, this repulsion is counterbalanced by mutually attractive forces of various kinds operating at shorter range [3]:

(1) hydrogen bonding
(2) van der Waals forces
(3) hydrophobic or nonpolar bonding.

The most important types of hydrogen bond are the hydroxy-ether, hydroxy-amine and imino-amine linkages (Figure 3.1). Thus one of the most significant forces of attraction between dye molecules containing hydroxy groups is identical with that governing mutual interaction in clusters of water molecules. Many water-soluble dyes (section 1.6) contain primary, secondary or tertiary amine groupings, all of which are capable of participating via hydrogen bonding in dye–dye association or dye–water solubilisation mechanisms. The van der Waals forces include dipole–dipole interaction between atoms of unlike polarity in neighbouring molecules and less specific *p*-bonding or dispersion forces between unsaturated groupings and aryl nuclei. Hydrophobic bonding between nonpolar segments of dye ions is particularly significant for acid dyes of high wet fastness solubilised by a single sulphonate group (section 1.6.7) and for basic dyes, which normally contain only one quaternary nitrogen atom (section 1.6.6).

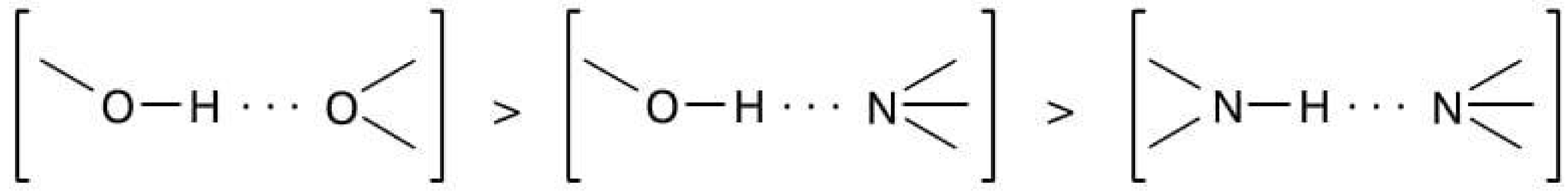


Figure 3.1 Types of hydrogen bond in order of relative strength (from the left: hydroxy-ether, hydroxy-amine and imino-amine)

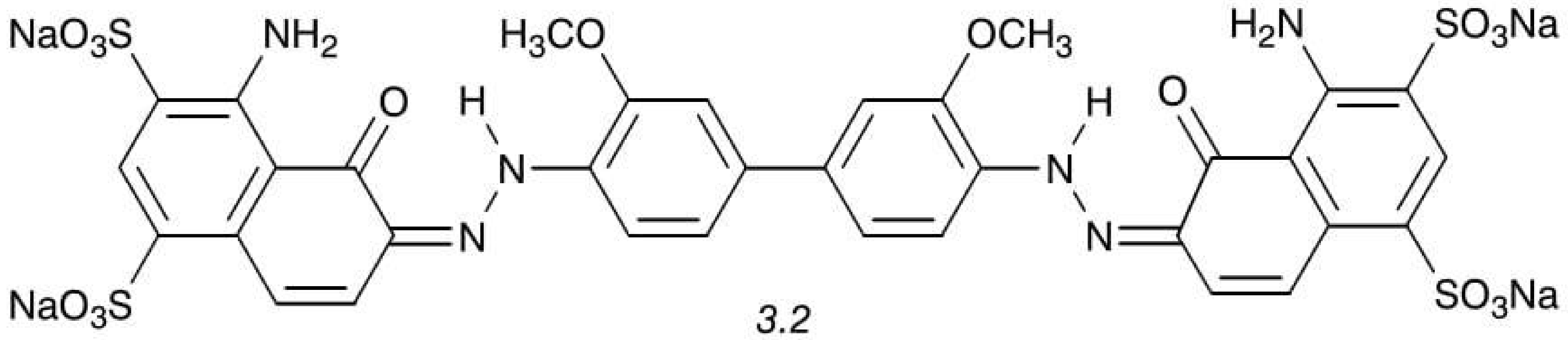
The bonding forces involved in hydrophobic interaction can be quite specific to the structure of the dye ions involved. A series of isomeric derivatives of 2-phenylazophenol-4-sulphonic acid, each containing a trifluoromethyl substituent, was synthesised recently. The aqueous solubility of these monosulphonated acid dyes was found to be dependent on the location of this specific grouping in the dye molecule [4].

The solubility of an ionic dye in water normally increases with temperature, since the enhanced mobility favours electrostatic repulsion between ions rather than closer approach to form aggregates by means of the short-range attractive forces. Addition of a simple inorganic electrolyte, on the other hand, normally lowers the solubility limit at a given temperature. Such additions enhance the ionic character of the aqueous phase and help to stabilise the structure of dye aggregates by forming an electrical double layer within the sheath of clustered water molecules around them.

In contrast, the addition of a water-miscible nonionic solute such as urea or an alkanol to an aqueous solution containing aggregates of dye ions has a disaggregating action at a given temperature and electrolyte concentration. Urea, for example, has a strong tendency to inhibit clustering because of the competitive influence of urea–water hydrogen bonds. Consequently the stabilising ‘iceberg’ cluster surrounding each dye aggregate tends to disintegrate. Dye–urea hydrogen bonds or dipole–dipole attractive forces further disrupt the hydrophobic interaction between pairs of dye ions.

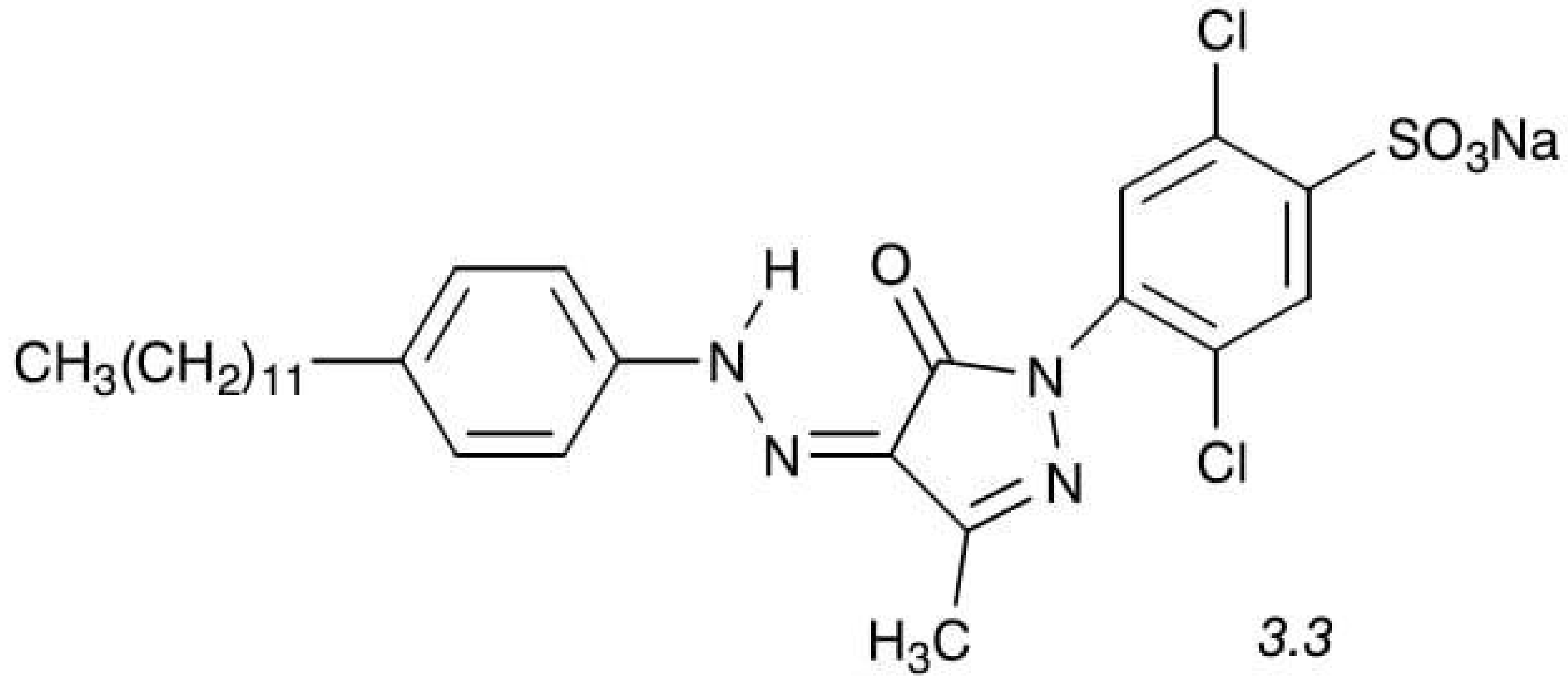
Nonionic solutes with a directional polar/nonpolar structural arrangement, such as long-chain alkyl polyoxyethylene adducts, destabilise the loose structure of dye aggregates by a somewhat different mechanism. These additives readily form micelles in which the hydrophobic alkyl groups form the core and the oxyethylene chains are hydrogen-bonded within an extensive sheath of water molecules clustered around them. The formation of these large clusters denudes the less firmly held envelopes surrounding the dye aggregates, which become thinner and less stable. The lower dielectric constant of the surfactant solution enhances the electrostatic forces of repulsion between monomeric dye ions. Hydrogen bonding or dipolar interaction between the oxyethylene chains and individual dye ions further weakens the hydrophobic attraction between pairs of dye ions.

All aqueous solutions of anionic or cationic dyes have lower surface tension than pure water. Solutions of the free sulphonic acids give lower values than solutions of the sodium salts of anionic dyes. The decrease in surface tension depends more on the degree of sulphonation of the dye than on its relative molecular mass, although alkyl substituents may exert a further lowering effect [5]. Thus a relatively hydrophilic tetrasulphonated disazo dye such as CI Direct Blue 1 (3.2) has comparatively little influence on surface tension, whereas a monosulphonated milling acid dye such as CI Acid Yellow 72 (3.3) can exhibit a mild detergency effect [6].



3.2

CI Direct Blue 1



3.3

CI Acid Yellow 72

Measurements of the surface tension of aqueous solutions of various sulphonated and unsulphonated phenylazonaphthol dyes showed that the degree of surface activity (that is, the lowering of surface tension) tended to increase progressively with the degree of alkyl substitution in the series of dyes [7]. The surface-active behaviour of such alkylated dye ions ensures that they become more concentrated at the interface between the dyebath and the fibre surface, just as they do at the air–water interface of the dye solution. Foaming of dyebaths can be a serious practical problem with relatively hydrophobic dye structures solubilised by means of a single ionised group.

Increasing concern about respiratory sensitisation by dust from dyes in powder form, especially reactive dyes, has generated extensive development work on concentrated solutions and low-dusting cold-dissolving granular forms of water-soluble dyes (section 1.7.1). Difficulties arise in attempting to market dissolved brands at concentrations close to the solubility limit, although these can be overcome by adding miscible solvents or solubilising agents. Hydrolysis during storage is another problem with reactive dyes of inherently high reactivity. Fluorotriazine dyes show maximum stability when buffered to pH 7–8, whereas sulphatoethylsulphone dye solutions require pH 4–5 to minimise premature hydrolysis. Dyes marketed as granules should show neither dusting nor hydrolytic instability, but the rate of dissolution may depend on average granule size and dust can be formed from granules during transportation [8].

Dyes marketed as aqueous solutions or dispersions should exhibit the following characteristics [8,9]:

(1) Constant flow properties under normal ambient conditions
(2) Complete and rapid homogenisation on stirring after a freeze/thaw cycle

(3) Ease of dispensing in automatic metering equipment
(4) Complete miscibility with water and other liquid products used in dyebath or print-paste formulations
(5) No drying-out or deposition of dye or other component on the inside of the container
(6) No crystallisation of solid particles from solution
(7) No agglomeration or sedimentation of particles in dispersion
(8) No microbial growth on storage.

Disperse liquid brands of sulphur, vat or disperse dyes, including mixed formulations of disperse and vat dyes in matching hues for the dyeing of polyester/cellulosic blends, have been commercially available for many years. The proportion of reactive dyes marketed as aqueous solutions is expected to increase markedly [10] because of:
(1) Optimum safety for operatives
(2) Versatility of formulation to suit specific customer needs
(3) Rapid cleaning of dispensing equipment when changing the target shade
(4) Ease of dispensing via automatic metering devices
(5) Unrestricted application with special suitability for continuous dyeing and printing.

3.1.2 Aggregation of dyes in aqueous solution

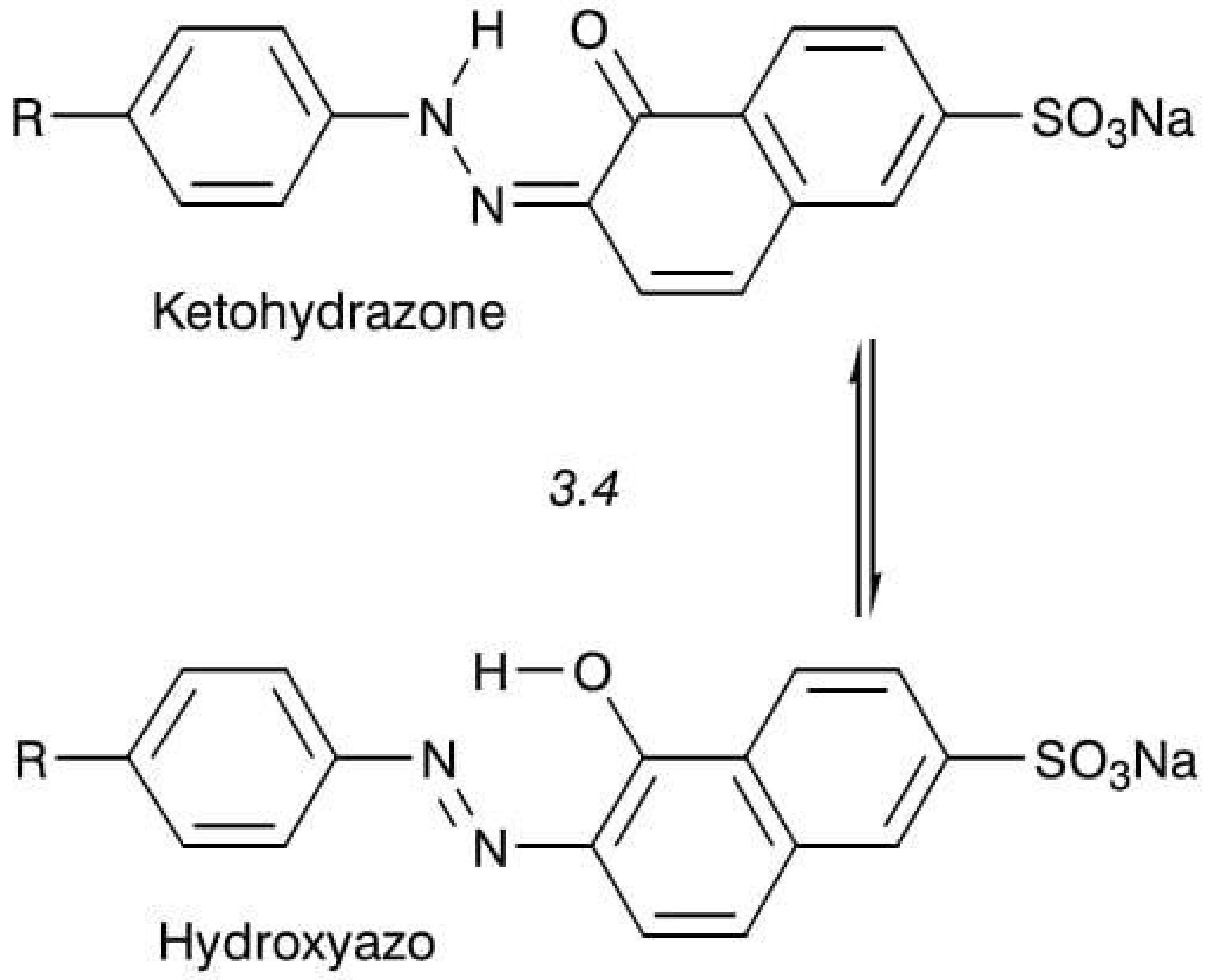
Dyes often exist in aqueous solution as aggregates of several ions or molecules rather than individual moieties. It is unlikely that all component anions in a multisulphonated dye aggregate are in the same state of ionisation. Unlike surfactants, dye molecules in general do not possess structures with directional polar and nonpolar segments. Thus they do not associate as micelles of ordered structure with a well-defined hydrophobic core and a charged hydrophilic sheath. Dye aggregates should be envisaged as relatively amorphous in composition with zones of more or less polar character distributed within them, although there will be a tendency for individual molecules to become oriented with their ionised groupings towards the aqueous phase.

Within a structural series, aggregation is usually greater for dyes with a higher ratio of relative molecular mass (M_r) to ionic group content, that is, a higher value for the equivalent mass per sulphonic acid group in the case of sulphonated anionic dyes. Multisulphonated dye anions may be stabilised as dimers in which the two components adopt a coplanar arrangement with the sulpho groups located if possible at opposite ends of the dimer. More hydrophobic structures of higher equivalent mass, especially monosulphonates, can readily form aggregates of larger sizes. Dimers are formed first, growing further by accretion of more dye anions to form lamellar micelles, in which the dye moieties are stacked like cards in a pack [3]. Planar chromogens, especially the sulphonated phthalocyanine dyes, are particularly prone to such stacking.

Equilibrium constants for dimerisation (K_D) have been determined [3] for several classical dyes from different chemical classes (Table 3.1). Although differing considerably in M_r and structural type, these values are all within the same order of magnitude ($\log K_D = 3$–4 at 25 °C). It seems likely that with most dyes the forces governing aggregation are mainly of the van der Waals type, including dipole–dipole and dispersion forces. Unlike hydrogen bonds, these are able to operate through successive layers of stacked molecules. An attempt to obtain equilibrium constants for the dimerisation of four *p*-substituted phenylazo-1-naphthol-6-

Table 3.1 Equilibrium constants for dimerisation of dyes [3]

CI Generic name	Chemical class	M_r	Log K_D
Basic Orange 14	Acridine	265	4.02
Basic Red 6	Azine	422	3.78
Basic Blue 9	Thiazine	284	3.77
Basic Red 1	Xanthene	443	3.36
Mordant Violet 5	Monoazo	344	3.29
Acid Orange 7	Monoazo	328	3.12



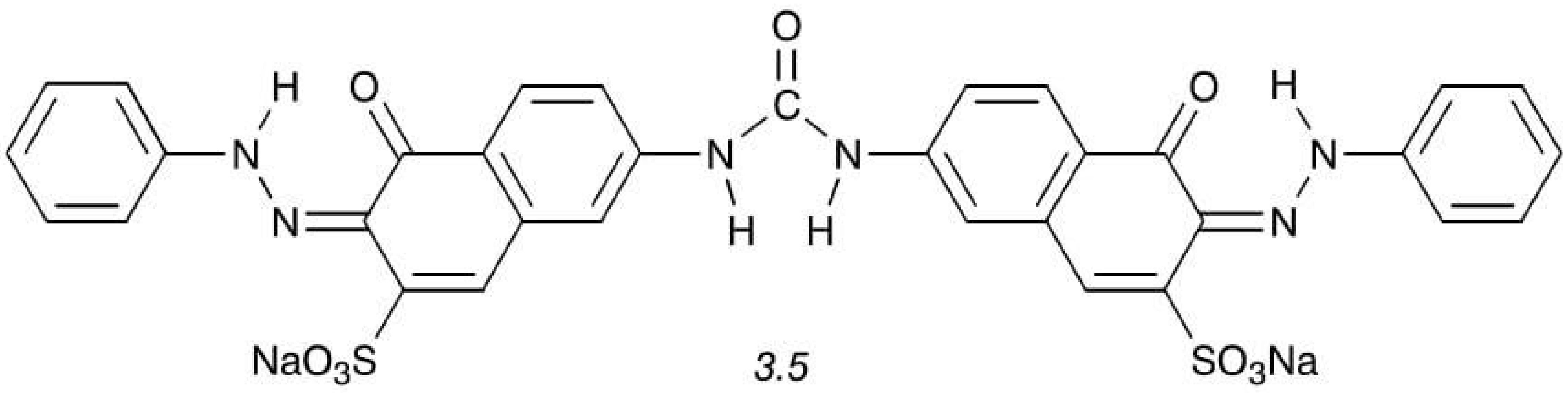
Scheme 3.1

sulphonic acids (3.4) failed because of the superimposed effects of acid-base, tautomeric (Scheme 3.1) and oligomeric equilibria [11].

Thermodynamic aspects of the aggregation behaviour of three monoazo acid dyes in aqueous solution have been studied by a potentiometric method. An anion-selective membrane electrode permitted the direct derivation of dye monomer concentration in the system. Graphs of e.m.f. against dye concentration were non-linear owing to dye–dye association at the higher concentrations. These deviations enable the dye monomer concentration to be determined at any total dye concentration. Adoption of an appropriate stepwise association model provided a framework for computing the successive multimerisation constants and the respective concentrations of dimers and higher multimers [12]. Another novel procedure to determine the aggregation constants of water-soluble dyes and the extinction coefficients of the monomeric dye ions has been proposed recently [13].

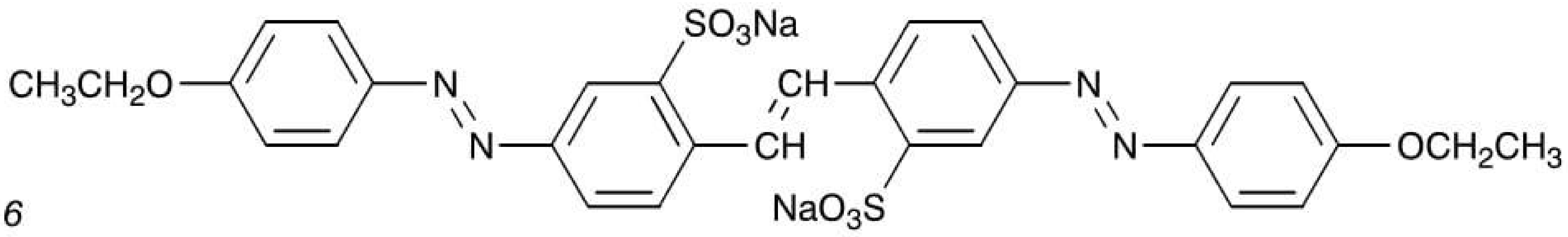
Most measurements of aggregation number (the average number of ions or molecules per aggregate) have been carried out on solutions of direct dyes, because these aggregate more readily than most of the other classes of water-soluble dyes. Regrettably, aggregation numbers determined for the same direct dyes under the same conditions using different methods of measurement are seldom consistent. Most results indicate, however, that such solutions contain a mixture of aggregates of various sizes in dynamic equilibrium, somewhat analogous to the mixed clusters of molecules in pure water. When individual anions or dimers are absorbed by a cellulosic fibre during dyeing, larger aggregates break down to maintain a similar overall distribution of aggregate sizes. The extent of aggregation of a direct dye increases with increasing concentration of dye or added electrolyte, but decreases as the dyebath temperature is increased. Although many direct dyes are highly aggregated at ambient temperature, the degree of aggregation is often negligible under exhaust dyeing conditions at the boil even in the presence of electrolyte.

Although quantitative agreement between the aggregation numbers obtained using different techniques of measurement is poor, meaningful conclusions can be drawn from them regarding the relative tendency of different direct dye structures to aggregate. Under given conditions of temperature and electrolyte concentration, CI Direct Orange 26 (3.5) is much more highly aggregated than CI Direct Yellow 12 (3.6). Both are disulphonated disazo dyes, but presumably the two *o*-ketohydrazone groupings and especially the ureido residue in the orange dye provide much greater scope for intermolecular hydrogen bonding than the etherified phenolic groups in the yellow dye. The sulpho groups on the central stilbene chromogen of Yellow 12 tend to inhibit aggregation. In a detailed study CI Direct Red 81 (3.7; X = H), an important dye that has good migration properties but low affinity and poor fastness to washing, was compared with its *p*-benzoylamino analogue (3.7; X = NHCOPh). The higher affinity and wet fastness but inferior migration of the latter was found to be associated with an increased tendency to aggregate, presumably due to the greater scope for hydrogen bonding via the amide groupings.



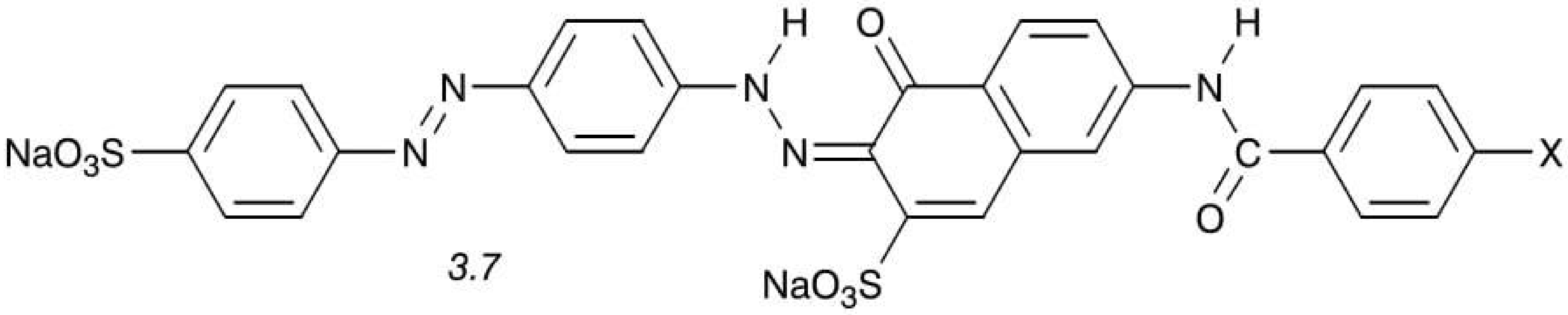
3.5

CI Direct Orange 26



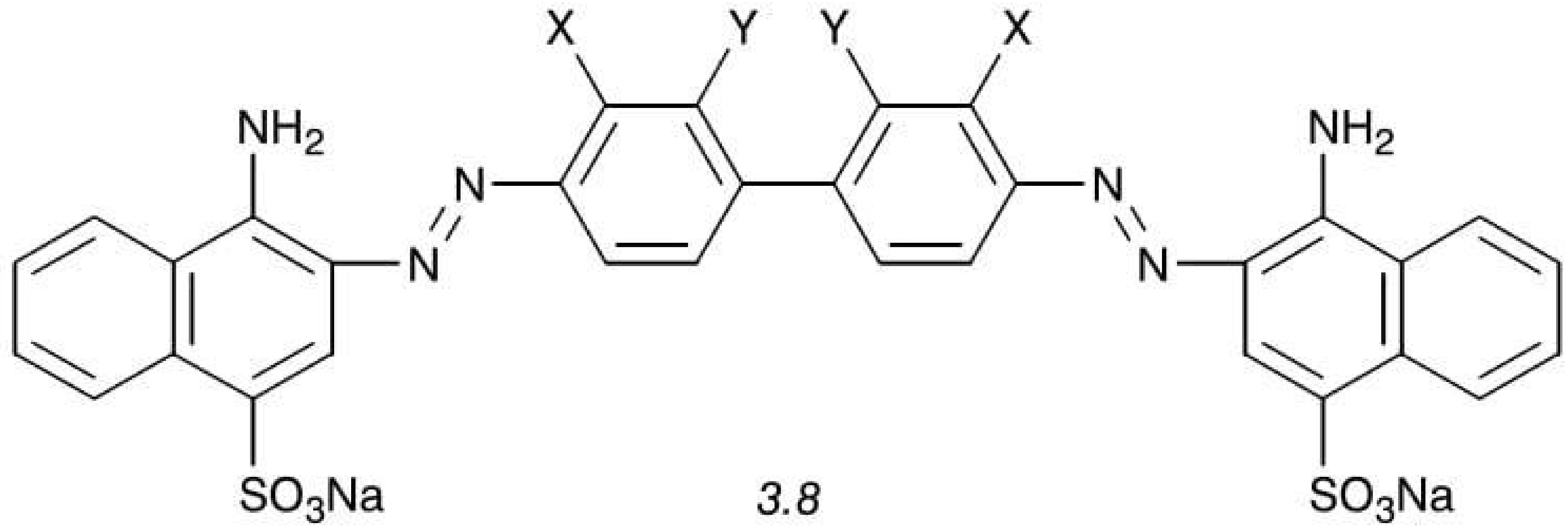
3.6

CI Direct Yellow 12



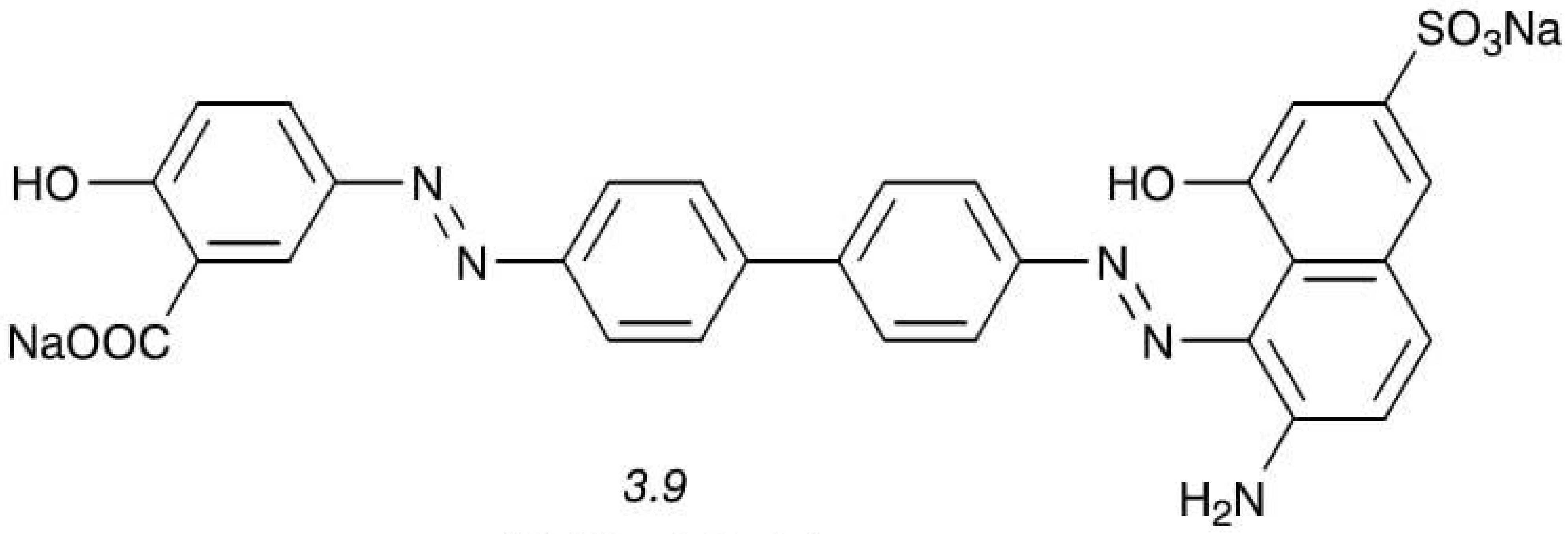
3.7

Three disazo analogues derived from naphthionic acid as coupling component are all highly aggregated in solution: CI Direct Red 28 (3.8; X = Y = H), CI Direct Red 2 (3.8; X = CH_3, Y = H) and its *m*-tolidine isomer (3.8; X = H, Y = CH_3). The two tolidine derivatives aggregate more readily than does Red 28, although the nonplanar *m*-tolidine dye is not so highly aggregated as the coplanar *o*-tolidine structure in Red 2, which is more sensitive to flocculation by salt and several times more substantive to cellulose than its *m*-tolidine isomer. The tetrasulphonated dye CI Direct Blue 1 (3.2) is considerably less aggregated than these disulphonated naphthionic acid derivatives.



3.8

In a recent investigation the aggregation of CI Direct Red 1 (3.9) in aqueous solution was studied as a function of pH, temperature and dye concentration [14]. At a given temperature and concentration, the high aggregation number at pH 4 confirmed that only the sulphonate group in the γ acid residue at one end of this disazo structure was ionised. At higher pH values the carboxyl group in the salicylic acid residue at the other end of the molecule became ionised, increasing the solubility and lowering the aggregation number. The degree of aggregation decreased with increasing temperature as expected, but this effect of pH on ionisation and disaggregation was evident at temperatures between 25 °C and 60 °C.



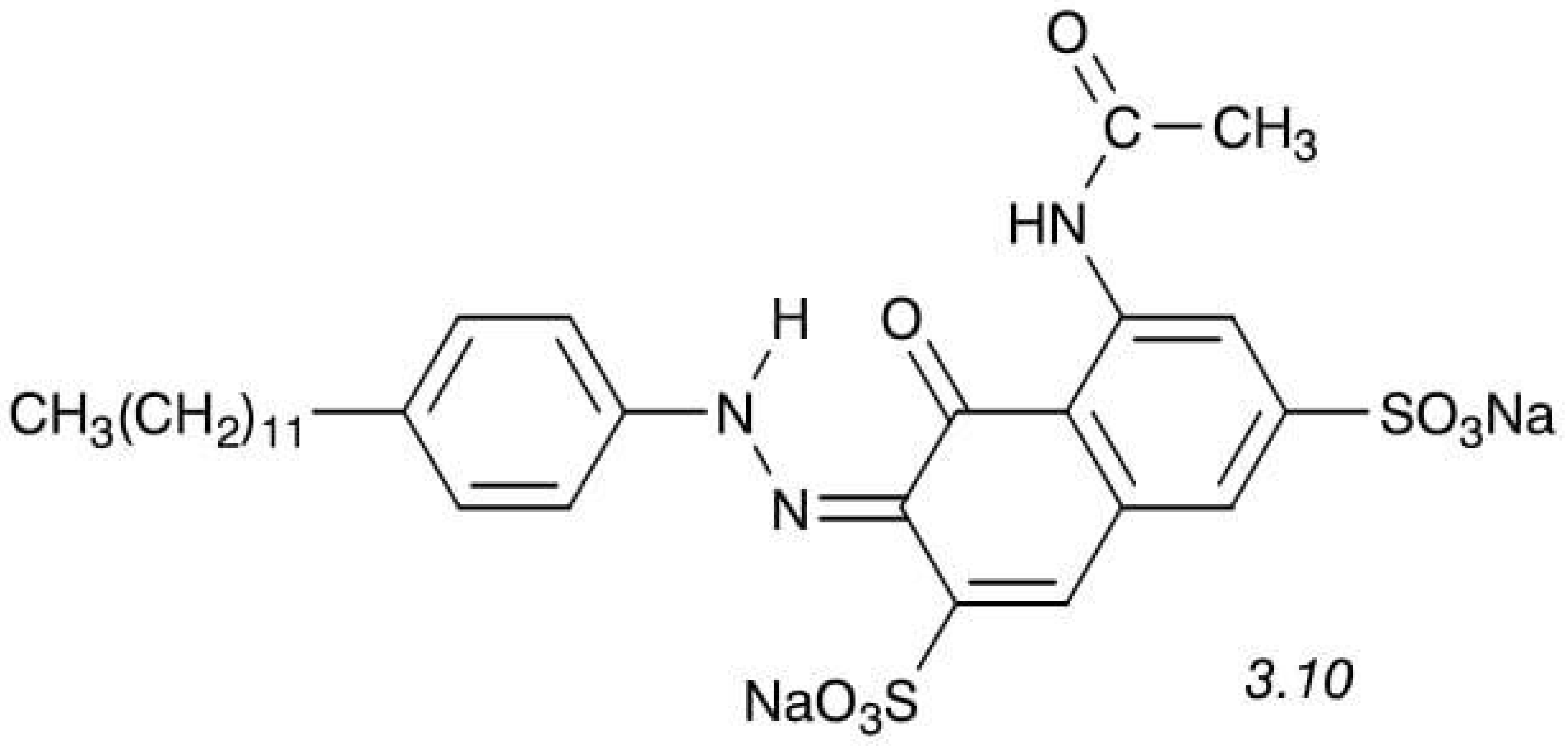
3.9

CI Direct Red 1

Although acid dyes in general are considerably less aggregated than direct dyes under similar conditions, they show broadly similar trends between structure and aggregation behaviour. Thus an increase in the size of the coplanar aryl nuclei in monoazo acid dyes (for example, replacement of a phenyl by a naphthyl residue) increases the tendency to aggregate. A recent spectrophotometric study of aggregation equilibria in a series of alkyl-substituted azo acid dyes revealed that only dimerisation took place with alkyl chain-lengths up to hexyl. Formation of multimers, however, was observed with octyl or decyl groups. As a general rule the dimerisation equilibrium constant increased progressively with the length of the n-alkyl chain, but the presence of a *sec*-butyl substituent produced an anomalous decrease in equilibrium constant attributable to steric interference with hydrophobic interaction between dye anions [15].

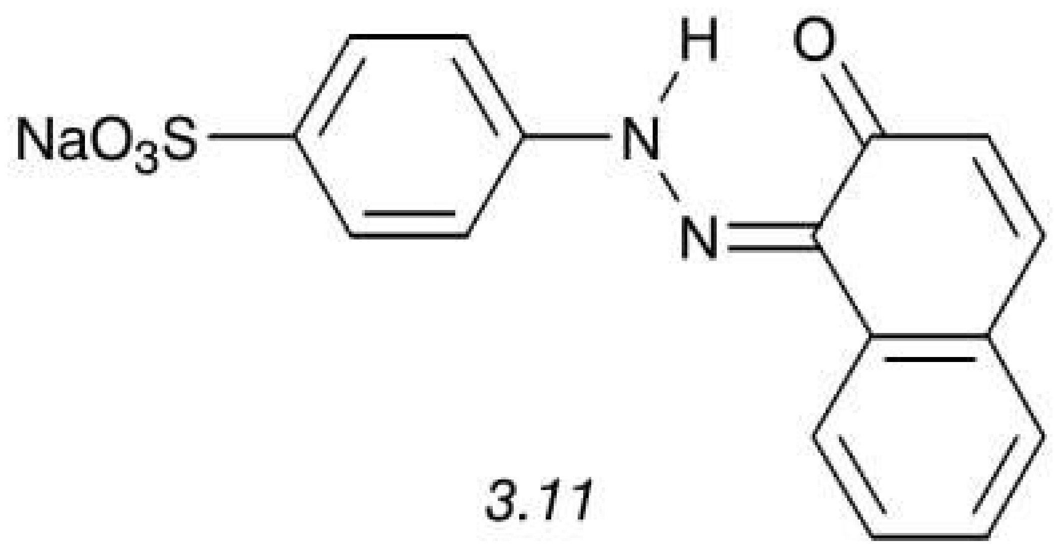
The aggregation and tautomeric equilibria of CI Acid Red 138 (3.10) have been examined recently. In spite of the length of the dodecyl substituent in the diazo component only monomers and dimers were present [16], presumably because the H acid residue contributes two sulpho groups to solubilise the molecule. Both monomer and dimer species were predominantly in the hydrazone form, as expected, and hydrophobic interaction between the terminal dodecyl chains played an important part in formation of the dimer.

An increase in the degree of sulphonation of a typical azo acid dye structure minimises aggregation, especially if the sulpho groups are widely separated from one another and from the azo group. Light-scattering studies demonstrated freedom from aggregation with the important monoazo monosulphonate CI Acid Orange 7 (3.11) and many simple monoazo di- or trisulphonates, but typical disulphonated milling dyes such as CI Acid Red 111 (3.12) showed salt-sensitive aggregation. With the disazopyrazolone disulphonate CI Acid Orange 63 (3.13) the aggregation appeared to be virtually independent of the concentrations of dye and electrolyte at low temperatures. Aggregation greatly decreased above about 60 °C, in good agreement with the anomalous dyeing properties of this dye. It may form stable micelles analogous to those of surfactants and this effect is apparently highly sensitive to temperature in the 50–70 °C region.



3.10

CI Acid Red 138



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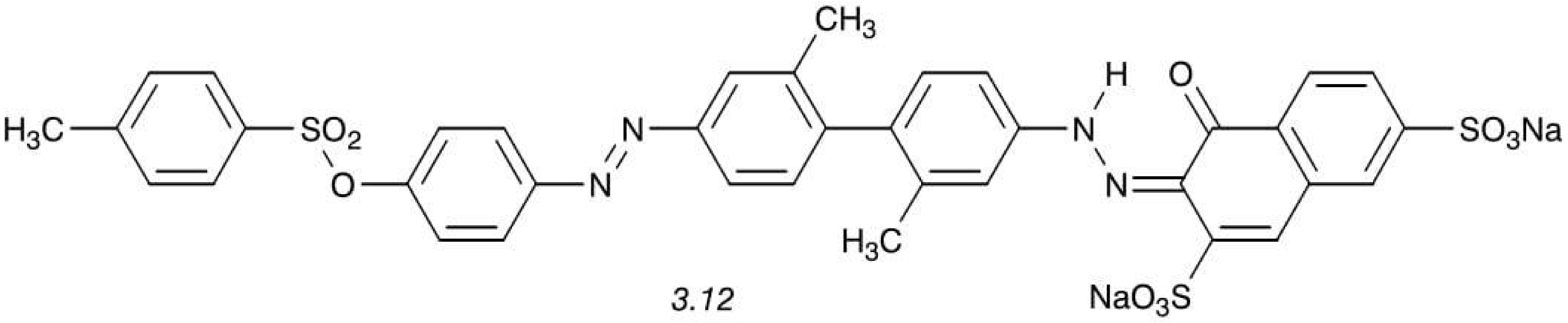
CI Acid Orange 7



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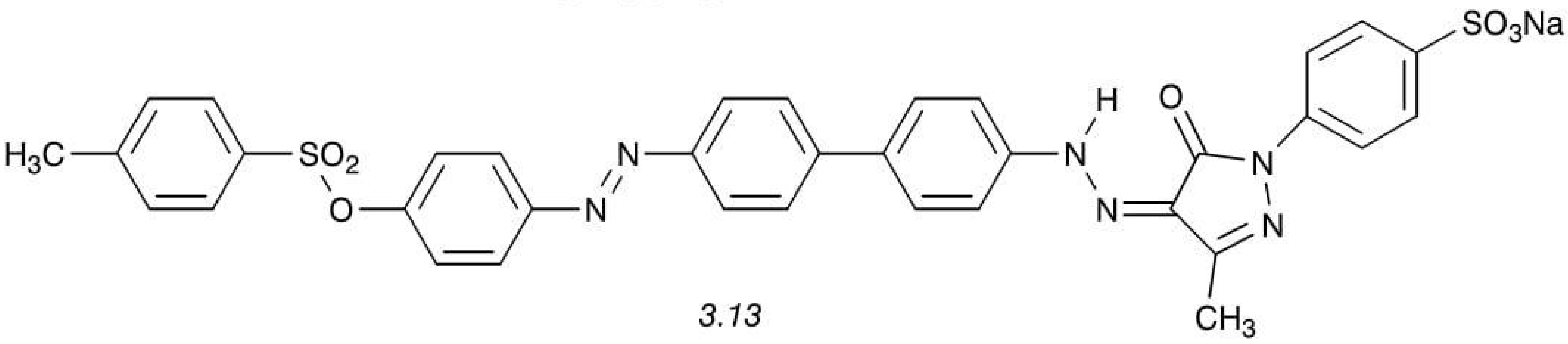
CI Acid Red 111

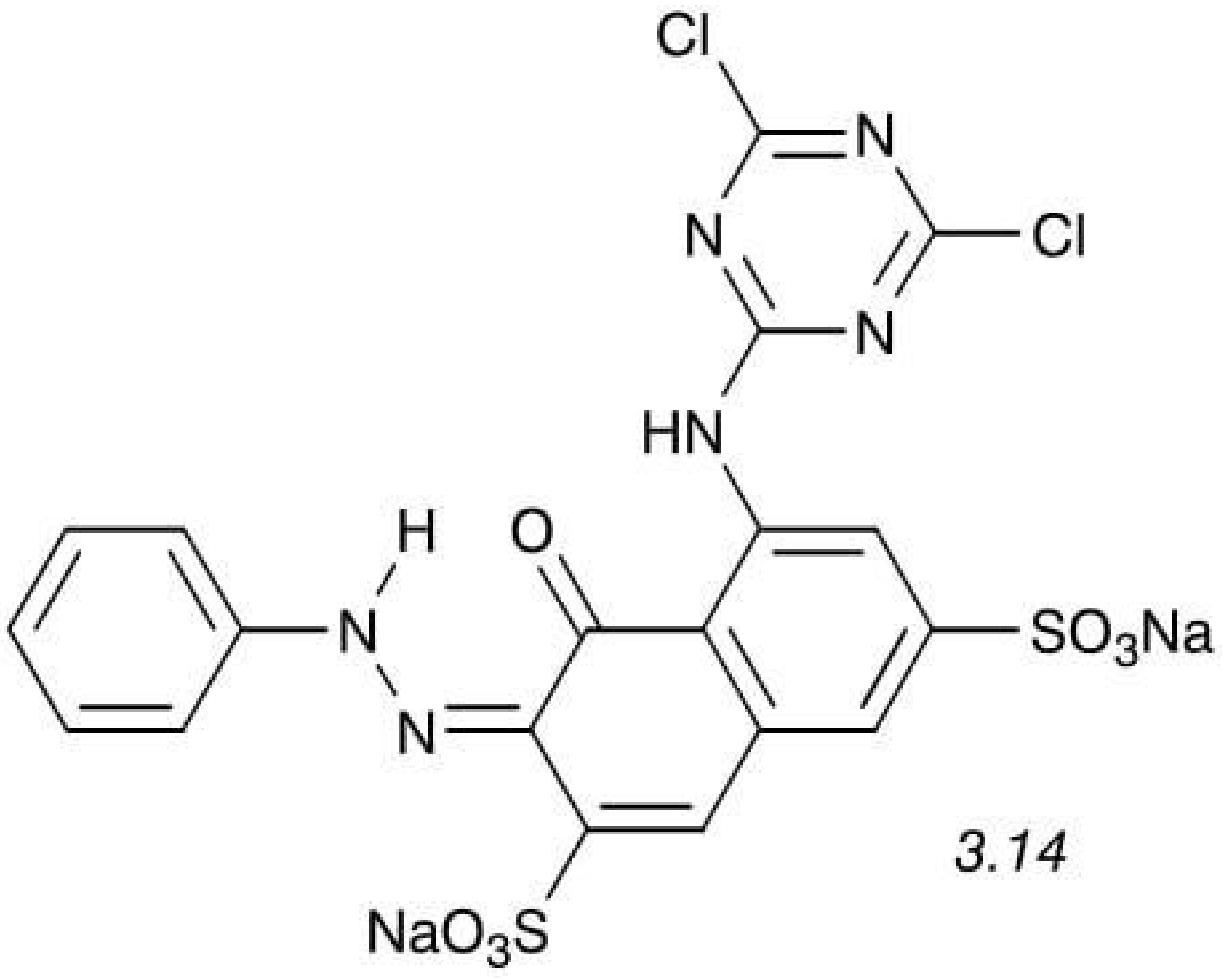


3.13

CI Acid Orange 63

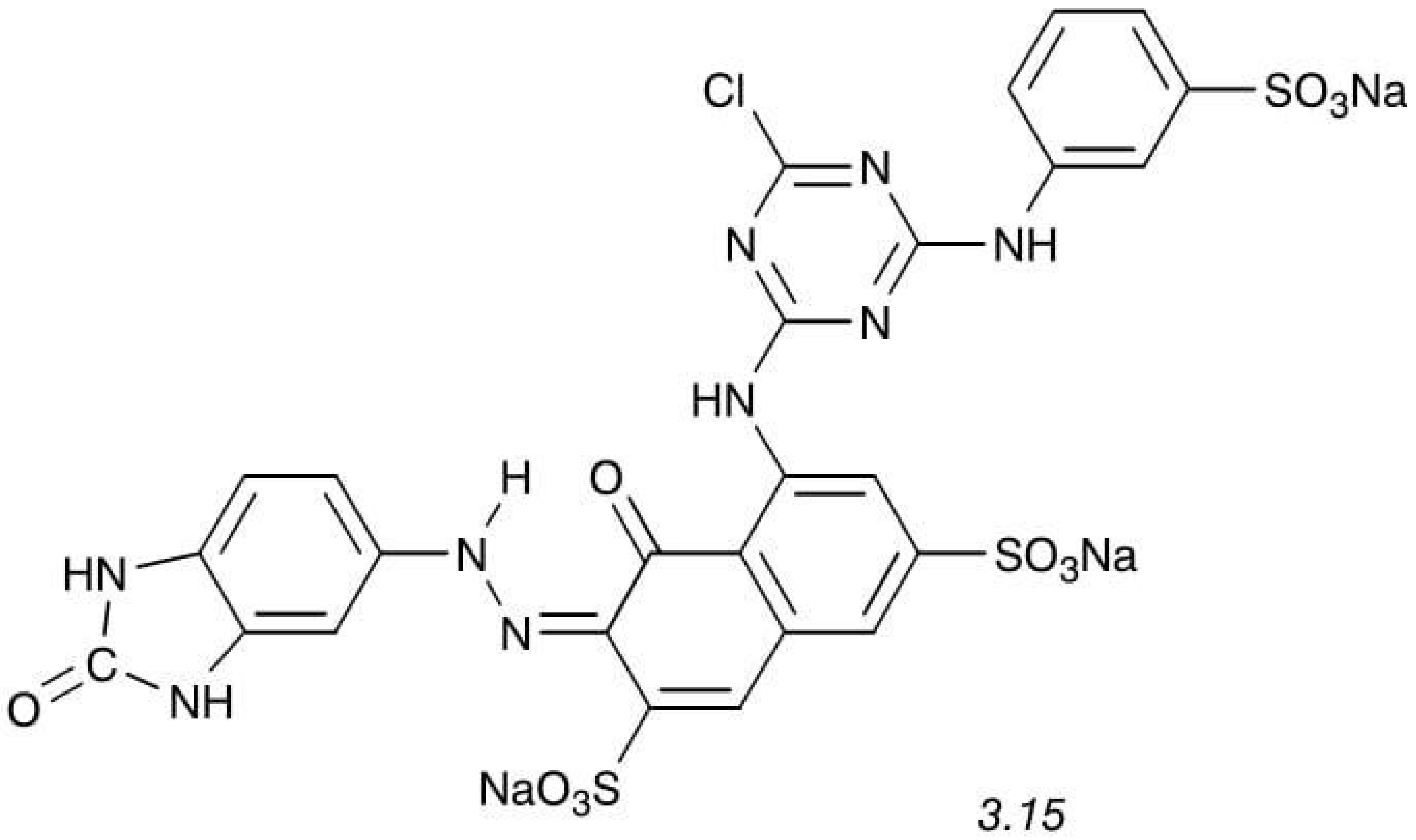
The aggregation behaviour and tautomerism of three *o*,*o*′-dihydroxy and one *o*-hydroxy-*o*′-methoxy monoazo dyes have been studied by UV-visible spectroscopy [17]. Evidence of monomer-dimer equilibria was obtained for all four of these mordant dye structures. Intermolecular hydrogen bonding between the hydroxy groups and hydrophobic interaction between aryl nuclei contribute to the dimerisation effect.

The influence of metal ions on the aggregation of CI Reactive Red 2 (3.14) in aqueous solution at various pH values has been examined in detail recently [18]. Sodium ions have a profound effect on these disulphonated dye anions, so that the enhancement of substantivity during the dyeing process is accompanied by aggregation attributable to hydrophobic interaction between the phenyl and s-triazine ring systems. Aggregation is much greater, however, in the presence of divalent calcium or magnesium ions, which can form intermolecular electrostatic linkages between sulpho groups in different dye anions. This accounts for the adverse influence of hard water on the level dyeing properties of reactive dyes.


3.14

CI Reactive Red 2

The introduction of a cyclic amide system into a monoazo dye molecule considerably enhances its substantivity for cellulose. This was demonstrated recently by evaluating a series of aminochlorotriazine structures derived from 5-aminobenzimidazolone as diazo component, typically the bluish red H acid derivative (3.15). The urea residue in the imidazolone ring is a powerful hydrogen bonding moiety. These dyes exhibited excessive aggregation when dyed at a temperature lower than 95 °C in the presence of a conventional salt concentration but showed markedly higher exhaustion at a relatively lower ionic strength, where the degree of aggregation was similar to analogous dye structures derived from aniline as diazo component. These results indicate that benzimidazolone-type reactive dyes are of potential interest as 'low-salt' products [19].

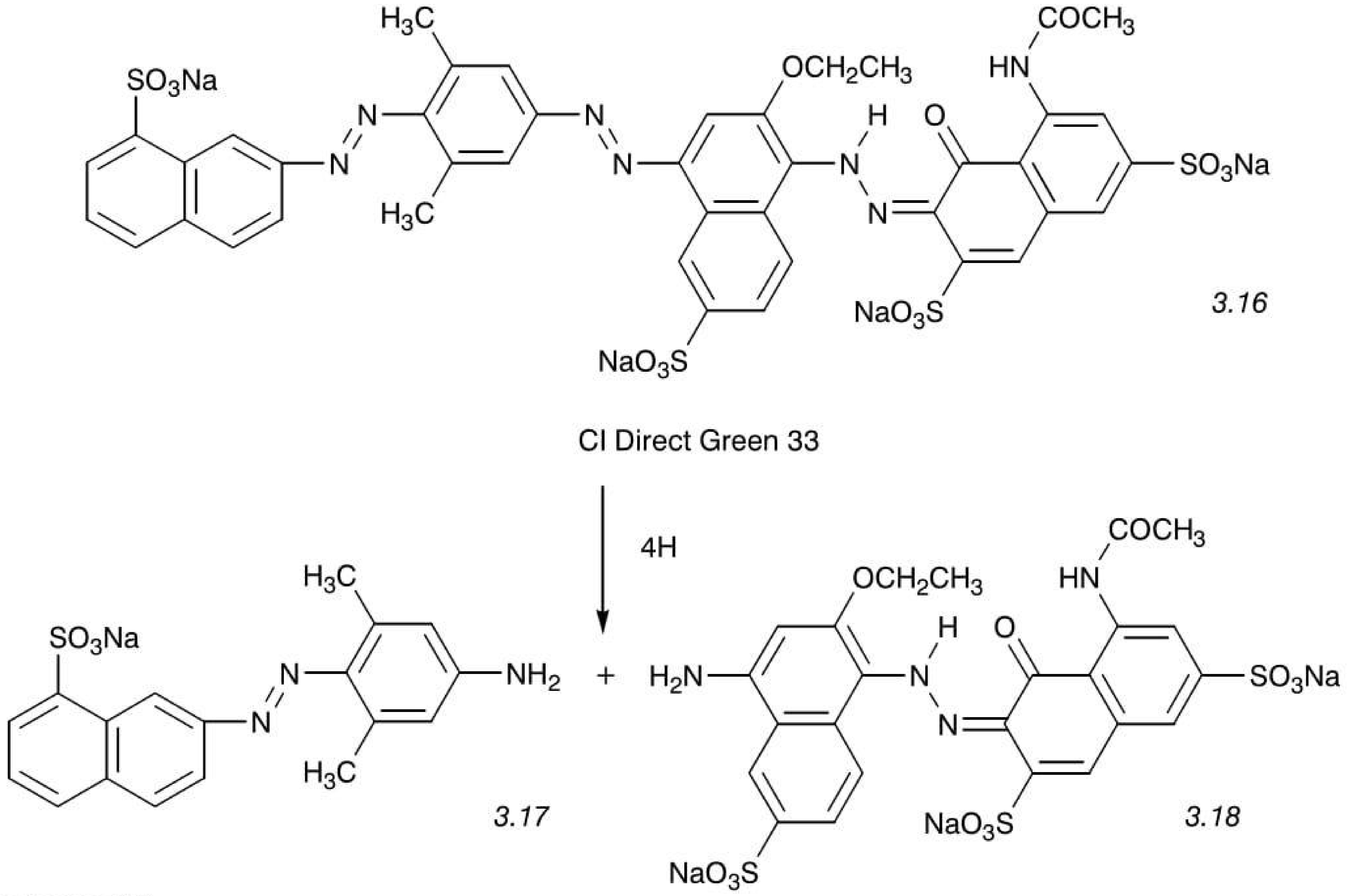

3.15

Owing to experimental difficulties, knowledge of aggregation effects in alkaline dithionite solutions of leuco vat dyes is sporadic [20,21]. Investigations based on absorption spectra have shown that, depending on concentration and temperature, planar polycyclic molecules such as the violanthrone derivatives CI Vat Blues 19, 20 and 22 and the perylene tetracarboxydiimide derivatives CI Vat Reds 23 and 32 are mainly present as monomers or dimers in leuco vat solutions. Violanthrones that do not have a coplanar structure because of the presence of alkoxy groups in the 16,17-positions, such as CI Vat Blue 16 and the widely used Greens 1, 2 and 4, are always present as single molecules under vat dyeing conditions.

3.1.3 Decomposition of dyes under reducing conditions

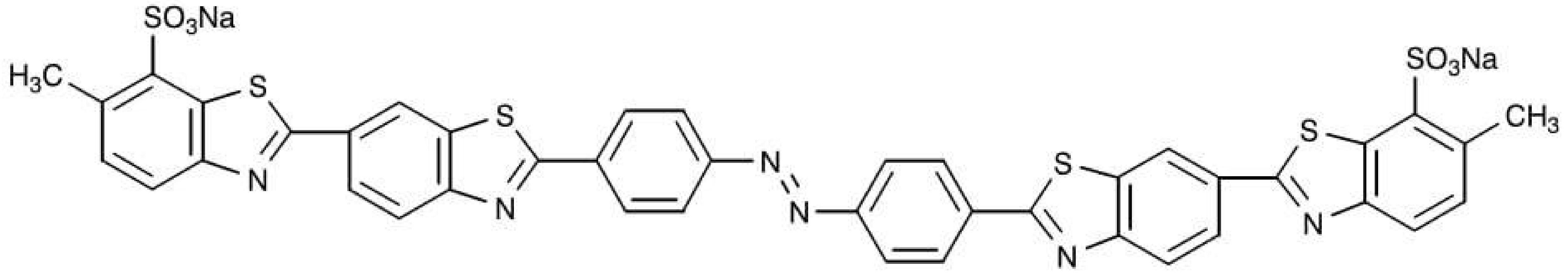
The primary objective of an exhaust dyeing process is to transfer as much as possible of the dye in the system from the dyebath into the fibre, provided this can be achieved with the dye uniformly distributed throughout the dyed material at the end of the process. If dyeing is unduly prolonged, either to improve the levelness or to attain an exact colour match to standard, decomposition of a minor proportion of the dye present may occur. The rate of decomposition is normally much more rapid in the dyebath phase than on the fibre and the onset of degradation can sometimes be observed as a change in colour of the exhaust liquor. This effect usually occurs as a hypsochromic shift, such as reddening of a blue or yellowing of a red solution.

Many direct dyes show instability of this nature if applied at a temperature above the boil, as in the dyeing of polyester/cellulosic blends, for example. A frequent cause of the problem is reduction of azo linkages. This may be accelerated in the presence of viscose, which has a reducing action under alkaline dyeing conditions. Direct dyes with exposed azo groups free from *o*-substituents, like the two azo links in CI Direct Yellow 12 (3.6), are particularly prone to reductive decomposition. However, some dyes with *o*-aminoazo groups, such as CI Direct Red 2 (3.8; X = CH_3, Y = H) or Red 28 (3.8; X = Y = H), are also reduction-sensitive. In the relatively unstable trisazo structure of CI Direct Green 33 (3.16), the most vulnerable of the three azo groups is the unprotected central linkage, so that the likely initial products of reduction (Scheme 3.2) are two monoazo dyes (3.17 and 3.18), resulting in a hypsochromic reddening and dulling of the blue-green solution.



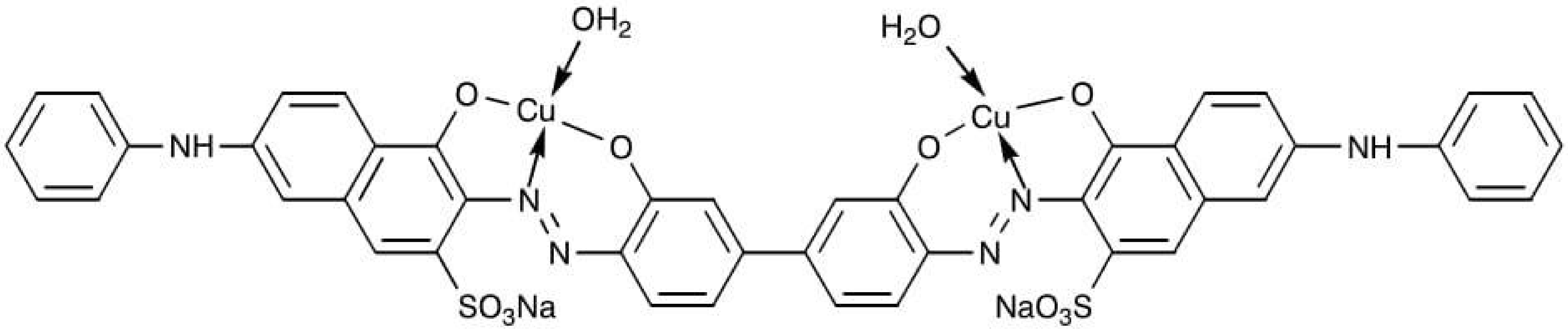
Scheme 3.2

Dyes containing azo links protected by *o,o′*-substituents, especially *o*-sulphonate groups, are generally relatively resistant to reductive breakdown during dyeing. Azothiazole dyes such as CI Direct Yellow 29 (3.19) and especially copper-complex structures such as CI Direct Blue 98, in which both azo groups are fully protected as the metal complex (3.20), show excellent stability in high-temperature dyeing conditions [22]. Buffering with ammonium sulphate confers a stabilising influence when dyes of inferior stability have to be used on viscose. Mild oxidants such as sodium *m*-nitrobenzenesulphonate are occasionally useful and more powerful inorganic oxidants, such as potassium chlorate or dichromate, can be most effective if used with care. Excessive use of these additives, however, can result in oxidative decomposition of azo dyes.



3.19

CI Direct Yellow 29



3.20

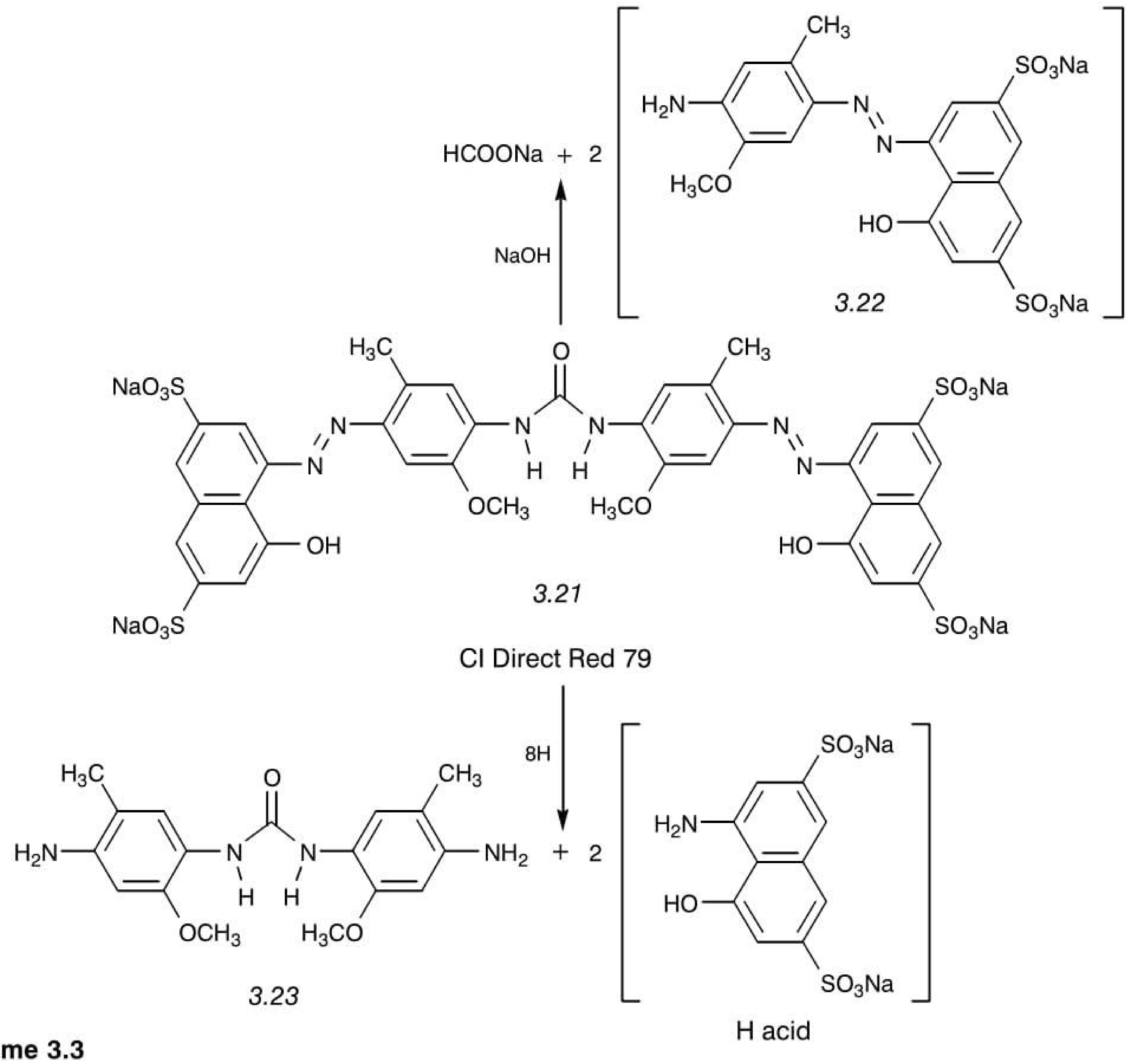
CI Direct Blue 98

Direct dyes of the disazo diarylurea type, such as CI Direct Orange 26 (3.5) and CI Direct Red 79 (3.21), are particularly prone to decomposition in high-temperature dyeing because molecular breakdown can occur by hydrolysis as well as by the reductive mechanism under alkaline conditions. Thus the ureido linkage in this red dye may be broken by hydrolysis to give two monoazo dye fragments (3.22), or the azo groups can be reduced to yield a diaminodiphenylurea (3.23) and two molecules of H acid (Scheme 3.3).

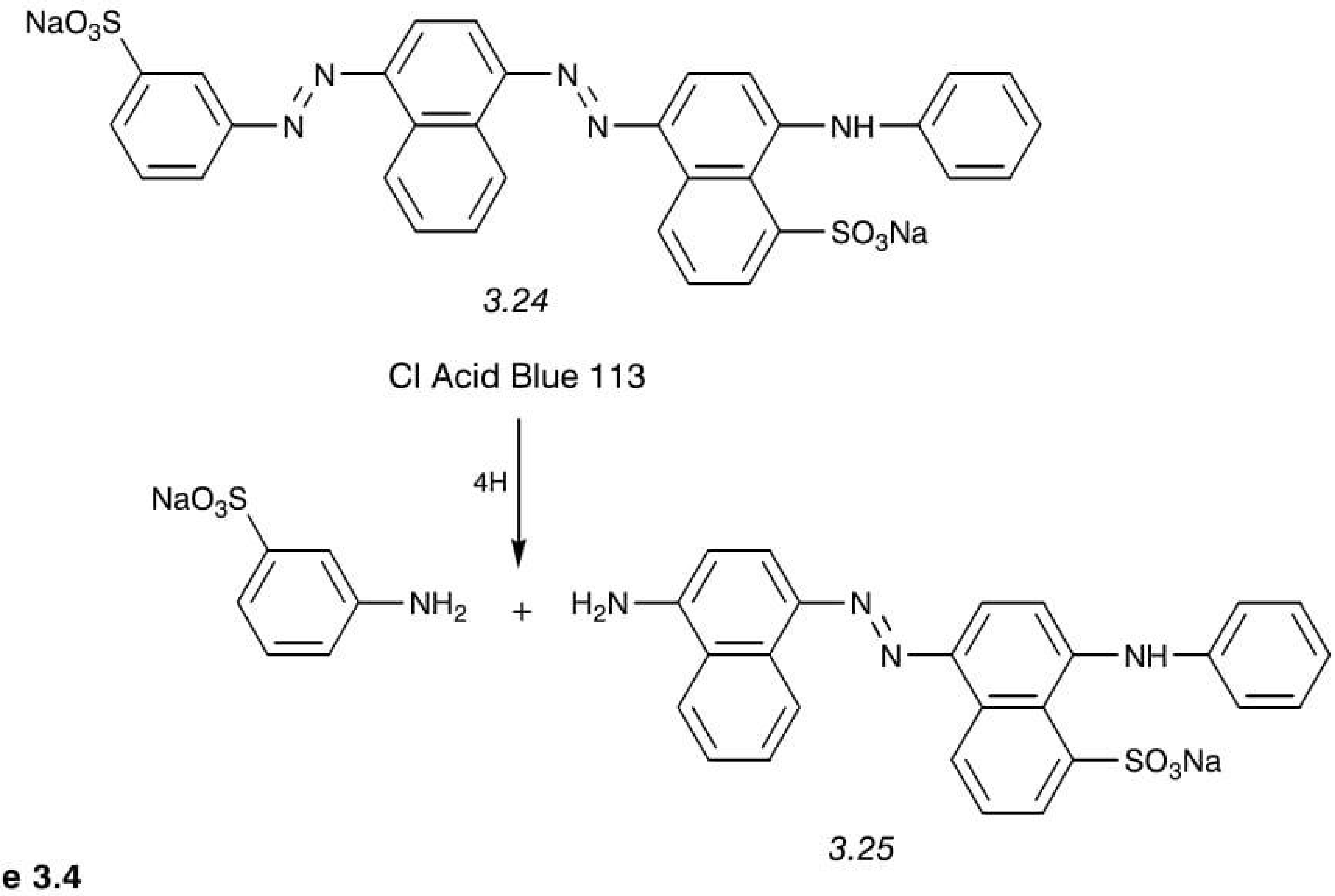
The azo linkage in some acid dyes is sensitive to the mild reducing action of the cystine and cysteine residues in wool under hot alkaline conditions. CI Acid Blue 113 (3.24) is a commodity dye showing good all-round wet fastness on wool and nylon, but it tends to turn brown during dyeing if exposed to alkaline reducing conditions at high temperatures. The degradation involves reduction to metanilic acid and a brown monoazo dye (3.25), the rate increasing rapidly above pH 7 (Scheme 3.4).

Hydrolysis of ester groups can also occur in certain wool dyes. For example, CI Acid Red 1 (3.26) loses its acetyl group (Scheme 3.5) on prolonged dyeing in an acid dyebath, the hue becoming bluer and duller and the dyeing much less fast to light.

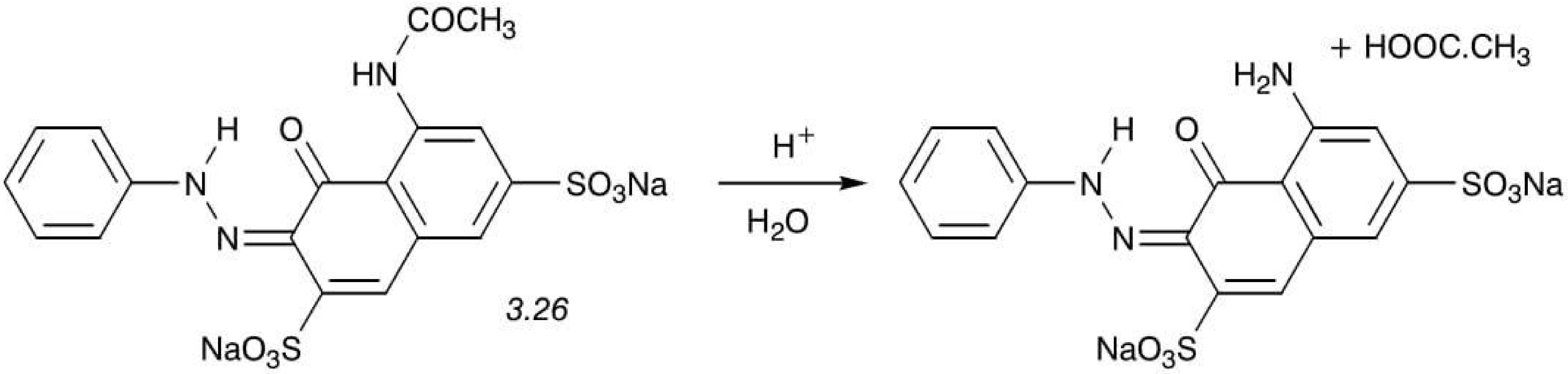
An interesting study of the relative rates of reduction of *N,N*-bis(2-chloroethyl)-aminoazobenzene and various monosubstituted derivatives (3.27) was initiated because of the ability of such dyes to inhibit the growth of animal tumours [23], even though some



Scheme 3.3



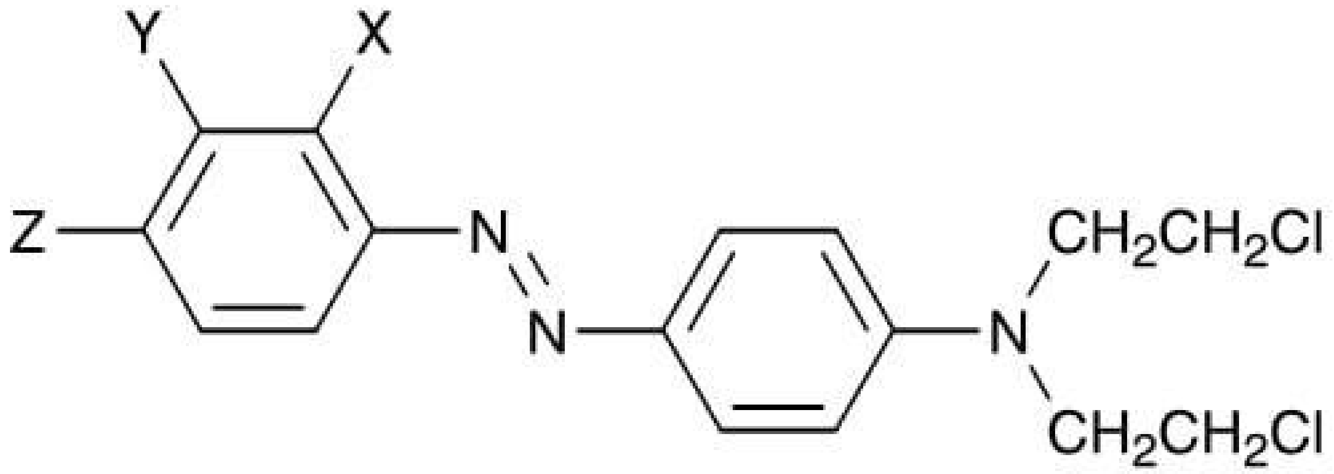
Scheme 3.4



CI Acid Red 1

Scheme 3.5

dialkylamino analogues such as 4-(dimethylamino)azobenzene have long been known to cause liver cancer in rats. A selection from the results is presented in Table 3.2, expressed in terms of the relative rate constant 100 k/k_0 where k and k_0 are the respective rate constants for the substituted and unsubstituted compounds. Electron-donating substituents (methyl, methoxy) in the 3- and 4-positions were found to retard reduction, whereas electron-withdrawing groups (bromo, chloro, acetyl, carboxy, sulpho) in these positions enhanced the rate. Steric effects tended to predominate, however, when relatively bulky substituents (phenyl, bromo, iodo) were present in the 2-position.

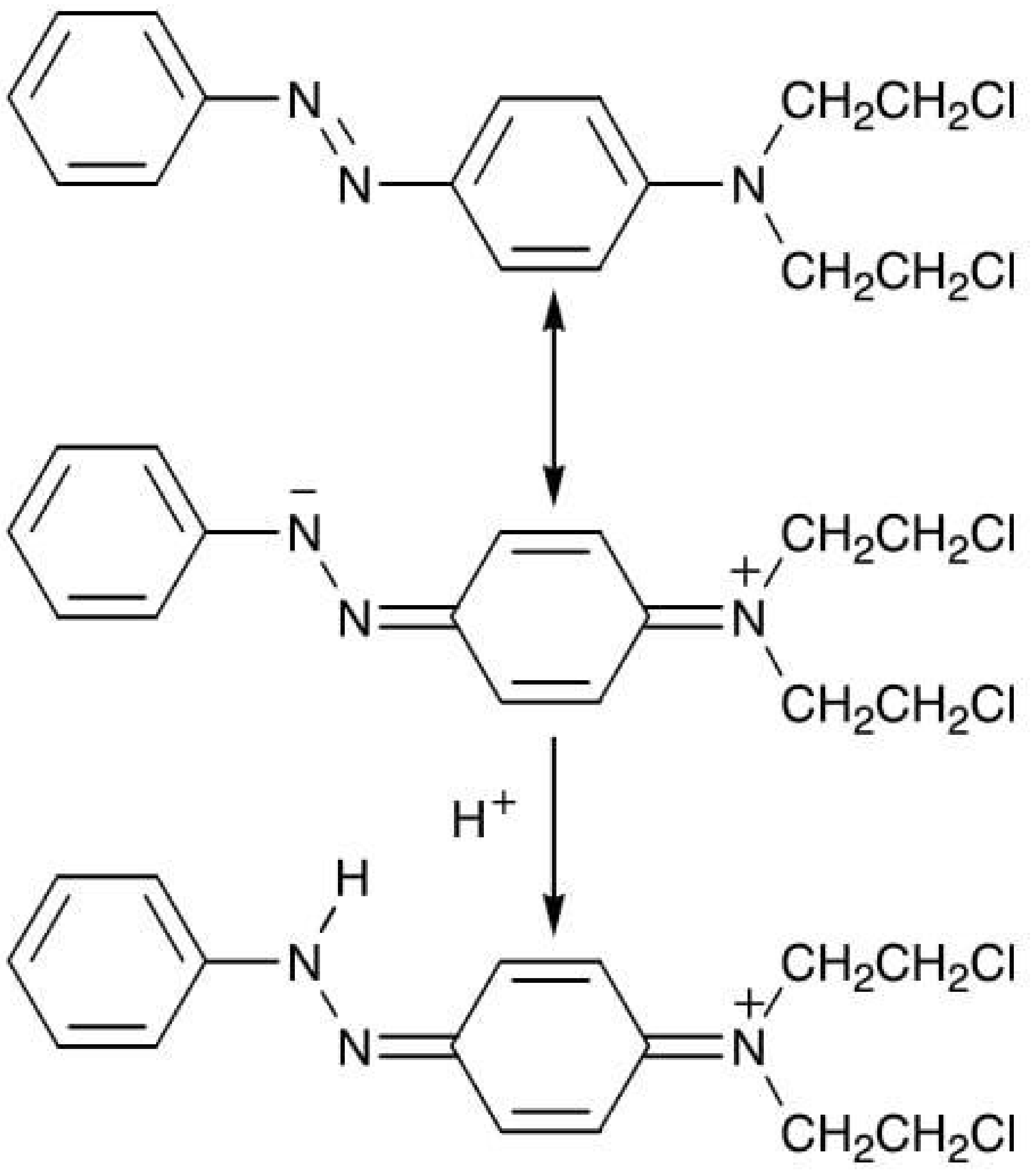


3.27

Table 3.2 Rates of reduction of monosubstituted monoazo dyes by tin(II) chloride [23]

Substituent in structure 3.27	Relative rate constant
X = nitro	very high
X = carboxy	very high
X = sulpho	2470
Z = acetyl	2100
Z = carboxy	1180
Z = sulpho	374
Z = bromo	254
Z = chloro	206
X = chloro	113
Z = phenyl	101
None	100
Y = methyl	94
X = bromo	80
X = phenyl	68
X = methyl	62
X = iodo	39
Z = methyl	36
Z = methoxy	20

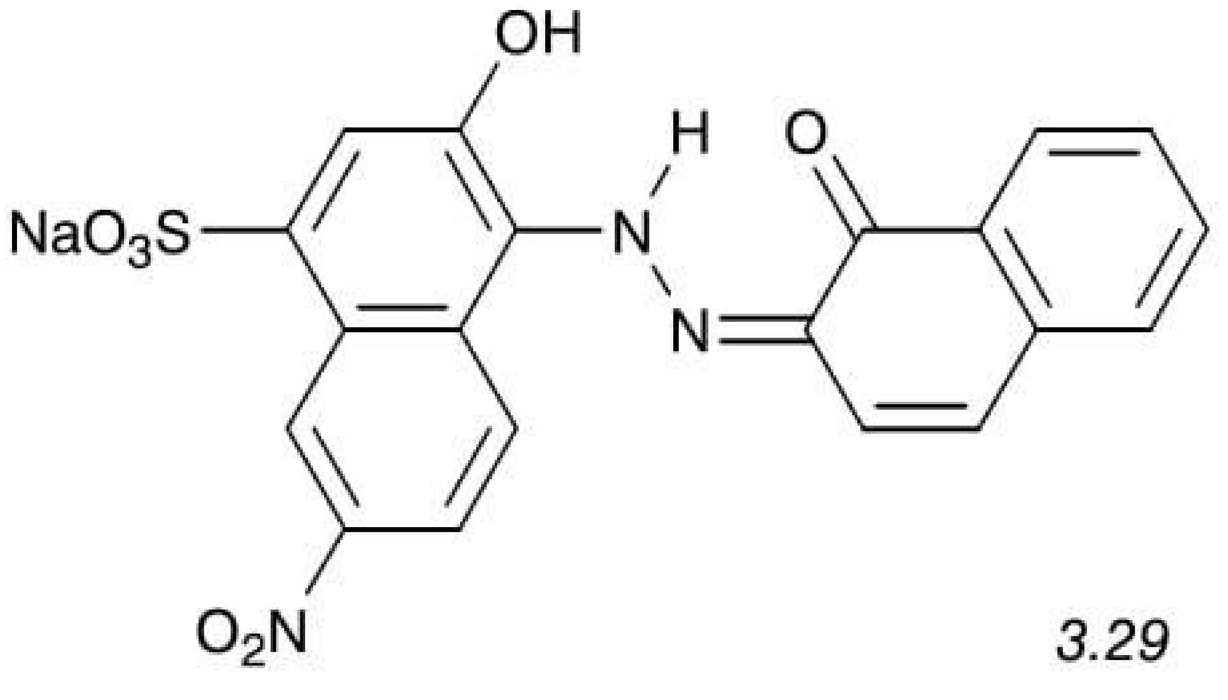
The mechanism of the reduction reaction involves the initial protonation of the azo nitrogen further from the *N*-chloroethyl groups (Scheme 3.6), formation of the quinonoid cationic species (3.28) being responsible for the bathochromic effect observed when dyes of this series are treated with acid. In the case of the 2-carboxy and 2-nitro derivatives of the parent dye, reduction of the azo linkage took place so rapidly that the rate could not be measured. The 2-carboxyphenylazo grouping readily chelates with metal ions and it seems likely that chelation of the tin(II) ion exerts a powerful catalytic effect on the reduction rate. In the 2-nitrophenylazo dye both the nitro and azo groups are potential sites for reduction to occur. In fact the azo linkage was reduced very rapidly but the yield of *o*-nitroaniline was quantitative, indicating that the nitro group was quite stable under these circumstances [23].



3.28

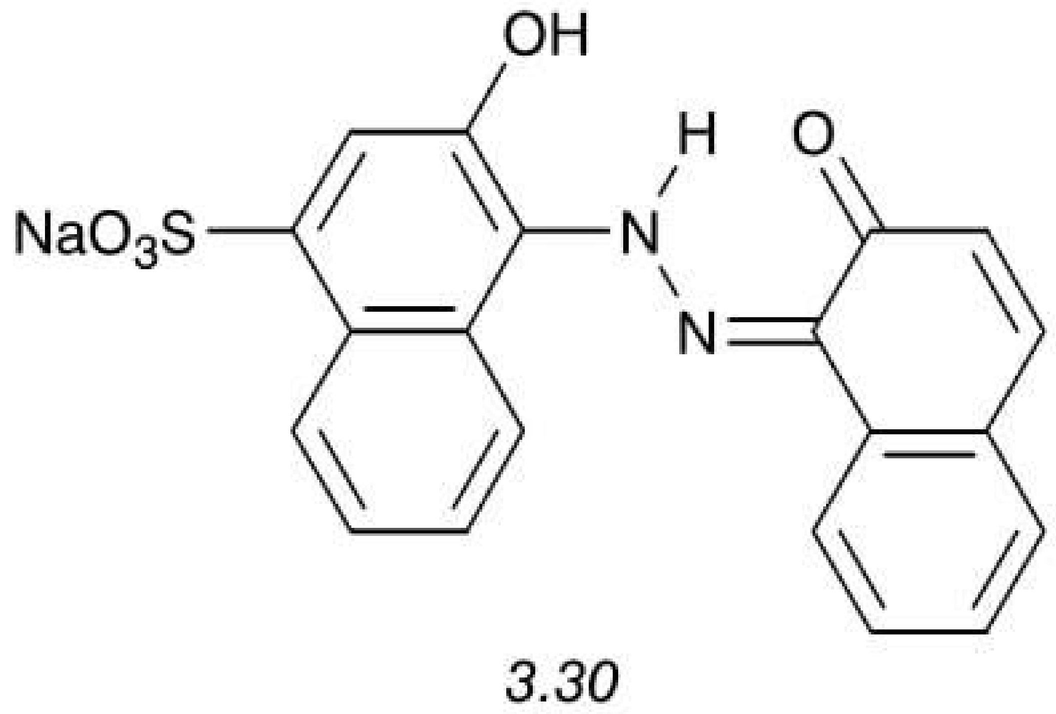
Scheme 3.6

Mordant dyes are notoriously troublesome from the viewpoint of colour matching because the hue of the chromium complex usually differs greatly from that of the unmetallised parent dye (section 5.4.1). If other metal ions are present in the treatment bath or on the fibre during chroming, the colour obtained is likely to differ from that of the pure chromium complex. Certain important chrome dyes, including CI Mordant Black 11 (3.29) and Black 17 (3.30), are particularly sensitive to traces of iron or copper. The hue of the black dyeings obtained is redder in the presence of copper and browner with iron contamination. The fastness to light and wet treatments may also prove inferior under these conditions. Even certain 1:2 metal-complex acid dyes show similar effects in the presence of these impurities,



3.29

CI Mordant Black 11

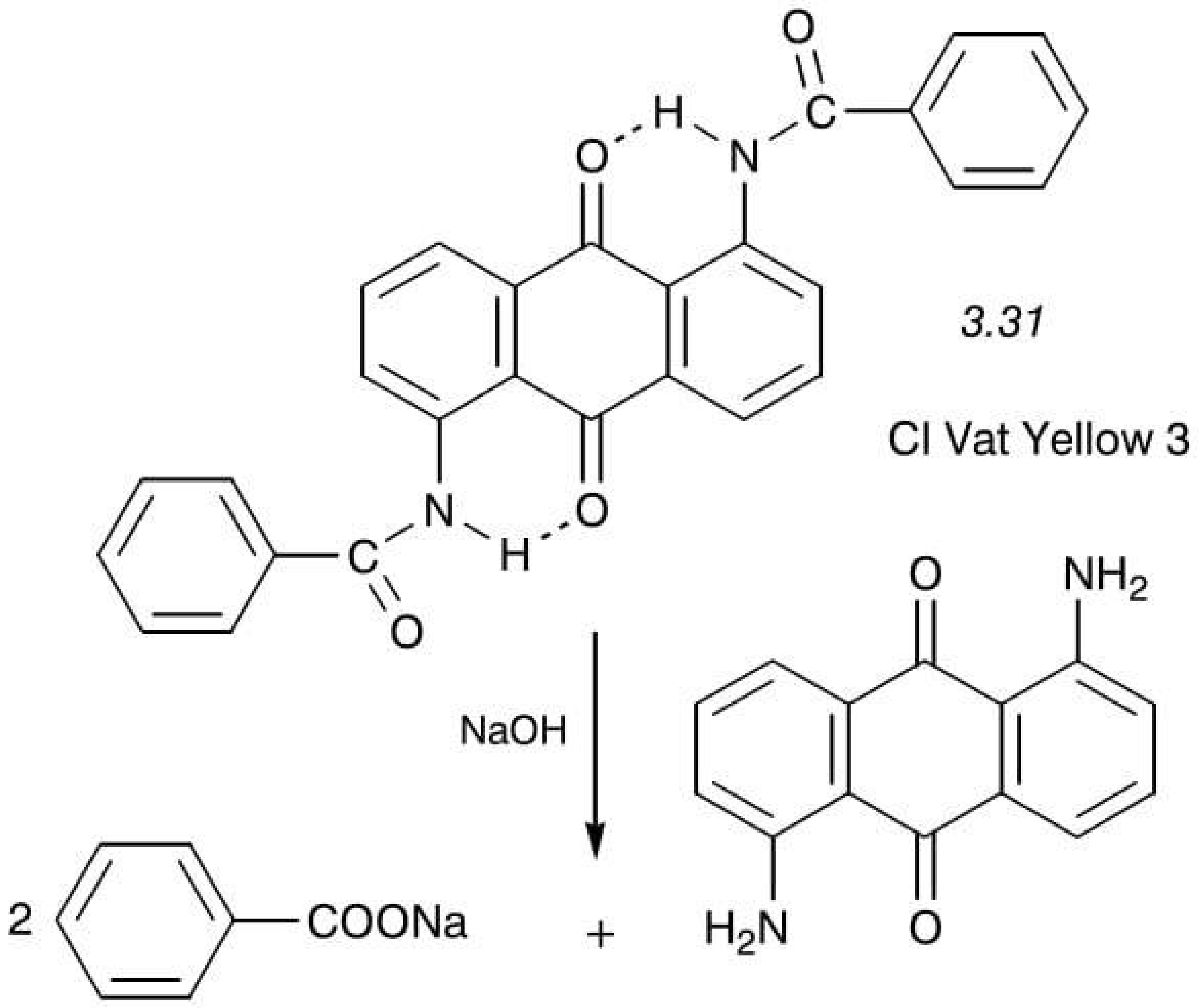


3.30

CI Mordant Black 17

indicating that the iron or copper ions are able to displace chromium from the desired chromium complex. Sequestering agents of the sodium polyphosphate type (section 10.2) can help to minimise these problems.

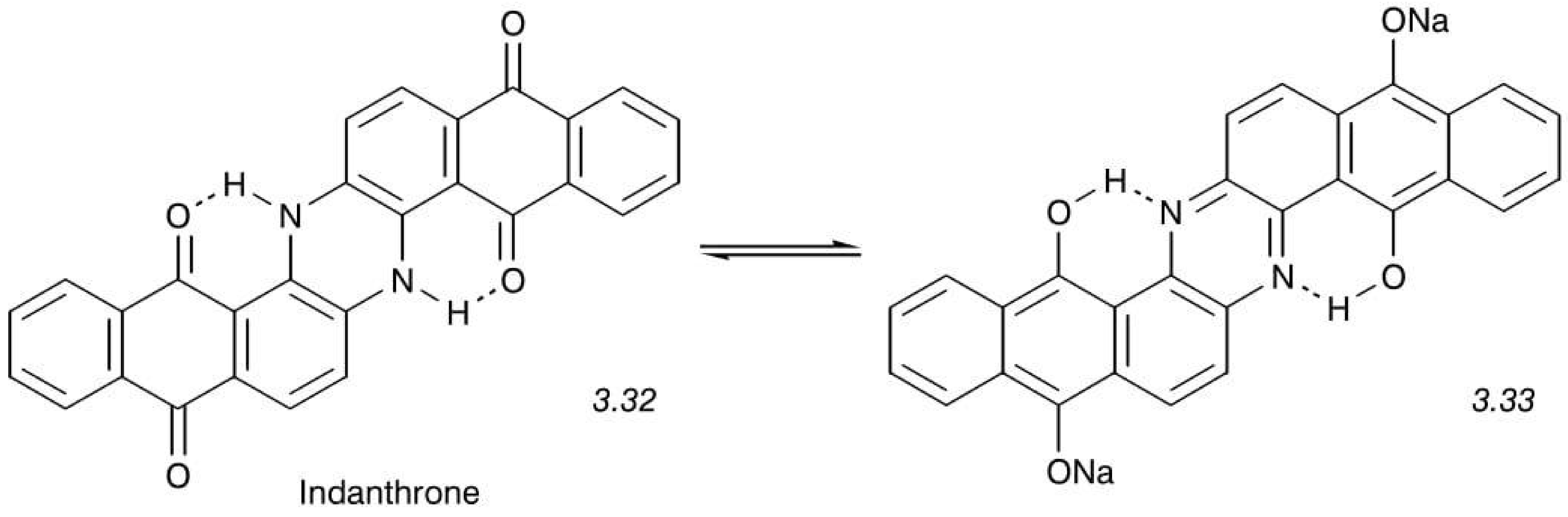
With some leuco vat dyes, chemical changes may take place in alkaline reducing media at high temperatures [24,25]. Many vat dyes contain benzoylamino substituents to confer higher affinity for cellulosic fibres. Alkaline hydrolysis of such dyes may result from prolonged treatment with loss of the benzoyl groups and a gradual lowering of substantivity, leading to unexpectedly low exhaustion of the dyebath. Thus CI Vat Yellow 3 (3.31) is hydrolysed under these conditions (Scheme 3.7), the hue becoming redder and duller because of the formation of the red 1,5-diaminoanthraquinone, and the dyeing exhibits lower fastness to washing.



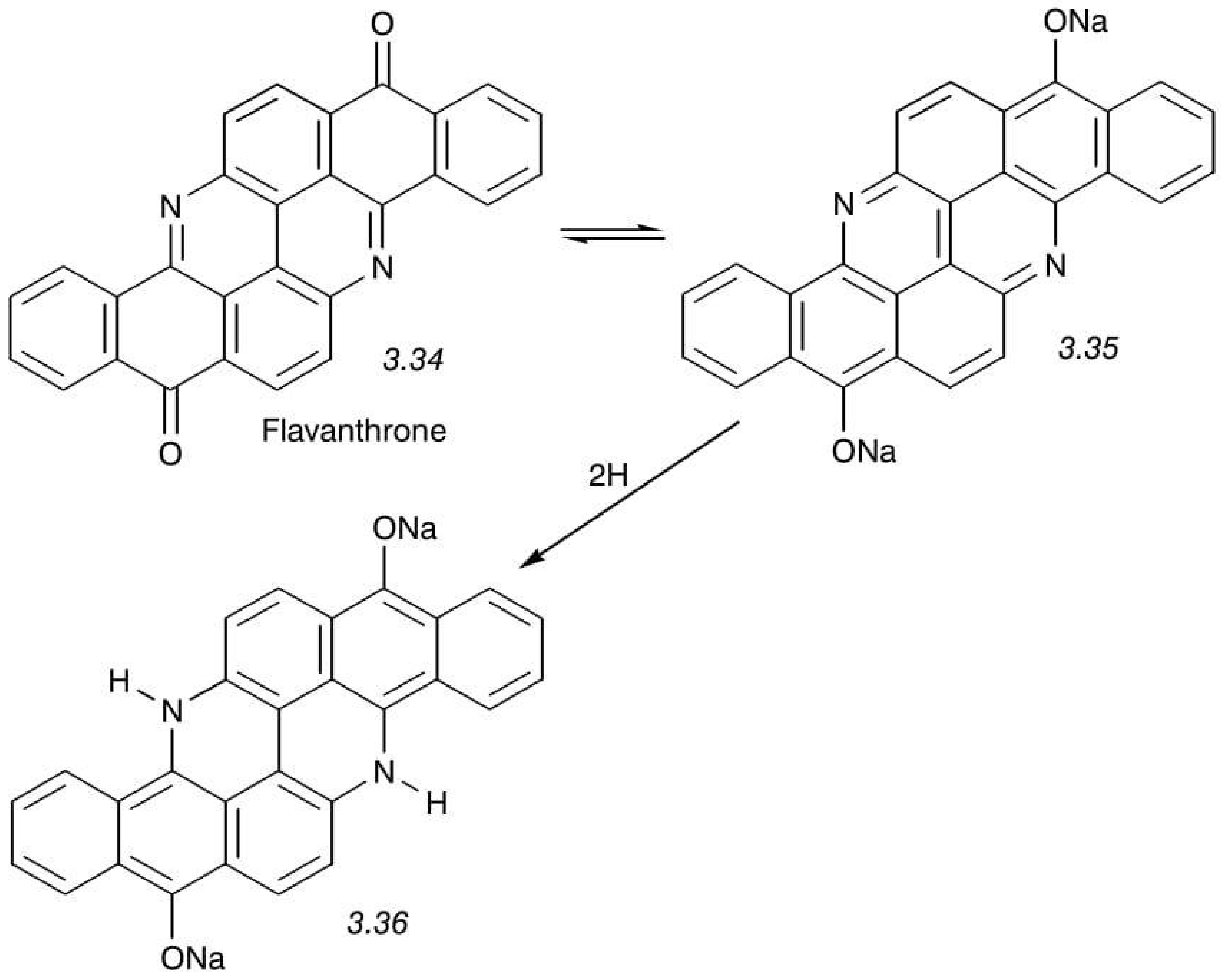
Scheme 3.7

High-temperature vatting or dyeing conditions may cause dehalogenation of vat dyes containing bromo or chloro substituents, resulting in a change of hue towards the parent chromogen. Thus if dichloro (CI Vat Violet 1) or monobromo (Violet 9) derivatives of isoviolanthrone are vatted and dyed on cotton at 90 °C rather than normally at 60 °C, a markedly bluer hue closer to the unsubstituted compound (Violet 10) is obtained. Under similar conditions, dyeings of dibromo (Green 2), dichloro (Blue 17) or trichloro (Blue 18) derivatives of violanthrone do become slightly redder and duller, but the contribution of the parent dye (Blue 20) formed is small because these halogenated structures are more stable than their isomeric analogues. Chlorinated acridone derivatives such as Red 39 and Violet 14 may also suffer dechlorination. Monochloro (Blue 14) or dichloro (Blue 6) derivatives of indanthrone lose chlorine even when dyed above 50 °C and this involves a deterioration in fastness to bleaching.

Indanthrone (3.32; CI Vat Blue 4) and its derivatives require the reduction of only two of the four keto groups to form the sparingly soluble disodium leuco compound (Scheme 3.8). Hydrogen bonding between the inner phenolic groups and the neighbouring azine nitrogen atoms stabilises the structure (3.33). Loss of oxygen atoms can occur, however, as a result of over-reduction at temperatures above 60 °C. The tendency for this irreversible reaction to ensue increases with time and temperature of reduction and with the concentrations of



Scheme 3.8



Scheme 3.9

alkali and dithionite. Additions of glucose or sodium nitrite have a stabilising influence on the disodium enolate solution. Over-reduction yields redder and duller dyeings because of the formation of a brown derivative that will not respond to the oxidising agents normally used after vat dyeing.

Flavanthrone (3.34; CI Vat Yellow 1) behaves in a similar way (Scheme 3.9). Only two hydrogen atoms are required to yield the blue disodium leuco form (3.35), but this is more stable than the analogous disodium enolate of indanthrone. Nevertheless, over-reduction to the brown flavanthraquinol (3.36) can take place under severe conditions of high alkalinity and temperature. In these circumstances the dyeings can no longer be reoxidised to flavanthrone even using acidified dichromate solution. These irreversible overreduction reactions are not known for any classes of anthraquinonoid vat dyes other than the indanthrone and flavanthrone chromogens.

3.1.4 Rates of reduction and redox potentials of vat dyes

The rate of reduction of a vat dye depends partly on the intrinsic chemical properties of the dye and partly on the size and physical form of the dispersed particles undergoing this reaction. The physical factors are much less important than the chemical aspects [26]. The vatting process entails conversion of the insoluble keto form into the soluble sodium enolate (section 1.6.1). The reaction takes place in two stages at ambient temperature. Extremely rapid reduction to the hydroquinone is followed by slower dissolution in the alkaline solution. At higher temperatures, however, the dissolution rate approximates more closely to the rate of reduction. Temperature and dithionite concentration are the important variables and the rate of reduction is much less dependent on dye or alkali concentration.

The ease of reduction of a vat dye depends on its chemical structure in relation to the reducing power of the agent selected. In practice this question is seldom critical because the reduction potential developed by a typical reducing agent is low enough to permit the reduction of all vat dyes of practical interest. Indeed, such dyes would never have been exploited commercially if they had not responded effectively to reduction under conventional conditions of application.

The times of half-reduction of five typical vat dyes are listed in Table 3.3. Most of the commercially important products give values within the range 25–500 seconds. Few dyes are as slow to reduce as CI Vat Red 1 and even fewer are reduced as quickly as flavanthrone. In fact, when these times were measured the average particle size of the sample of flavanthrone under test was greater than that of the CI Vat Green 1 sample, which was reduced at least ten times more slowly [26].

Table 3.3 Times of half-reduction of typical vat dyes [26]

CI Vat	Chemical name	Time(s)
Yellow 1	Flavanthrone	<5
Blue 17	16,17-Dichloroviolanthrone	31
Orange 9	Pyranthrone	36
Green 1	16,17-Dimethoxyviolanthrone	50
Red 1	6,6′-Dichloro-4,4′-dimethylthioindigo	2880

Vat dye reduction is a reversible reaction leading to the formation of an equilibrium mixture of the oxidised and reduced forms. The relative rates of reduction of vat dyes bear no obvious relation to their intrinsic reduction potentials, which determine the position of the equilibrium reached when the keto form of the vat dye is dissolved under a given set of reducing conditions. The relative stabilities of the reduced and oxidised forms can be estimated from the reduction potential developed at a bright platinum electrode (Table 3.4). An unstable leuco compound tends to revert to the oxidised form by transfer of electrons to the electrode, developing a high negative reduction potential. On the other hand, a dye with a small negative reduction potential is easy to reduce because the leuco form is relatively stable.

Few vat dyes are as difficult to reduce as CI Vat Yellow 3 (3.31) in which the amide NH groups form hydrogen bonds with the keto groups, or as easy to reduce as tetrabrominated

Table 3.4 Standard reduction potentials of vat dyes in pyridine [26]

CI Vat	Chemical name	Potential(mV)
Yellow 3	1,5-Dibenzoylaminoanthraquinone	–490
Orange 9	Pyranthrone	–270
Green 1	16,17-Dimethoxyviolanthrone	–250
Yellow 4	1,2,4,5-Dibenzopyrenequinone	–240
Yellow 1	Flavanthrone	–230
Red 6	6-Chloro-6′methoxy-4-methylthioindigo	–220
Blue 1	Indigo	–220
Blue 4	Indanthrone	–220
Blue 20	Violanthrone	–220
Blue 17	16,17-Dichloroviolanthrone	–210
Red 1	6,6′-Dichloro-4,4′-dimethylthioindigo	–190
Blue 5	5,5′,7,7′-Tetrabromoindigo	–70

indigo. Most dyes of commercial interest have reduction potentials within the range –200 to –300 mV. It is interesting to note from Tables 3.3 and 3.4 that CI Vat Yellow 1 is inherently less stable in the reduced form than is CI Vat Red 1, even though the yellow flavanthrone is reduced approximately a thousand times quicker than is the red thioindigo derivative. Although standard reduction potentials have to be measured in anhydrous solvent solution for practical reasons, the results appear to be in general agreement with the qualitative behaviour of vat dyes in aqueous media. Thus indigoid dyes are more stable in the leuco form than are the anthraquinone derivatives in general, but they tend to be reduced more slowly and need a higher temperature for complete reduction.

Cyclic voltammetry has been used to determine the standard heterogeneous rate constants and standard Gibbs free energy for the oxidation-reduction of thioindigo (CI Vat Red 41) on cellulose. The substrate plays an active role in these reactions of the dye when they take place during dyeing, including lowering of the activation energy of the redox processes. This technique allows the vat dyeing mechanism to be modelled more closely [27].

The application of indirect electrolysis as a reduction technique in indigo dyeing has been reported recently. The build-up, penetration and final depth attained were similar to those observed in conventional dyeing with alkaline dithionite. Various reversible redox systems were evaluated as potentially suitable for indigo dyeing, particularly an iron(II)-triethanolamine complex. The iron(III) form of this complex can be transformed into the iron(II) form by cathodic reduction, thus leading to a regenerable reducing agent. This approach offers the prospect of improved process stability, because the reduction state of the dyebath can be monitored by measuring the reduction potential. By regenerating the mediator system, significant reductions in consumption of chemicals and water can be achieved. The process engineering involved can readily be applied to the commercial production of indigo-dyed denim [28].

3.1.5 Substantivity and ionisation of indigo

Indigo was in short supply during the 1970s and development work at Dan River Inc. (USA) demonstrated that the consumption of indigo in the dyeing of cotton denim yarn could be markedly reduced using a sodium carbonate/hydroxide buffer rather than caustic soda alone to generate lower dyebath pH values. Dyebaths produced in this way were less stable, however, resulting in a variable pH, more deposition of inadequately dissolved dye and a greater risk of unlevel dyeing. In recent years the effect of dyebath pH on the yield and penetration of indigo dyeings has been studied in greater detail [29].

Measurements of apparent colour yield, expressed in terms of the reflectance absorptivity coefficient of the indigo-dyed yarn, showed this to be a maximum at pH 10.5–11.5 and to decrease progressively with pH, until at pH 13.5 the colour yield was only about one-sixth of that at pH 11 (Figure 3.2). The degree of penetration of the dyeings was also highly dependent on dyebath pH, poorly penetrated ring dyeings being obtained at pH 11 and almost fully penetrated ones at pH 13. This is attributable to a rapid rate of strike onto the fibre surface under conditions of much higher substantivity at the lower pH.

It is well-known that the reduction of indigo (3.37) proceeds according to Scheme 3.10, to give firstly the monoionised sodium hydrogen enolate (3.38) and then its conjugate base the disodium enolate (3.39). The relative amounts of these species present is governed by the dyebath pH. By extrapolation from the data for the pK values of the various sulphonated derivatives of indigo, it was shown that approximate pK values of 8.0 and 12.7 respectively can be taken to represent the ionisation equilibria in Scheme 3.10. Using these statistically estimated values, the fractions of reduced indigo present as species 3.34 and 3.35 at a given pH can be calculated [29].

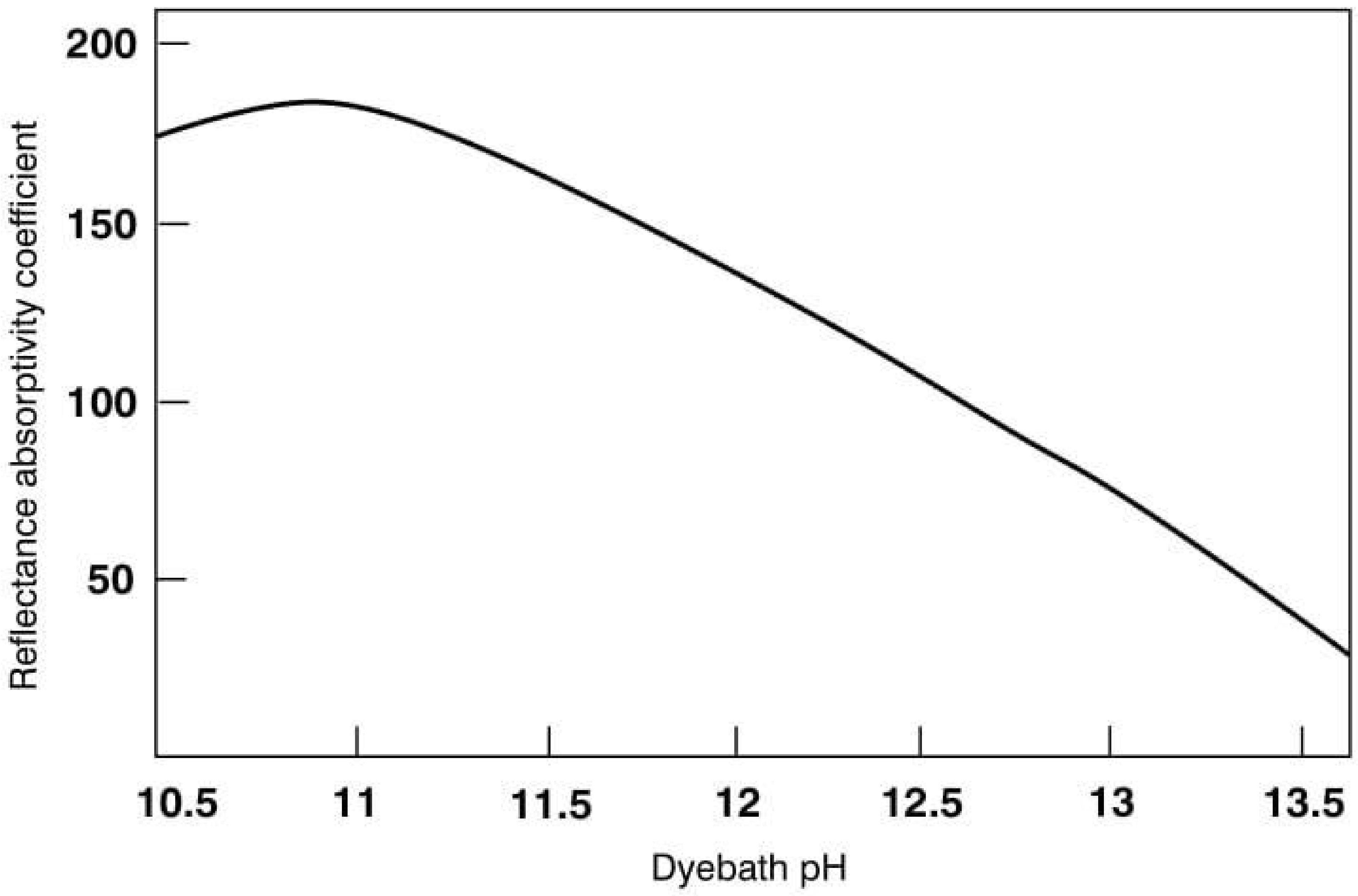
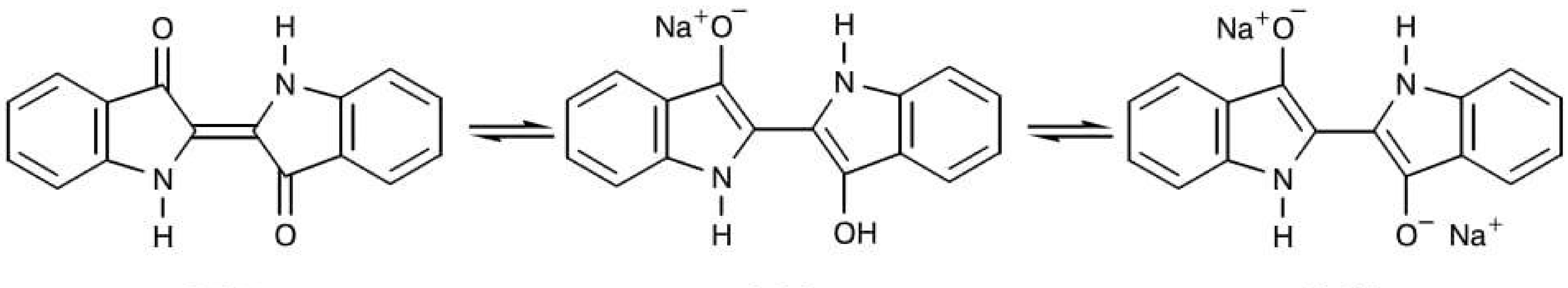


Figure 3.2 Effect of dyebath pH on apparent colour yield in a five-dip indigo dyeing process [29]



3.37
Indigo

3.38
Mono-enolate

3.39
Di-enolate

Scheme 3.10

Sorption studies have revealed that both equilibrium sorption and the ratio of the monoionised to diionised forms of indigo are markedly higher at pH 10.5–11.5, where the highest colour yield is achieved in indigo dyeing [30]. Above this region of pH, the fraction of indigo that exists as the monoionised species decreases rapidly with increasing pH. Above about pH 12.7, a greater proportion of the leuco dye is present as the disodium enolate (3.39). Good linear correlation was obtained (Figure 3.3) between the colour yield data converted to a fractional scale and the fraction of indigo present in the dyebath as the monoionised form over the pH range 10.5–13.5. Improved formulation of buffered alkalis has enabled the degree of ring dyeing obtained in the commercial indigo dyeing of cotton denim yarn to be closely controlled [29].

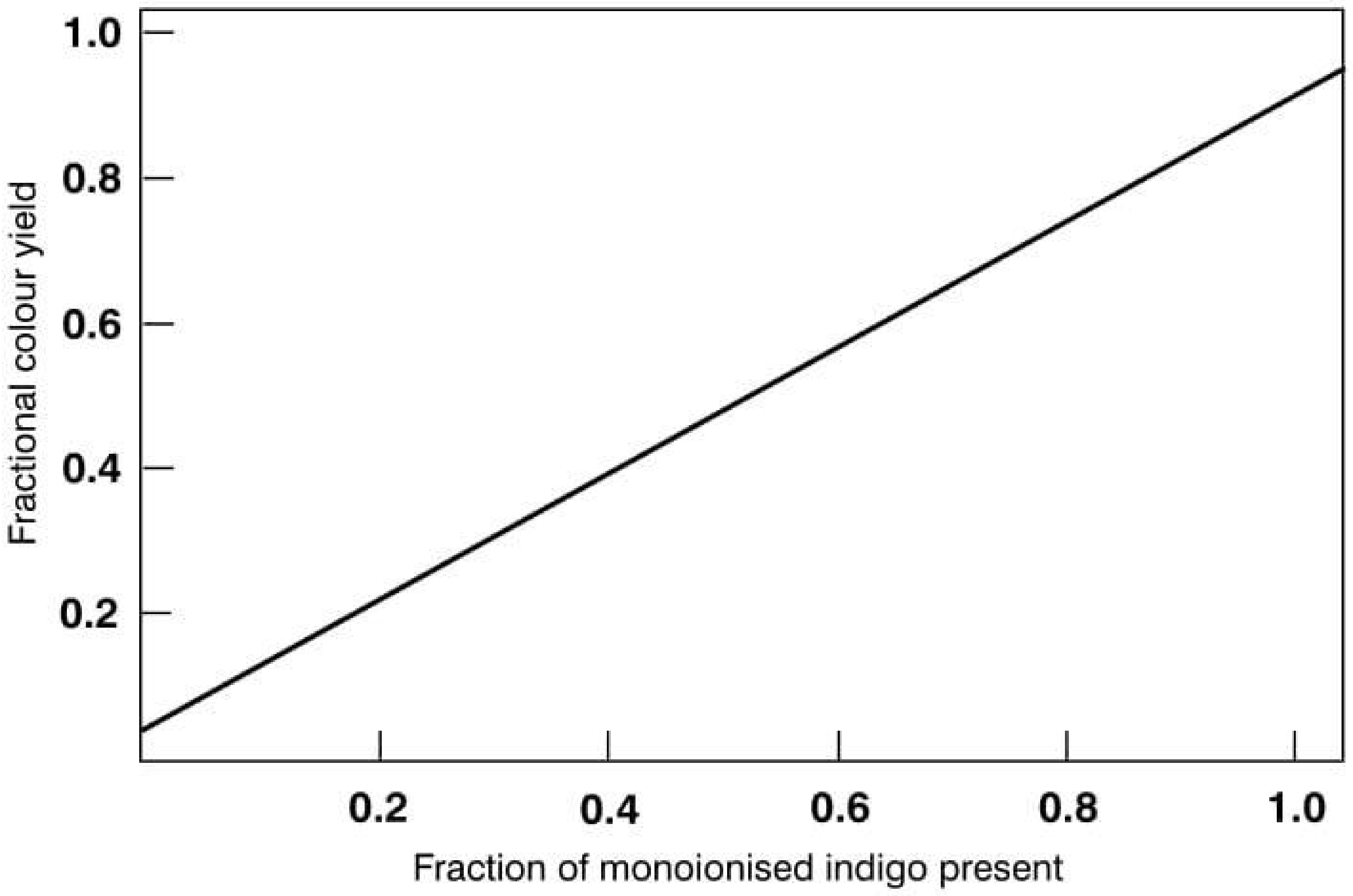
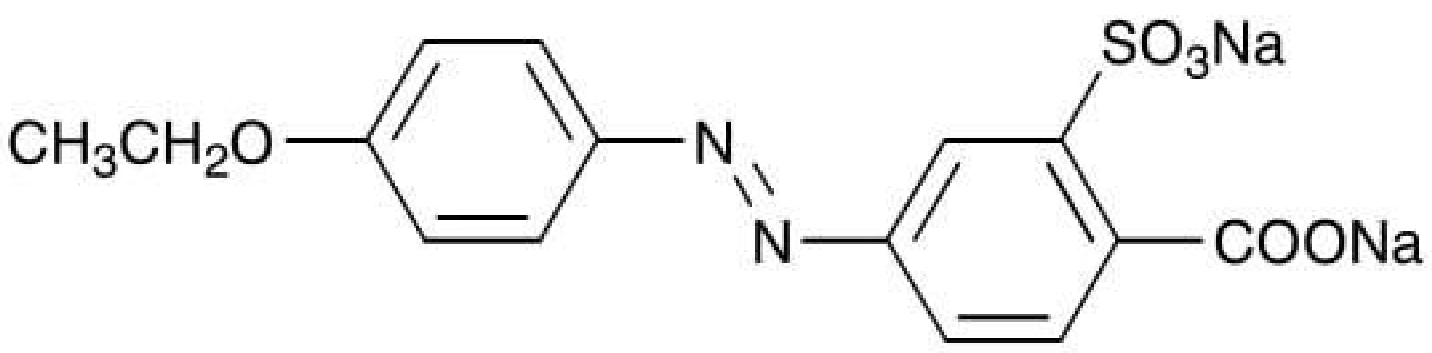


Figure 3.3 Relation between fractional colour yield and fraction of monoionised indigo [29]

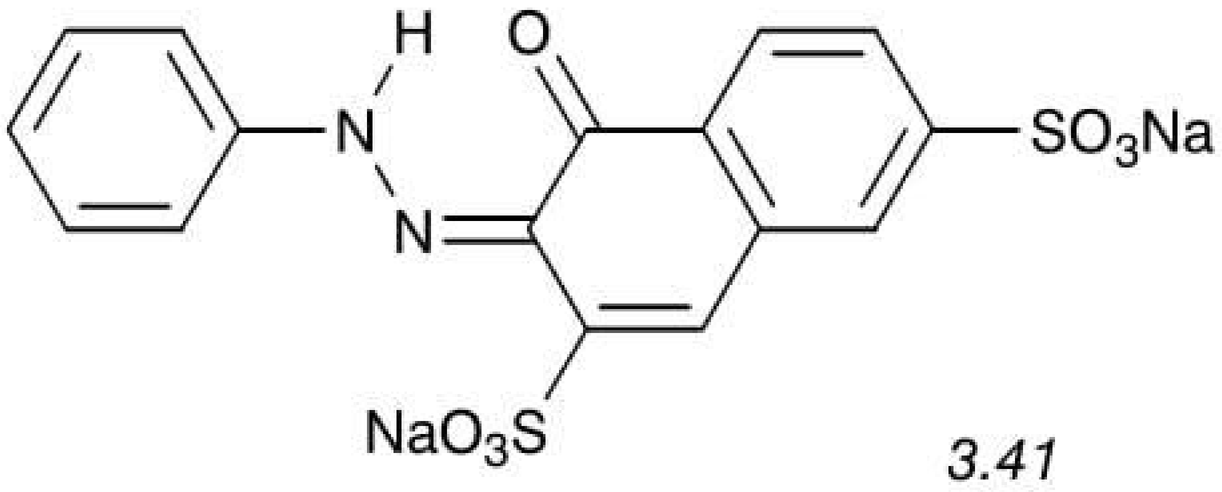
3.1.6 Oxidative decomposition of dyes

Oxidising agents have always been important reagents for the dyer and printer, not only for the reoxidation of vat or sulphur dyes but also in bleaching, stripping and discharge treatments. In recent years, interest in the oxidative decomposition of dyes has greatly increased as a means of dealing with the problem of colour in waste-water (section 1.7.3). Catalytic oxidation is probably the simplest approach to decolorisation of residual dyes. Poly-*p*-phenylene-1,3,4-oxadiazole may be used to induce oxidative decomposition under UV irradiation [31]. Azo acid dyes derived from H acid or K acid can be degraded by photo-assisted catalysis in an aqueous suspension of titanium dioxide. The reaction followed apparent first-order kinetics, the effect of pH varying with the dye structure [32]. Hydroxyl radicals play an essential role in the oxidative fission of the azo groups. The triplet state lifetimes of the dye species are almost independent of the presence of titanium dioxide, implying that the triplet state does not react with hydroxyl radicals or anionic superoxide free radicals [33].

Ozone treatment has potential as a powerful means of decolorising exhaust dyebaths with at least 95% colour removal for good reproduction of bright shades after recycling [34]. The effect of ozone concentration on the decomposition of reactive dye hydrolysates (eight orange or red monoazo and two blue anthraquinone dyes) was investigated [35]. The ecological properties of ozone-treated *N*-containing hydrolysates and the influence of surfactants on the ozonolysis reaction were evaluated. GLC, HPLC and mass spectrometry are valuable techniques for following the reactions and identifying the products of decomposition [35,36]. Fundamental study of the ozonolysis mechanism has shown that the azostilbene CI Direct Yellow 12 (3.6) yields mainly 4-carboxy-4′-ethoxyazobenzene-3-sulphonate (3.40) and hydrogen peroxide, indicating that the stilbene group is more oxidation-sensitive than the azo linkages in spite of the protection afforded by the two *o*-sulphonate groups [37]. The stability to ozone of 2-arylazo-1-naphthol-3,6-disulphonate dyes (3.41) was investigated. Electron-withdrawing nitro or bulky perfluoroalkyl substituents in the diazo component conferred increased resistance to ozone attack [38].



3.40



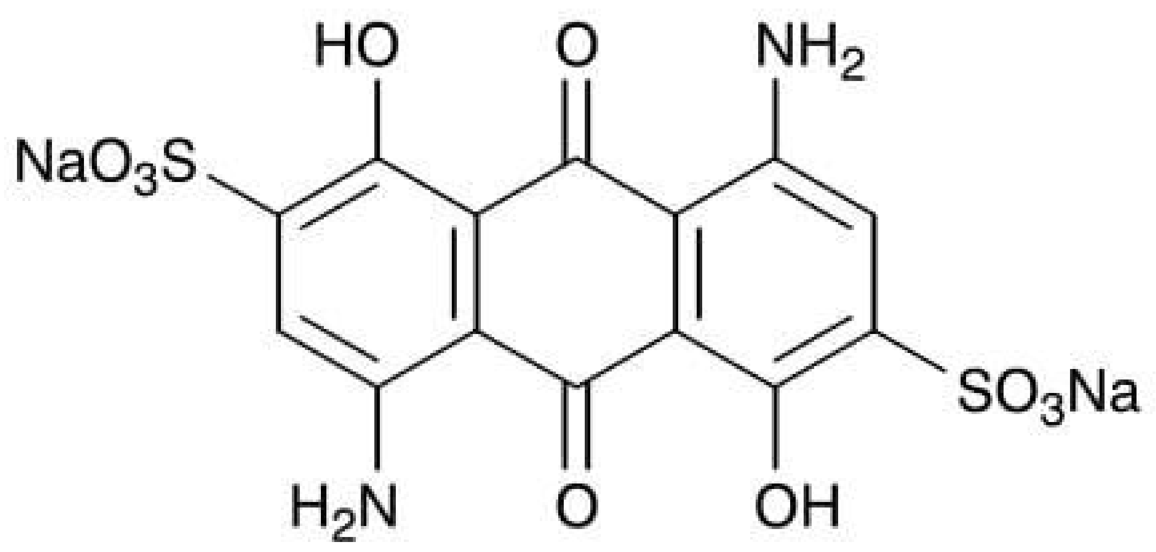
3.41

Commercially viable systems for the decolorisation of spent dyebaths can be based on hydrogen peroxide treatment initiated by UV radiation. A representative selection of six disulphonated monoazo acid dyes and two disazo disulphonated types was exposed for various times in a pilot-scale photochemical reactor of this kind. The controlling parameters were dye structure, pH, peroxide dosage and UV light intensity [39]. In a wider survey of the response of various classes of dyes to the combination of UV radiation and hydrogen peroxide, viable candidates for further in-plant treatment trials were the water-soluble reactive, direct, acid and basic classes. On the other hand, water-insoluble colorants such as disperse and vat dyes did not appear to be viable [40].

The photo-oxidation of several water-soluble monoazo dyes was studied in hydrogen peroxide solution, irradiation being carried out using a low-pressure mercury vapour lamp. The reaction was found to be pseudo-first-order with respect to dye concentration. A labile hydrogen atom in the dye molecule was the primary target of attack and the predominant hydrazone form of the chromogen was more sensitive to oxidation than the azo tautomer [41]. An alternative hydrogen peroxide treatment at temperatures close to 100 °C in the absence of UV irradiation was evaluated using three repreeentative anionic dyes of commercial importance: a monosulphonated anthraquinone milling dye (CI Acid Blue 25), a tetrasulphonated disazo dye (CI Direct Blue 25) and a sulphatoethylsulphone phthalocyanine dye (CI Reactive Blue 21). The effects of pH, temperature and Fe(II) or Fe(III) ions as catalysts were examined and a reaction mechanism proposed [42].

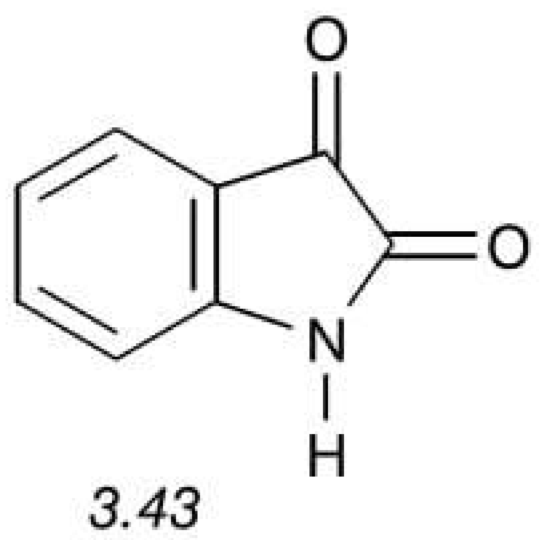
The influence of substituents on the rates of degradation of arylazo reactive dyes based on H acid, caused by the action of hydrogen peroxide in aqueous solution and on cellulose, has been investigated [43]. The results suggested that the oxidative mechanism involves attack of the dissociated form of the *o*-hydroxyazo grouping by the perhydroxyl radical ion [·OOH]. The mechanism of oxidation of sulphonated amino- and hydroxyarylazo dyes in sodium percarbonate solution at pH 10.6 and various temperatures has also been examined. The initial rate and apparent activation energy of these reactions were determined. The ketohydrazone form of such dyes is more susceptible to attack than the hydroxyazo tautomer [44].

The anthraquinone derivative CI Acid Blue 45 (3.42) is somewhat sensitive to oxidation (by sodium nitrite for example), especially in the presence of trace metals such as Fe(III) or Cu(II) ions, forming the dull reddish blue tetrahydroxyanthraquinone disulphonate, which exhibits inferior levelling properties. The formation of isatin (3.43) and anthranilic acid (3.44) as oxidative decomposition products from indigo (3.37) during the acid washing of denim with permanganate has been confirmed. Either of these compounds is capable of causing undesirable yellowing and dulling of the indigo dyeing if not removed in subsequent hot water rinsing [45].



3.42

CI Acid Blue 45



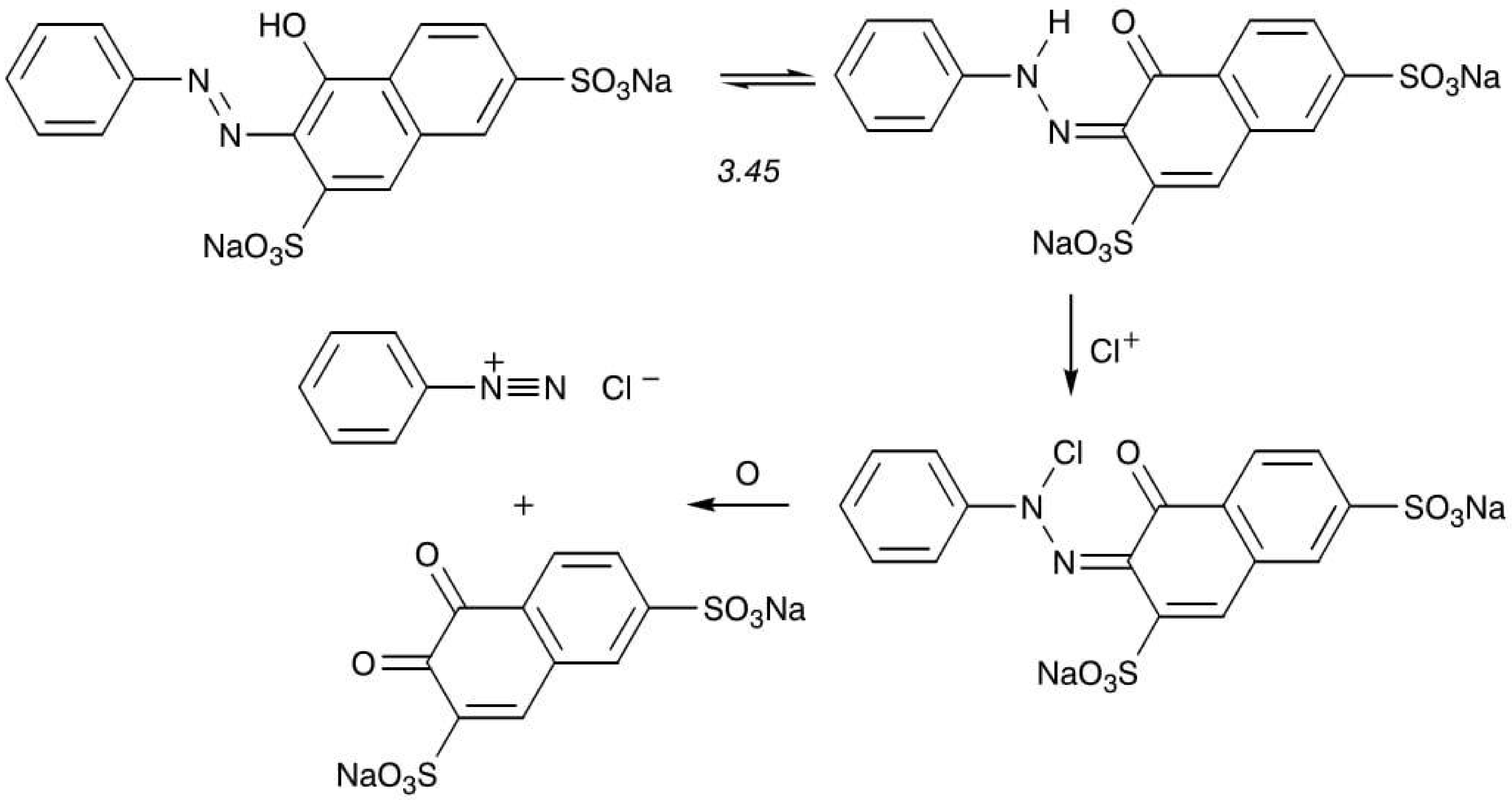
3.43

Isatin

3.44

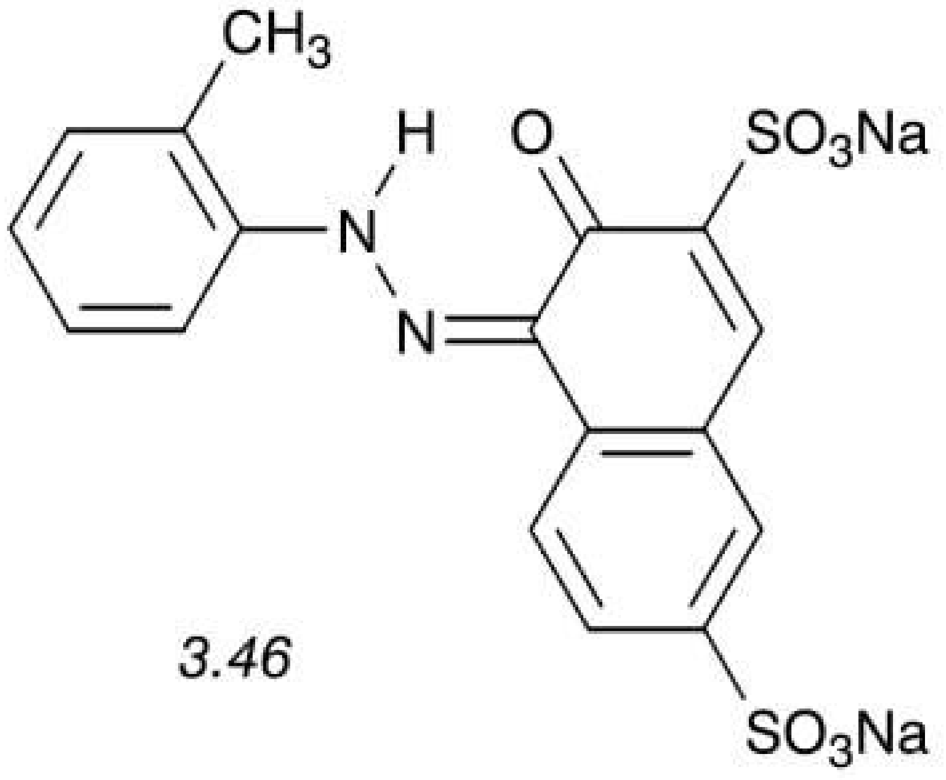
Anthranilic acid

The decolorisation of disodium 1-phenylazo-2-naphthol-6,8-disulphonate (CI Acid Orange 10) and CI Direct Red 2 (3.8; X = CH_3, Y = H) by aqueous sodium hypochlorite was followed by UV spectroscopy. The rates of degradation of both dyes in the initial stage of the reactions conformed to a second-order rate equation [46]. The mechanism of oxidation of a series of orange disodium 2-arylazo-1-naphthol-3,6-disulphonates (3.45) in dilute sodium hypochlorite involved initial attack at the imino nitrogen of the dye in its ketohydrazone tautomeric form by the electrophilic chloronium ion (Cl^+). The diazo component is regenerated and the naphthol residue is oxidised to the *o*-quinonoid analogue (Scheme 3.11). Sulphonic or carboxylic acid groups located *ortho* to the azo linkage are particularly effective in retarding the rate of azo decomposition [47].



Scheme 3.11

The effect of ionic strength on the aggregation and degradation rates of the orange dye disodium 1-(2′-methylphenylazo)-2-naphthol-3,6-disulphonate (3.46) in sodium hypochlorite solutions was studied by visible absorptiometry. The slowest rate of decomposition of the dye was observed under conditions in which the degree of aggregation was at a maximum. This confirmed that the dye molecules shielded inside aggregates are oxidised significantly more slowly than the free monomer in solution [47]. When this oxidation reaction was followed in surfactant solutions, the rate of degradation was markedly dependent on the chemical structure of the surfactant molecule [48]. The influence of substituents on the rates of degradation of red arylazo reactive dyes based on H acid, caused by the action of hypochlorite in solution and on cellulose, has been evaluated [49]. At pH values above 5 only the dissociated form of the *o*-hydroxyazo grouping undergoes attack by the chloronium ion, so that the pK_a value of this group becomes a decisive criterion for the fastness to hypochlorite treatment.



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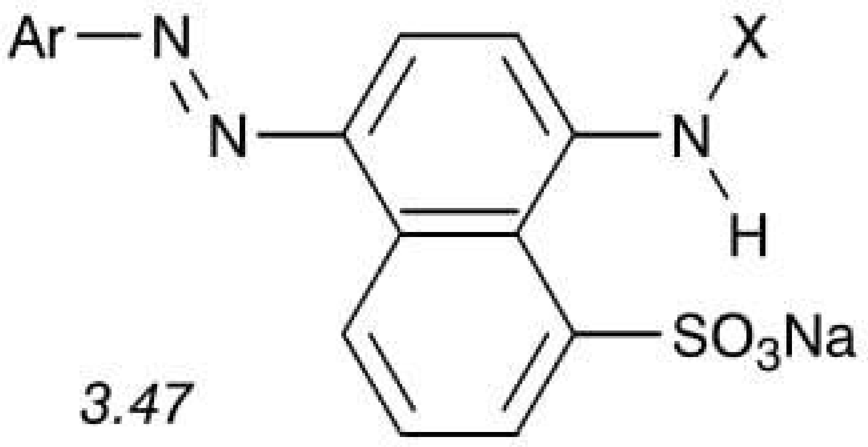
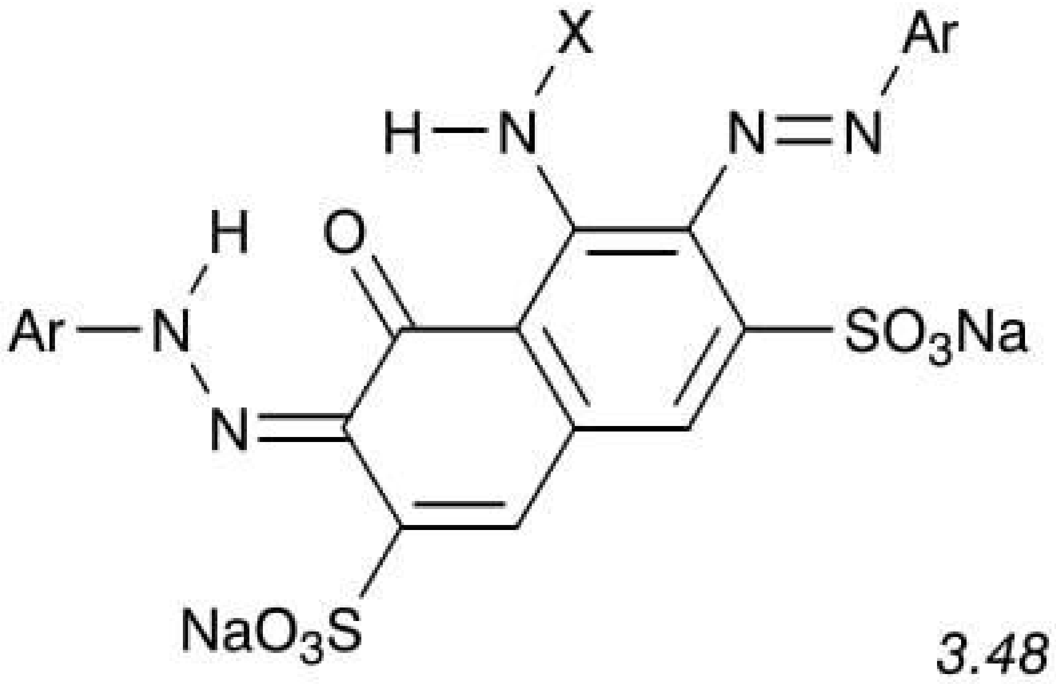


3.47

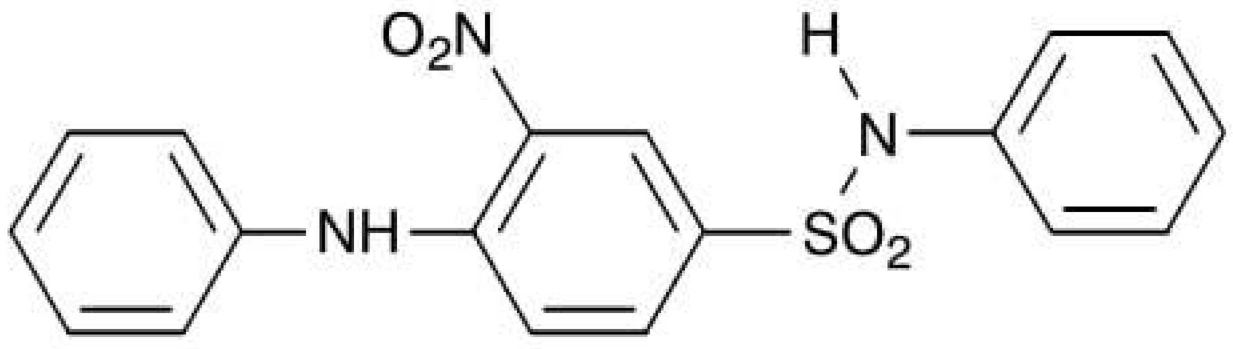


3.48

The influence on colour fastness to chlorinated water resulting from incorporating a sulpho group into various positions of the arylazo-1-naphthol chromogen in typical orange reactive dyes was examined. Enhanced fastness could be attributed to steric protection of the imino site in the predominant ketohydrazone form of these dyes [50]. In a similar study of orange reactive dyes based on the arylazoarylamine system, it was found particularly effective to incorporate the sulpho group into the 8-position of these 4-arylazo-1-naphthylamine dyes (3.47; Ar = aryl, X = reactive group), *peri* to the imino group bearing the reactive system. In the case of blue disazo reactive dyes derived from twice-coupled H acid (3.48), the two phenylazo groups located in the 2,7-positions make a major contribution to protecting the imino group in the 8-position. In all such imino-substituted acid, direct or reactive azo dyes of these or related types, electrophilic attack on the imino group by the chloronium ion in sodium hypochlorite solution initiates the degradation process, drastically accelerating the subsequent cleavage of the azo linkage [51].

3.1.7 Dispersion properties and aqueous solubility of disperse dyes

An aqueous dispersion of a disperse dye contains an equilibrium distribution of solid dye particles of various sizes. Dyeing takes place from a saturated solution, which is maintained in this state by the presence of undissolved particles of dye. As dyeing proceeds, the smallest insoluble particles dissolve at a rate appropriate to maintain this saturated solution. Only the smallest moieties present, single molecules and dimers, are capable of becoming absorbed by cellulose acetate or polyester fibres. A recent study of three representative CI Disperse dyes, namely the nitrodiphenylamine Yellow 42 (3.49), the monoazo Red 118 (3.50) and the anthraquinone Violet 26 (3.51), demonstrated that aggregation of dye molecules dissolved in aqueous surfactant solutions does not proceed beyond dimerisation. The proportion present as dimers reached a maximum at a surfactant:dye molar ratio of 2:5 for all three dyes, implying the formation of mixed dye-surfactant micelles [52].



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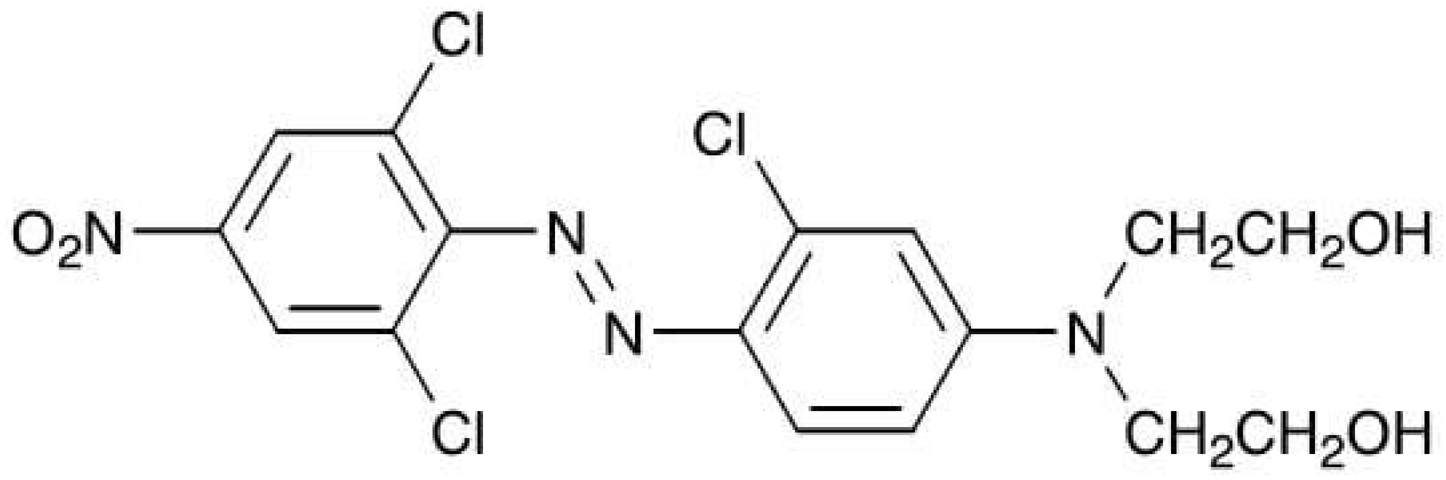
CI Disperse Yellow 42



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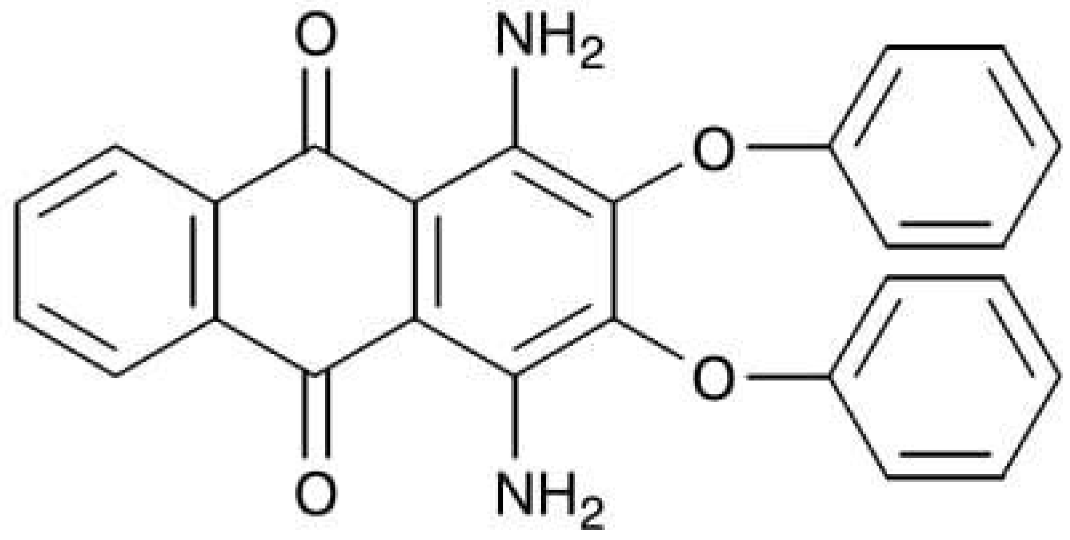
CI Disperse Red 118



3.51

CI Disperse Violet 26

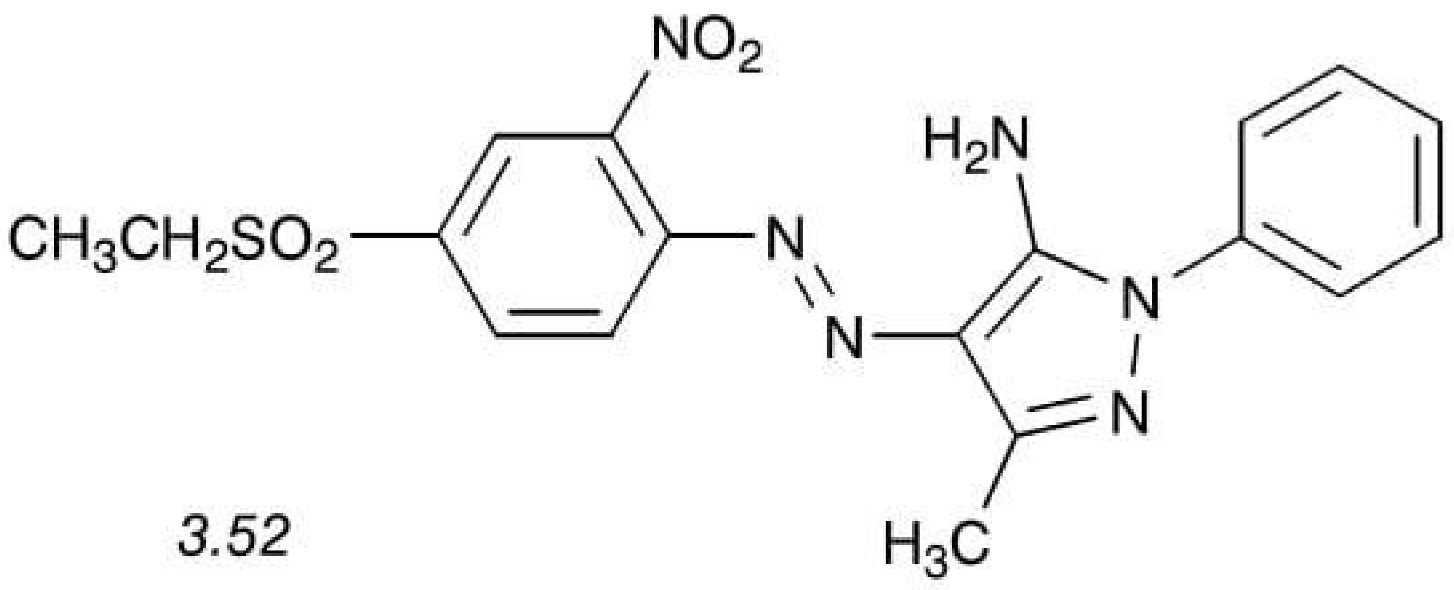
Surfactants are invariably incorporated in the formulation of commercial disperse dye powders, grains or liquid brands. Further additions of surfactants to the dyebath may be made in batchwise or continuous application. The initial purpose of the agents included by the manufacturer is to prevent the finely divided particles of dye from agglomeration during milling or spray drying. They also help to maintain concentrated dispersions in a stable condition during transportation and handling, to minimise agglomeration and settling during storage of liquid brands.

In the dyeing process, where the dispersion is much less concentrated, the function of the surfactant addition is to control a process of dynamic change rather than to preserve a static equilibrium for as long as possible. Here the agents play an active part in accelerating the disintegration and dissolution of dispersed particles and thus in increasing the concentration of dissolved dye present in the dyebath. This has the secondary effect of increasing the rate at which dye can be adsorbed onto the fibre surface. During cooling of the dyebath surrounding the dyed material, the presence of a surfactant helps to retard agglomeration, coalescence or crystallisation of dye particles from the saturated solution as it cools.

Coalescence of dyes during cooling is characteristic of their existence in a viscous state at elevated temperatures [53]. Surfactants minimise the redeposition of insolubilised dye onto the surface of the fibres from the cooling bath.

Numerous disperse dyes are marketed in a metastable crystalline form that gives significantly higher uptake than the corresponding more stable modification. The molar free enthalpy difference can be used as a criterion of the relative thermodynamic stabilities of two different modifications [53]. Certain dyes can be isolated in several different morphological forms. For example, an azopyrazole yellow disperse dye (3.52) was prepared in five different crystal forms and applied to cellulose acetate fibres. Each form exhibited a different saturation limit, the less stable modifications giving the higher values [54].

In a later investigation three different crystal modifications of each of three commercially important monoazo CI Disperse dyes, namely Yellow 3 (3.53), Yellow 42 (3.49) and Red 54 (3.54), were characterised in terms of melting point, X-ray diffraction pattern and dyeing behaviour on polyester fibres. Different fibre saturation values were found for the various forms of Yellow 42 and Red 54, but the three modifications of Yellow 3 did not differ in this respect [55]. A dispersing agent may influence the aqueous solubility of crystal modifications of the same dye to differing extents, so that the rate of change from a metastable to a more stable form on heating may be modified in the presence of an agent. On the other hand, a metastable form of Yellow 3 showed no tendency to revert to the stable form in the absence of any dispersing agent [56].



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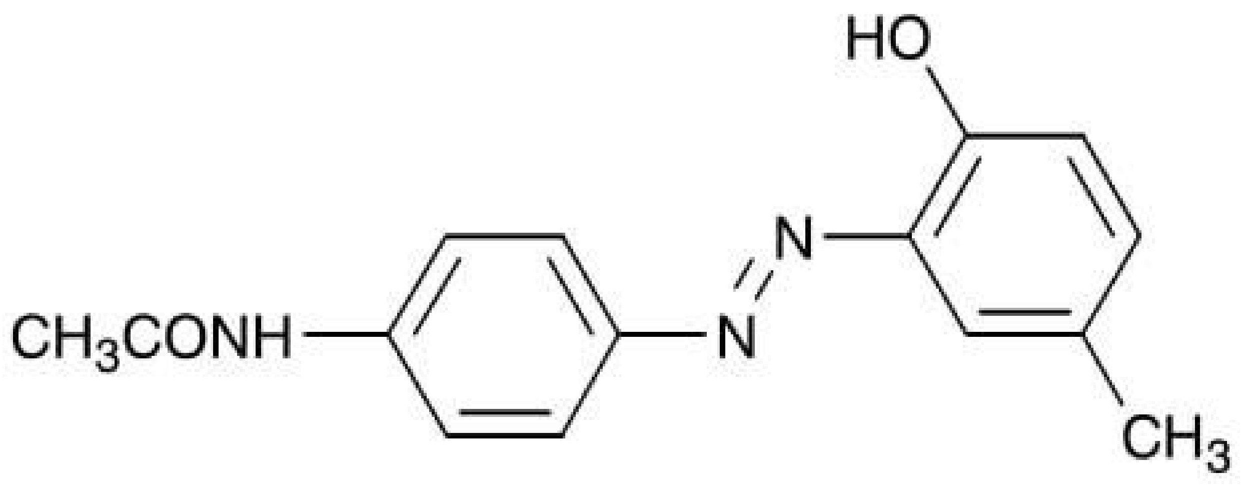

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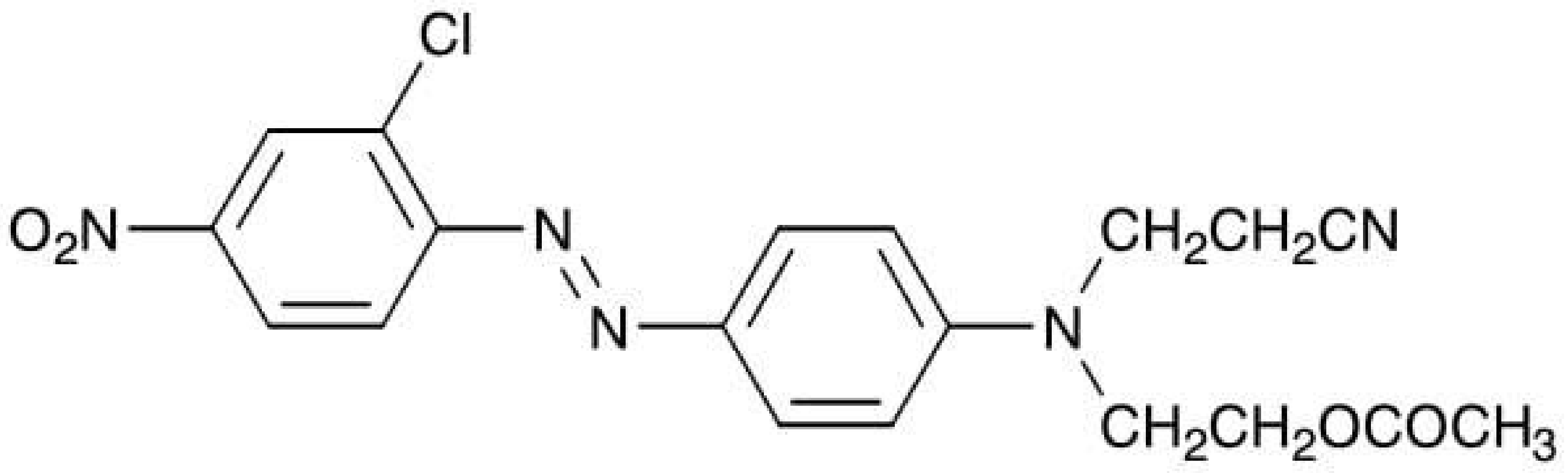
CI Disperse Yellow 3



3.54

CI Disperse Red 54

The saturation solubility of a disperse dye in water at a given temperature may be defined as the maximum amount of pure dye that will give a single homogeneous phase when dissolved in a given volume of pure water. The qualification as 'saturation solubility' implies that any further addition of dye would remain undissolved as a separate solid phase. Solubilisation of a disperse dye refers to the marked increase in saturation solubility that occurs when a water-soluble solubilising agent is added. If a water-miscible co-solvent such as acetone or ethanol is added to an aqueous suspension of a disperse dye, there is a gradual increase in the amount of dissolved dye that is proportional to the quantity of co-solvent added.

A disperse dye suspension responds somewhat differently when a surface-active solubilising agent is added. At low concentrations of this type of additive the saturation solubility of the dye remains relatively little changed, but when the critical micelle concentration of the surfactant is reached a sudden marked increase in dye solubility is observed [57]. When micelles of the surfactant begin to form in the solution, these provide a more amenable environment into which the dye molecules or dimers can transfer. Above the critical micelle concentration the increase in solubility of the dye is directly proportional to the concentration of surfactant present [1,56].

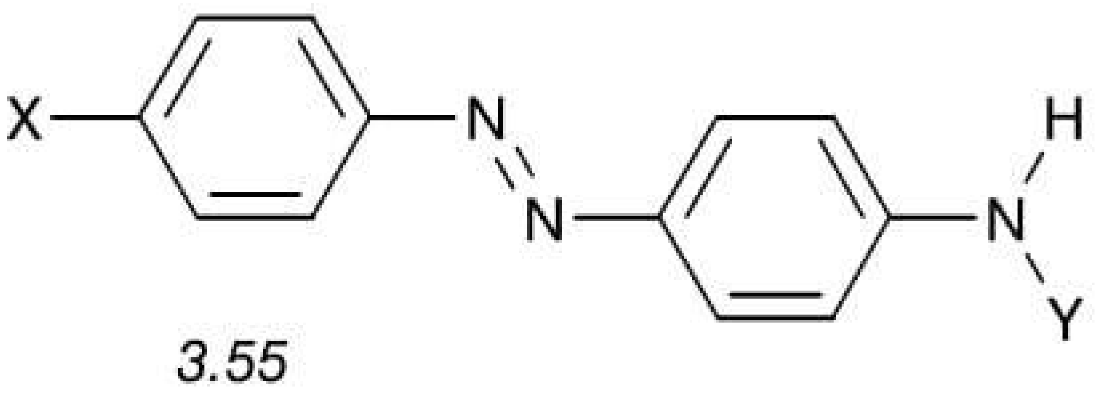
The saturation solubility of pure disperse dyes in water is often extremely low at ambient temperature. An early survey of about forty typical dyes for cellulose acetate yielded values within the range 0.1 to 32 mg/l [58]. Raising the temperature to 80 °C results in a considerable increase in saturation solubility, but the solubilising power of surfactants is essential for the satisfactory dyeing of cellulose acetate with the less soluble dyes. Dyes for polyester tend to be more hydrophobic in structural balance. These require considerable solubilisation by agents even at 130 °C in order to give satisfactory dyeing behaviour and freedom from agglomeration or redeposition on cooling.

The hydrocarbon groupings in disperse dye molecules represent the most hydrophobic portions and these favour dimerisation and agglomeration in an aqueous environment. Substituents containing electronegative atoms (such as nitrogen, oxygen or sulphur), especially when bearing hydrogen atoms (as in =N–NH–, $–NH_2$, –CONH–, –OH, –SH groups) are able to interact strongly with water to form hydrogen bonds and thus to contribute to solubility in water [1].

Much of the available published data on the aqueous solubility of disperse dyes was accumulated during the 1960s in the course of studies of the mechanism of dyeing cellulose acetate with disperse dyes. Most of the dyes examined were low-energy types for dyeing acetate (Table 3.5). Particular attention was given to monoazo dyes derived from aniline or

Table 3.5 Aqueous solubility of disperse dyes of related structure [59-63}

		Solubility(mg/l)					
		Temp (°C):	60	80	80	90	100
CI Disperse	Structure	Lit. ref.:	59	60	61	62	63
	3.55; X = H, Y = H		141				
	3.55; X = NH_2, Y = H		74				
Orange 3	3.55; X = NO_2, Y = H		3			16.6	
Orange 1	3.55; X = NO_2, Y = Ph					1.1	
	3.56; X = Ph		214				
	3.56; X = 1-naphthyl		7.8				
Red 19	3.57; X = Y = CH_2CH_2OH			26.4			
Red 1	3.57; X = CH_2CH_3, Y = CH_2CH_2OH			7.7			
	3.57; X = Y = CH_2CH_3			ca 0.2			
Blue 23	3.58; X = Y = $NHCH_2CH_2OH$				61		
Blue 3	3.58; X = $NHCH_3$, Y = $NHCH_2CH_2OH$				30		
Blue 14	3.58; X = Y = $NHCH_3$				2		
Violet 1	3.58; X = Y = NH_2				21.7		
Red 15	3.58; X = OH, Y = NH_2				11.7		38
	3.58; X = Y = OH						17



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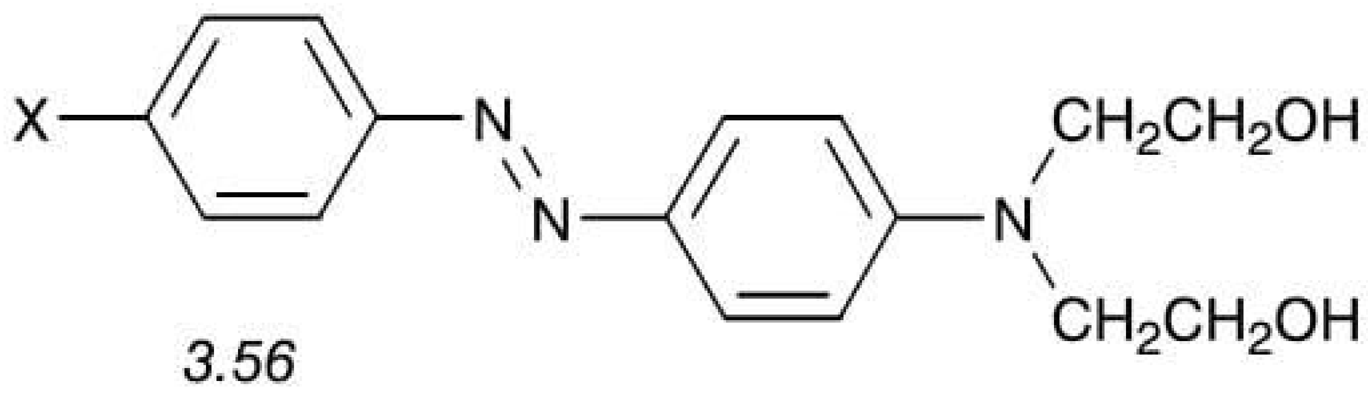

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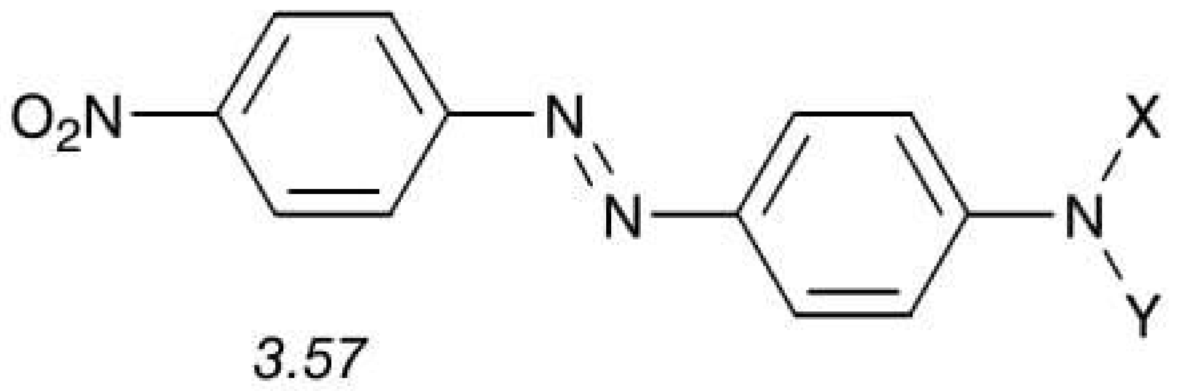

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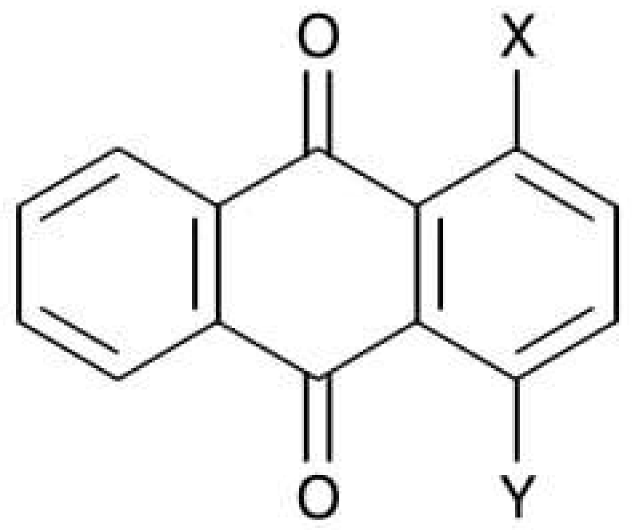


3.58

p-nitroaniline coupled to *N,N*-disubstituted anilines with ethyl or 2-hydroxyethyl substituents and to 1,4-disubstituted anthraquinones containing potential hydrogen bonding groups (–OH, $-NH_2$, $-NHCH_3$ or $-NHCH_2CH_2OH$).

In the azo series, unsubstituted aniline as a diazo component gave more soluble dyes than did *p*-phenylenediamine or *p*-nitroaniline, in that order. Introduction of an additional aryl ring resulted in a marked decrease in solubility, as shown by comparing CI Disperse Orange 1 with Orange 3, or phenylazo-*N,N*-bis(2-hydroxyethyl)aniline (3.56; X = Ph) with its 1-naphthylazo analogue. Hydroxyethyl groups are readily solvated in water by hydrogen bonding and therefore confer much higher solubility than alkyl substituents in analogous dyes. Examples are given in Table 3.5 from both the monoazo (3.57) and the anthraquinone (3.58) series. The solubility is approximately doubled if two hydroxyethyl groups are introduced instead of one. Aminoanthraquinone dyes are markedly more soluble than their hydroxy analogues.

In a recent study of twenty disperse and solvent dyes, data for water solubility, octanol/water partition coefficient, entropy of fusion and melting point were subjected to regression analysis. Complicating factors such as impurities, polymorphism, tautomerism, polarisation and hydrogen bonding precluded the development of reliable predictions of solubility and partition coefficient. Anthraquinone dyes exhibited much lower entropy of fusion than many of the azo dyes [64,65].

3.2 DYEABILITY OF FIBRES IN RELATION TO DYE STRUCTURE

The chemical forces that operate between dye molecules and fibrous polymers are essentially the same as those governing the clustering of water molecules, dye solubilisation in aqueous media and the aggregation or agglomeration of dyes. In dyeing systems depending on an essentially ionic mechanism, such as the dyeing of acrylic fibres with basic dyes or the application of anionic dyes to nylon, silk or wool, a decisive role is played by electrostatic attraction between the charged dye ions and sites of opposite charge in the substrate. Shorter-range forces make a notable contribution to the affinity of the dye ion but their function is essentially supportive.

In all other dyeing systems, however, the charge (if any) on the dye ion or molecule does not enhance affinity. A cellulosic fibre, for example, normally carries a negative charge like that of an approaching dye anion and measures must be taken to minimise the forces of repulsion arising from this similarity. Under these circumstances the less specific shorter-range forces (hydrogen bonding and van der Waals or dispersion forces) make a much more substantial contribution to dye-fibre bonding.

3.2.1 Dyeing of cellulosic fibres with anionic dyes

Within a structural series of direct dyes, the lower the equivalent mass (that is, the ratio of relative molecular mass to sulphonic acid group content) the higher will be the aqueous solubility of the dye. As already noted, the converse of this general trend is that dye molecules of higher equivalent mass tend to aggregate together more readily because of the greater opportunity for hydrophobic interaction. In the presence of a cellulosic substrate, such dyes will tend to escape more readily from the aqueous dyebath by adsorption onto the fibre surface. It is reasonable to assume that the dye molecules will become adsorbed in such a way that as far as possible the hydrophilic sulphonate groups are directed outwards towards the aqueous phase.

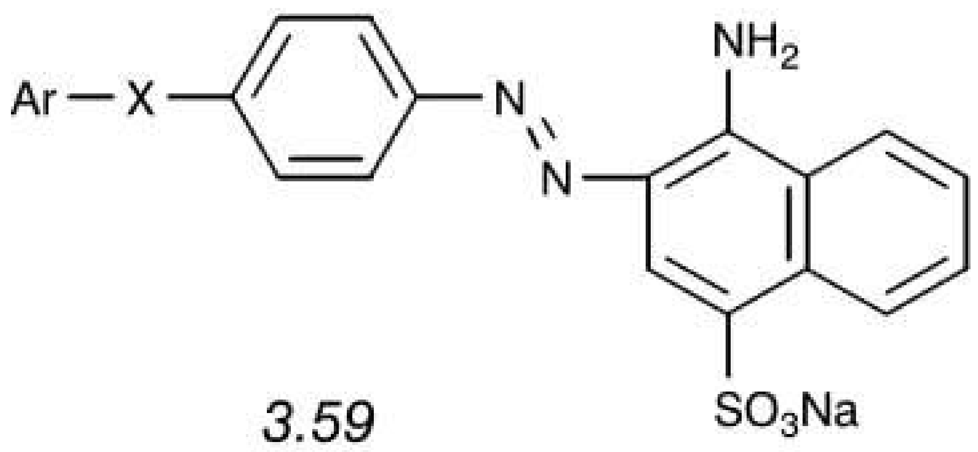
Just as addition of an electrolyte to a solution of a direct dye tends to lower the electrostatic repulsion between the negatively charged dye ions and promote aggregation, the effect of the presence of salt when dyeing a cellulosic fibre is to overcome the long-range forces of repulsion between the dye anions and the negatively charged fibre surface. The closer approach then allows hydrogen bonding and other short-range attractive forces to operate between the dye molecules and the glucoside units of cellulose. This favourable influence of electrolyte addition is as useful with anionic leuco forms of vat or sulphur dyes as it is with sulphonated direct or reactive dyes.

Hydrogen bonding between the hydroxy groups of cellulose and centres of electronegativity (nitrogen, oxygen or sulphur), especially those substituted with hydrogen atoms (as in $=N–NH–$, $–NH_2$, $–CONH–$, $–OH$, $–SH$ groups), is widely acknowledged to contribute to adsorption and retention of the dye molecules. Stereochemical studies have shown that hydrogen bonding is possible for almost all cellulose hydroxy groups in the amorphous regions of the fibre. Measurements of the heat of dyeing confirm that a typical adsorption process entails the formation of at least two hydrogen bonds per molecule of dye adsorbed [66,67]. It is obvious that retention of the adsorbed molecule will be favoured the higher the number of potential dye–fibre bonding points and the more widely they are spaced along the length of the dye molecule. The more hydrogen bonds that a dye can form with the glucosidic polymer, the more readily it can compete with and rupture the fibre–fibre bonds in order to penetrate more deeply into the amorphous structure of the fibre.

The recognition that the existence of conjugation in all organic colorants was essential to provide intense colour (section 1.5) and that an increase in the length of the conjugated chain produced a bathochromic shift of the main waveband in the absorption spectrum led to the adoption of related ideas in the context of the theory of substantivity. Many direct dyes with high affinity for cellulose are disazo or trisazo structures in which the azo groups are located in *para* positions relative to one another, so that the longest conjugated chain through the azo-linked aryl nuclei tends to be as near linear as practicable. The presence of an amide group that is conjugated via a 1,4-phenylene or 2,6-naphthylene residue to the nearest azo group, as in the commercially important CI Direct Red 81 (3.7; X = H), enhances the substantivity of the molecule by lengthening the conjugated chain, a modification that also causes a bathochromic shift.

A methine group oriented *para* to an azo group through an intervening aryl nucleus boosts substantivity even more than does an amide group in a similar position. This was demonstrated for a series of azostilbene and related dyes (3.59; Ar = Ph, X = CH=CH, CONH or CO) with their thiophene analogues (Table 3.6). Affinity increased in the order of increasing electron mobility (CH=CH > CONH > CO) and was greater for the heterocyclic derivatives than for the corresponding phenyl-substituted dyes [68]. A series of analogues of the most substantive of these dyes (containing both the thiophene ring and the methine linkage) proved to be highly sensitive to the nature of the coupling component at the opposite end of the conjugated chain, however (Table 3.7). The presence of an amino group favours substantivity (naphthionic acid > NW acid, H acid > chromotropic acid) but the extra sulpho group in the three disulphonated couplers affects it adversely.

The significance of conjugation as a contributor to the substantivity of dyes for cellulose is not always easy to distinguish from the effect of the degree of linearity of the molecule. Almost all direct dye molecules possess flexible chains of aryl nuclei linked by azo or other unsaturated groups. Such structures can readily adopt a near-linear spatial conformation, as



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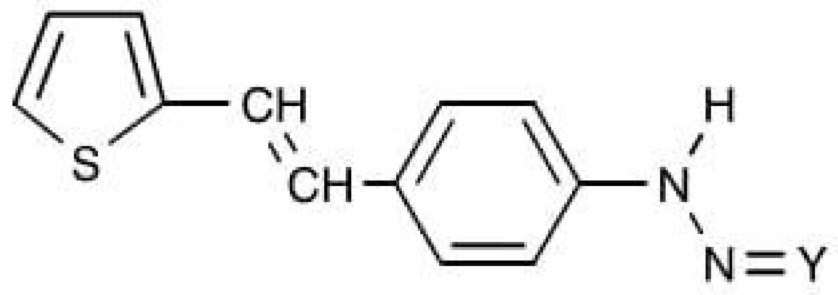

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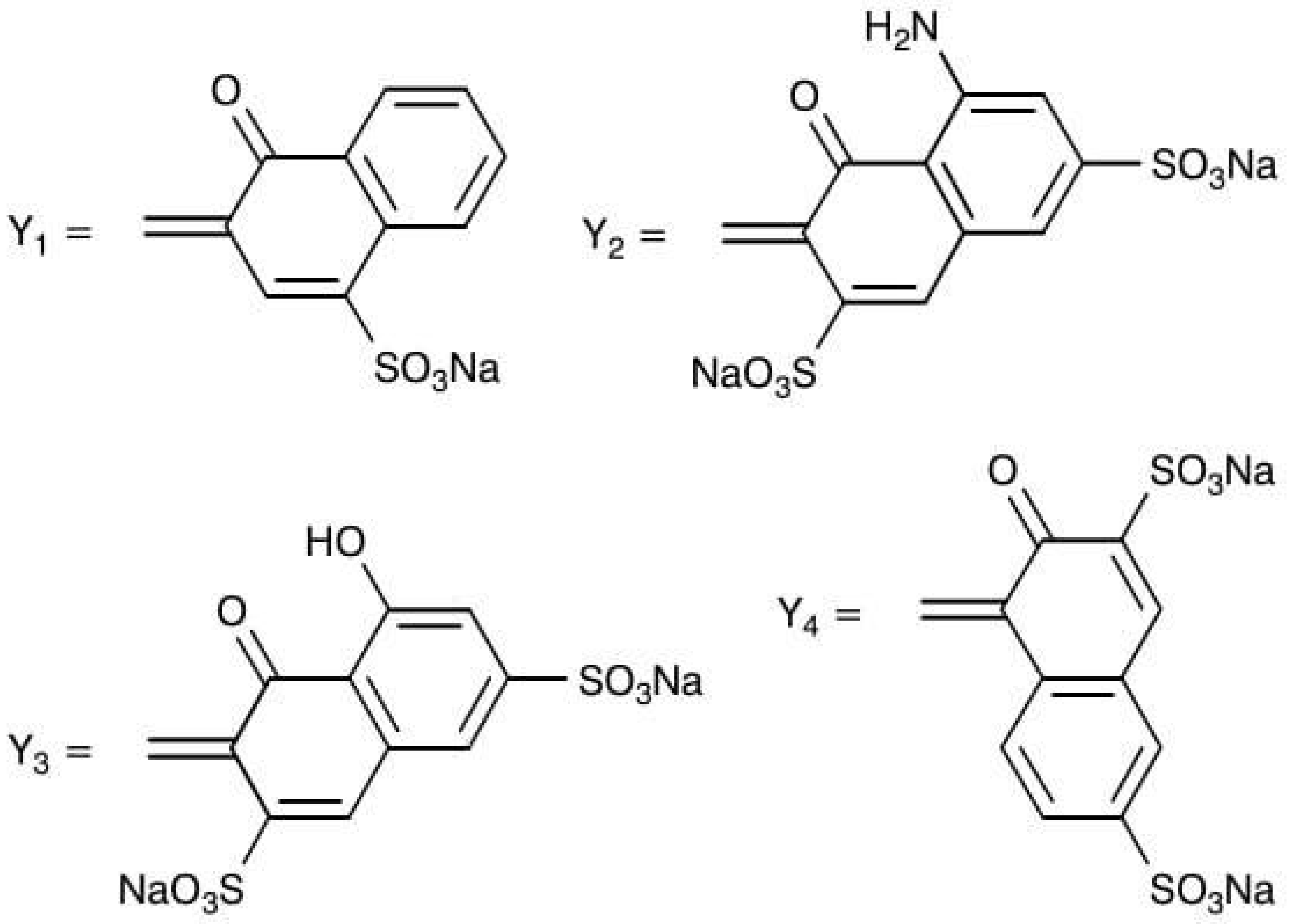


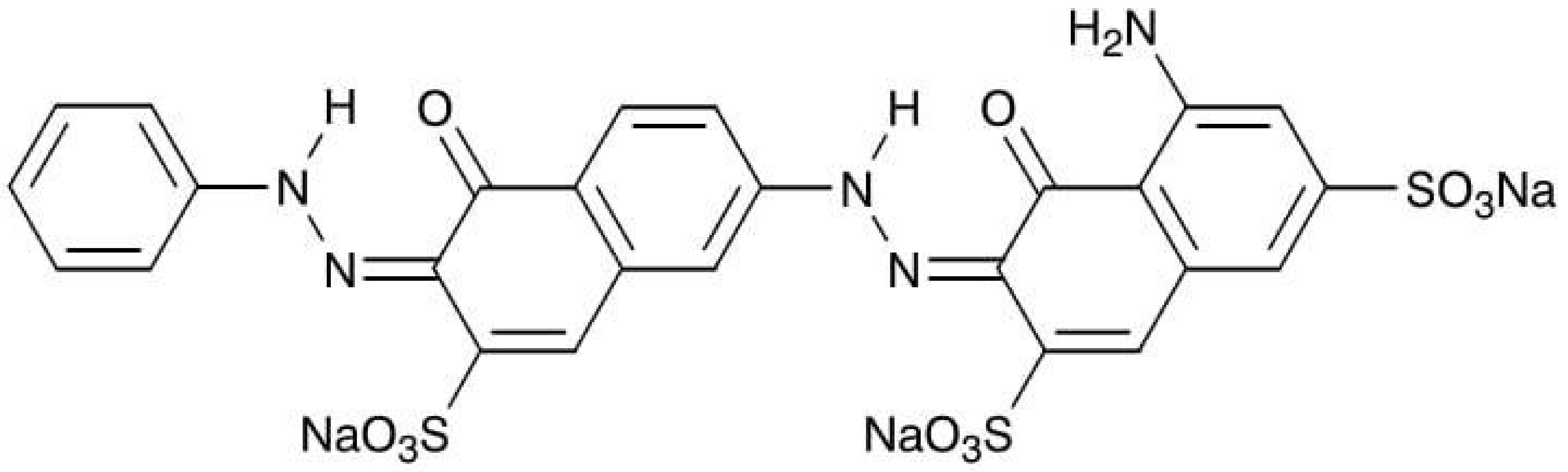
Table 3.6 Substantivity and structure of *p*-substituted monoazo naphthionic acid derivatives [68]

Substituents in structure 3.59		
Ar	X	Affinity (kJ/mol)
Thienyl	CH=CH	–15.8
Phenyl	CH=CH	–14.3
Thienyl	CONH	–13.1
Phenyl	CONH	–12.0
Thienyl	CO	–8.8
Phenyl	CO	–7.0

Table 3.7 Substantivity of thienyl monoazo dyes with various coupling components [68]

Coupling component	Structure	Affinity(kJ/mol)
Naphthionic acid	3.59; Ar = thienyl, X = CH=CH	–15.8
NW acid	3.60; Y = Y_1	–9.7
H acid	3.60; Y = Y_2	–9.4
Chromotropic acid	3.60; Y = Y_3	–7.1
R acid	3.60; Y = Y_4	–6.3

far as the angular constraints of the participating bonds will allow. Azo groups attached to central naphthylene residues are frequently oriented in 1,4- or 2,6-positions relative to one another. Typical central diamines that give linear dyes on tetrazotisation include *p*-phenylenediamine, benzidine, *p,p′*-diaminostilbene, *p,p′*-diaminodiphenylamine and *p,p′*-diaminodiphenylurea. For similar reasons, 1,4-bis(arylamino)anthraquinone vat dyes are markedly more substantive than their 1,5-disubstituted analogues.



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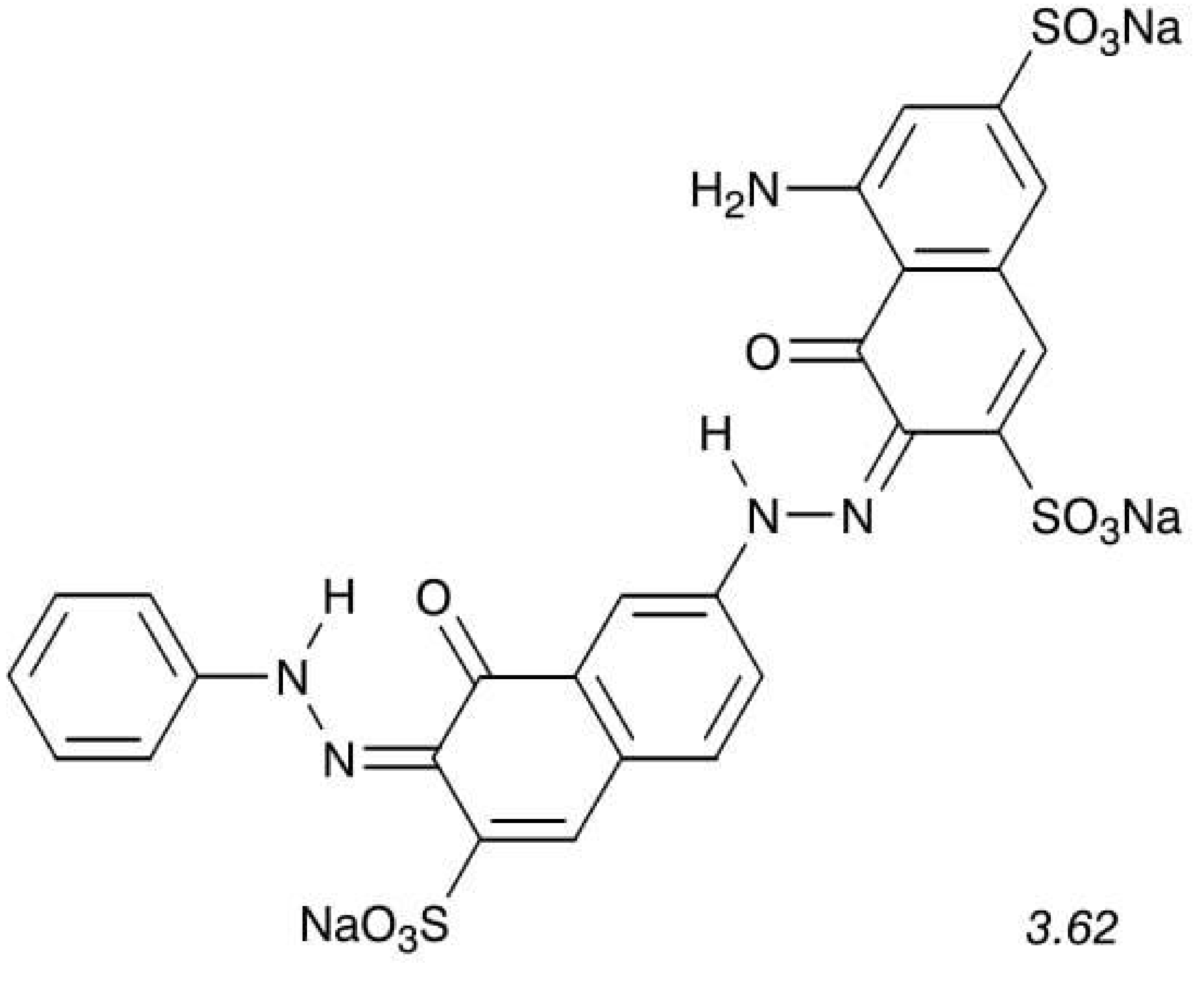

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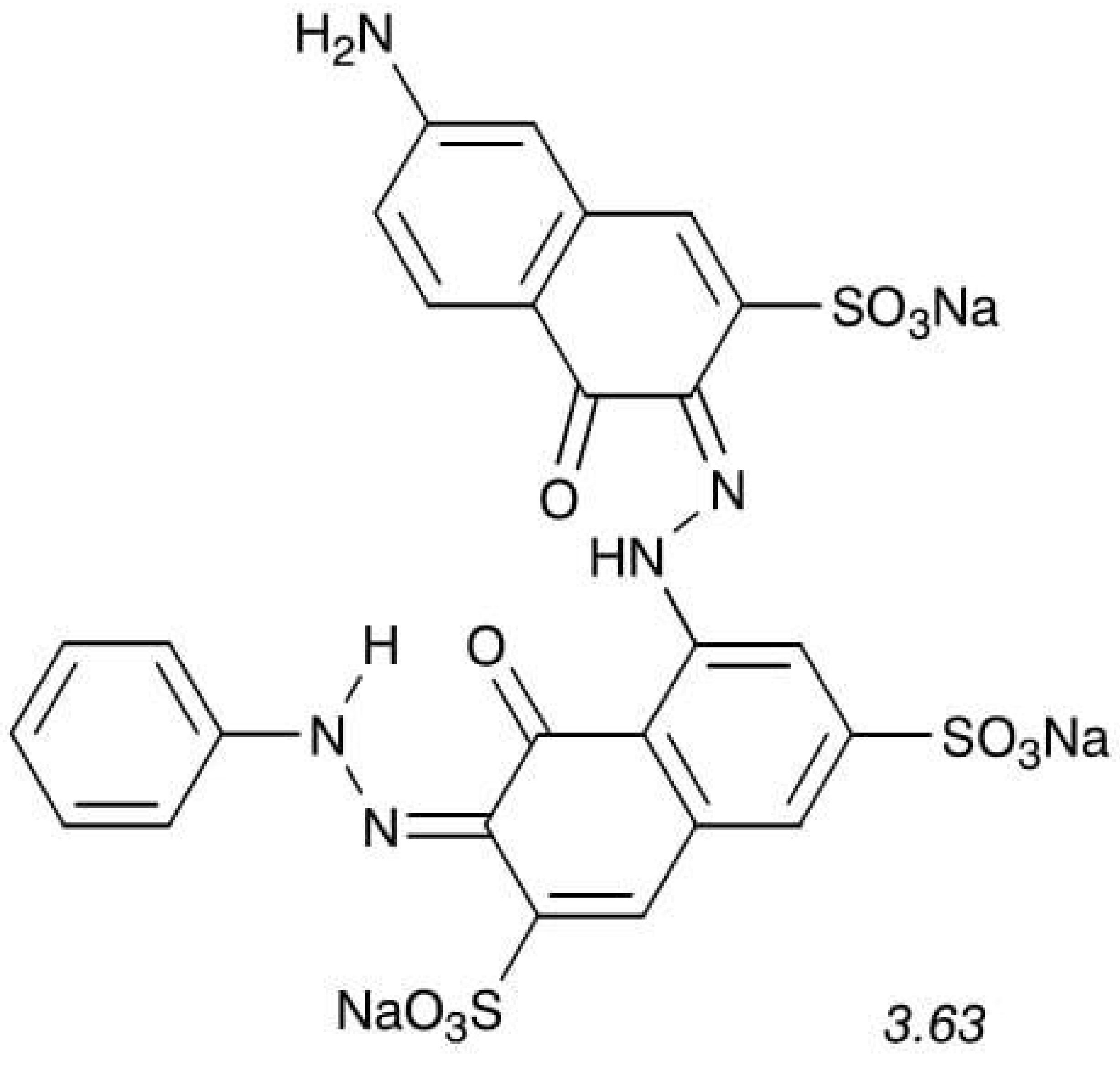
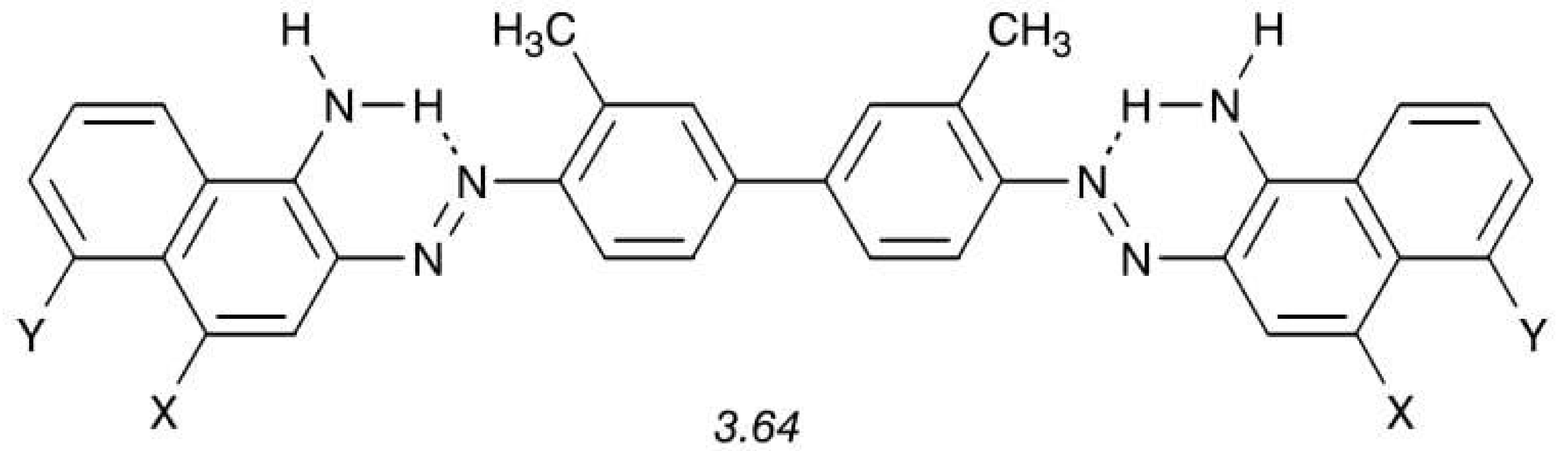


3.63

The ability to adopt an extended configuration has been recognised for many years to be a desirable feature of substantive dyes. It helps to explain why J acid is such a popular choice as a central component in unsymmetrical disazo dyes. For example, it is much easier for aniline→J acid→H acid (3.61) with the 2,6-naphthylene substitution pattern to adopt a linear conformation than for the similar disazo dyes aniline→γ acid→H acid (3.62) and aniline→H acid→J acid (3.63) with 2,7- and 2,8-disubstitution respectively.

A further refinement of the concept that linear conjugated systems such as aryl–azo–aryl–azo–aryl represented the preferred design for highly substantive molecules was the stipulation that the aryl nuclei must be able to adopt a coplanar conformation [69]. This favours the adsorption of one dye molecule onto another during the formation of laminar aggregates, as well as the multipoint adsorption of a dye molecule onto two or more glucoside units of a cellulose chain via hydrogen bonding sites. There are unequivocal examples that clearly demonstrate the validity of this interpretation. Thus CI Direct Red 2 (3.8; X = CH_3, Y = H) and other 3,3′-disubstituted analogues are markedly more substantive than their *meta* analogues with 2,2′-disubstitution (such as 3.8; X = H, Y = CH_3). These substituents adjacent to the central bond in these symmetrical disazo structures inhibit free rotation of the phenylene nuclei and thus prevent the adoption of a coplanar conformation.

The scope for intramolecular hydrogen bonding between each azo group and coupling component in symmetrical disazo structures of this kind also contributes significantly to the maintenance of coplanarity and hence to the affinity for cellulose. The number of commercial direct dyes in which coupling has been directed *para* to the amino or hydroxy substituent in the coupling component is much smaller than those manufactured by *ortho* coupling. Within the series of symmetrical *o*-tolidine disazo dyes in which the naphthionic acid of CI Direct Red 2 (3.64; X = SO_3Na, Y = H) is replaced in turn by Laurent's acid, Cleve's 6 and 7-acids, and finally Peri acid (Table 3.8), there is a marked lowering of affinity for the 6-, 7- and 8-sulpho derivatives compared with the first two members of the series [70]. Naphthylamine-4- and –5-sulphonic acids can only couple *ortho* to the amino substituent and the derived dyes preferentially adopt an extended coplanar arrangement (3.64) by intramolecular hydrogen bonding of the amino group to the more distant nitrogen atom of the adjacent azo group. In the remaining members of the series, however, coupling readily takes place in the *para* position (3.65) and the amino groups are no longer able to form intramolecular hydrogen bonds. Free rotation is possible on either side of the azo linkages and the preferred coplanar arrangement is no longer preferentially stabilised.



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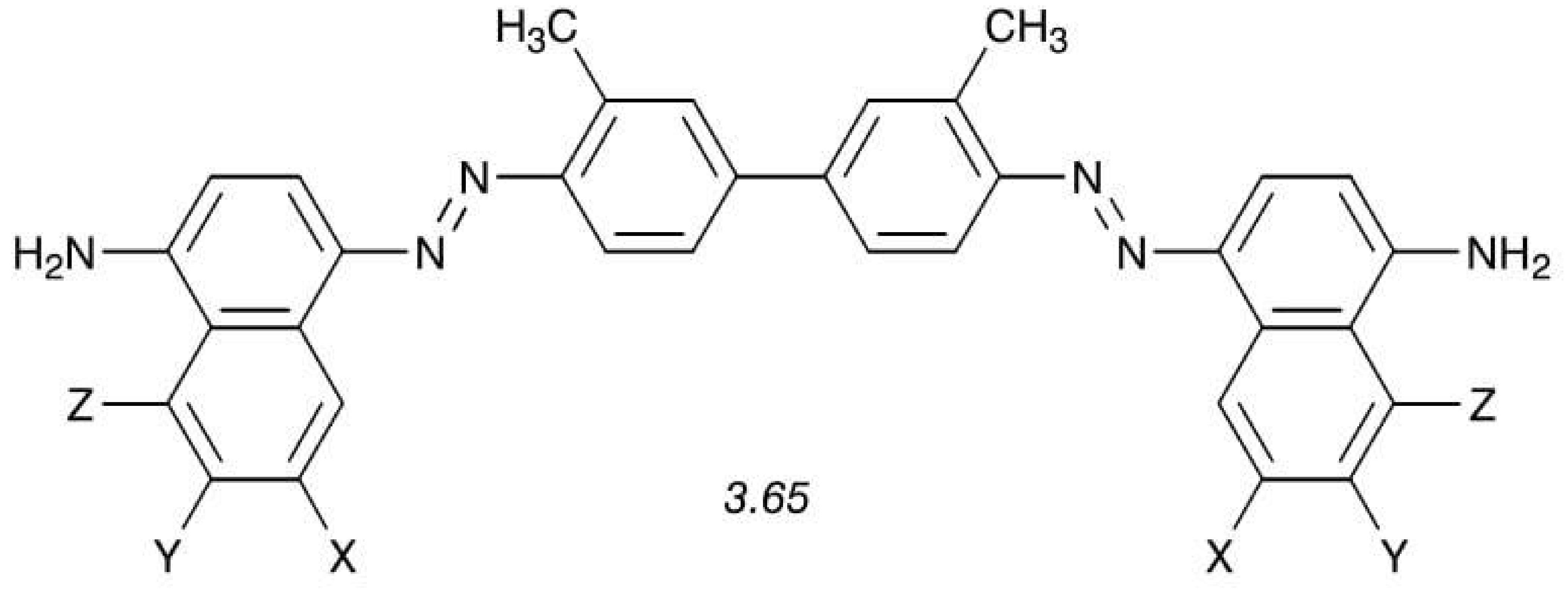

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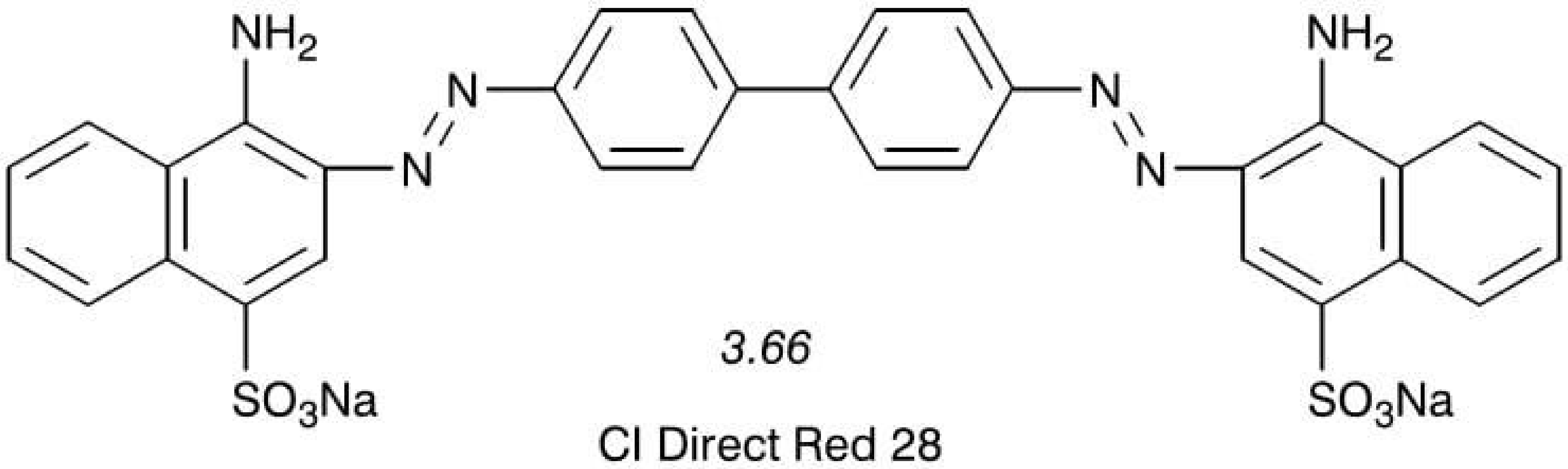
Table 3.8 Substantivity of symmetrical disazo dyes derived from naphthylamine monosulphonic acids [70]

Coupling component	Structure	Affinity(kJ/mol)
Naphthionic acid	3.64; X = SO_3Na, Y = H	–26.8
Laurent's acid	3.64; X = H, Y = SO_3Na	–28.0
Cleve's 6-acid	3.65; X = SO_3Na, Y = Z = H	–22.6
Cleve's 7-acid	3.65; Y = SO_3Na, X = Z = H	–22.2
Peri acid	3.65; Z = SO_3Na, X = Y = H	–23.4

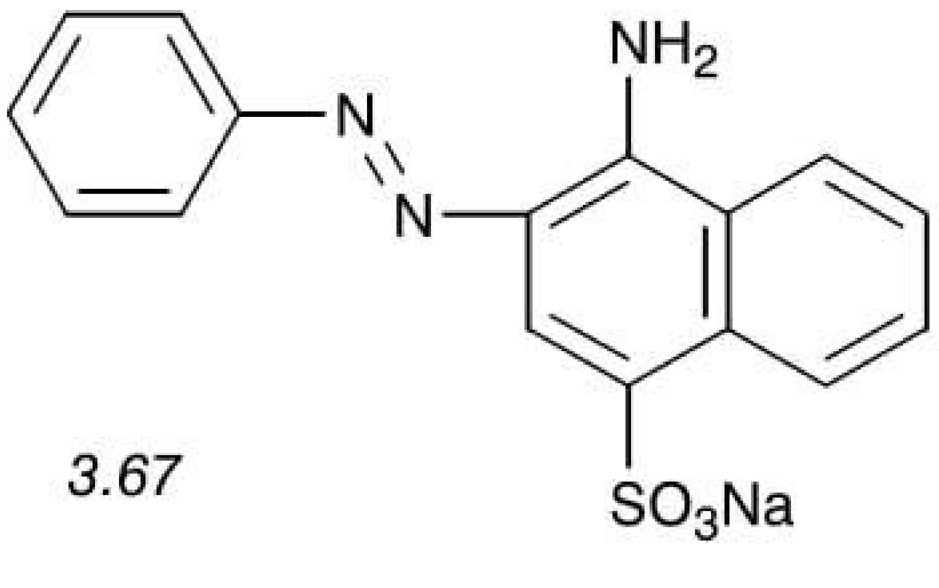
Vat dye molecules are relatively hydrophobic and are usually capable of assuming a coplanar configuration that favours aggregation in a laminar arrangement as well as the formation of multiple attachments to a segment of the cellulose chain. Hydrogen bonding can be invoked to account for the favourable influence of arylamino or benzoylamino substituents on the affinity of the parent anthraquinonoid nuclei in vat dye structures. Purely carbocyclic quinones such as pyranthrone, violanthrone and dibenzopyrenequinone must depend mainly on coplanarity, hydrophobic interaction and hydrogen bonding between dye keto groups and cellulose hydroxy groups. In any closely related series of vat dyes the affinity does seem to increase with molecular size, but the differences between members of different subclasses emphasise the specific influence of their characteristic structural features, especially nitrogen-containing groupings, on the forces of affinity.

A full interpretation of the relationships between direct or vat dye structure and substantivity for cellulose must take into account the contribution of multilayer adsorption of dye molecules within the pore structure of the fibre [71]. The great difference in substantivity between CI Direct Red 28 (3.66) and the monoazo acid dye (3.67) that is the 'half-size' analogue of this symmetrical disazo dye may be interpreted in terms of their relative tendencies to form multilayers within the fibre pores as a result of dye–dye aggregation. Saturation adsorption values of these two dyes on viscose fibres at pH 9 and 50 °C corresponded to monolayer coverage areas of approximately 90 and 11 m^2/g of internal surface respectively [72]. In view of the smaller molecular area and greater mobility of the 'half-size' acid dye, higher uptake than the direct dye would be anticipated if there were only a limited area of internal surface available for true monolayer adsorption.



3.66

CI Direct Red 28



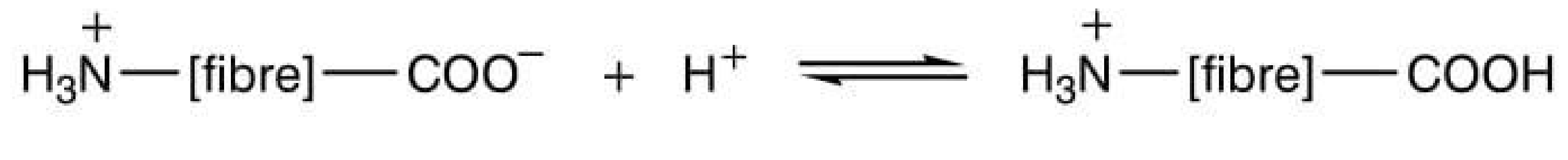
3.67

The much higher adsorption of the direct dye at saturation equilibrium can be explained satisfactorily on the basis that both dyes are adsorbed initially on essentially the same internal surface area, but the direct dye has a much greater tendency to aggregate and so build up readily into multilayers. The greater length of the direct dye molecule relative to the acid dye of similar cross-sectional area favours penetration into the intermicellar spaces between the cellulose fibrils, followed by multipoint adsorption onto the glucoside units or another dye molecule already adsorbed. Inorganic electrolytes assist powerfully in promoting these interactive forces leading to multilayer adsorption of direct dyes, since they are present in the intermicellar pore spaces as well as the external phase. Acid dyes aggregate much less readily in solution (section 3.1.2) and are thus less likely to form multilayered aggregates in the fibre pores.

The pore structure of cellulosic fibres has a decisive influence on direct dyeing. It can be defined using probe molecules of specific graduated sizes, measurement being by either the stationary non-solute water method or by chromatographic elution on a cellulose column. The distribution of pores can be determined from chromatographic values, revealing the accessibility of the inner voids to dye molecules of different sizes [73]. Pore structure data have been related to the adsorption and diffusion kinetics of the disazo dyes CI Direct Blue 1 (3.2) and Red 81 (3.7; X = H). The specific pore surface can be decisive for equilibrium uptake, whereas the porosity or the amount of free water can be important when interpreting differences in diffusion rate [74].

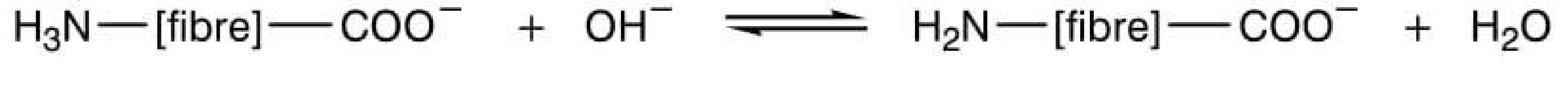
3.2.2 Dyeing of amide fibres with anionic dyes

Wool, silk and nylon contain both basic and acidic groups, amongst which by far the most important are amino and carboxy groups respectively. Just like the parent amino acids from which protein fibres are derived, all three of these polymeric amides show zwitterionic characteristics at pH values close to the isoelectric point, the pH at which the fibre contains equal numbers of protonated basic and ionised acidic groups. As the pH decreases below this point, the carboxylate anions are progressively neutralised by the adsorption of protons and the fibre acquires a net positive charge (Scheme 3.12). Conversely, as the pH rises above the isoelectric point, the fibre becomes negatively charged as a result of deprotonation of the amino groups by adsorption of hydroxide ions or other simple anions (Scheme 3.13).



$$\mathrm{H_3\overset{+}{N}{-}[fibre]{-}COO^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_3\overset{+}{N}{-}[fibre]{-}COOH}$$

Scheme 3.12



$$\mathrm{H_3\overset{+}{N}{-}[fibre]{-}COO^-} + \mathrm{OH^-} \rightleftharpoons \mathrm{H_2N{-}[fibre]{-}COO^-} + \mathrm{H_2O}$$

Scheme 3.13

The capacity of nylon or the protein fibres to adsorb simple organic or inorganic acids is closely equivalent to their respective contents of accessible amino groups. More complex dye anions, however, differ in their affinity for these fibres owing to nonpolar bonding between the hydrophobic portions of the dye molecule (alkyl substituents and unsubstituted aryl nuclei) and nonpolar side-chain or main-chain segments in the fibrous polymer. The contributions to dye anion affinity of electrostatic attraction to protonated amino groups in the fibre and hydrophobic interaction with nonpolar segments tend to mask any further influence of hydrogen bonding forces, although this form of bonding seems likely to reinforce the effects of the other factors. According to specific adsorption studies on wool, silk and nylon, the tendency of proton donor molecules to form hydrogen bonds with amide groups in these polymers is in the order: $ArOH > ArNHCOCH_3 > ArNH_2$, $ArNHR$, $AlkOH$.

As a general rule, the lower the dyebath pH the more rapid is the rate of initial adsorption by the amide fibre and the subsequent approach towards equilibrium exhaustion. Consequently, the attainment of a safely controllable rate of dyeing becomes easier the higher the pH at which dyeing begins. Eventually, however, a pH is reached at which the dyebath is no longer exhausted within a reasonable time.

Dyeing conditions are usually controlled to give a moderate initial rate of dyeing for optimum levelling, followed by a gradual lowering of pH by acid release to achieve as much exhaustion as possible at the end of the process. Selection of the preferred initial pH and rate of acidification is determined by the affinity of the dyes at neutral pH values. Neutral-dyeing affinity is dependent on the structural features and hydrophilic-lipophilic balance of the dye molecule.

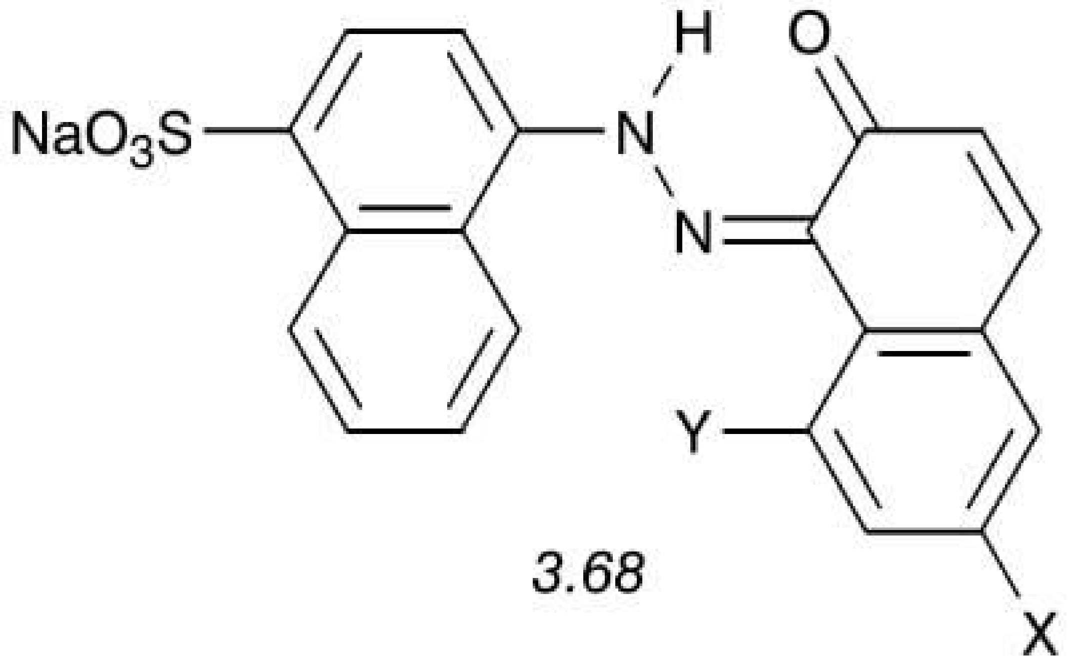
The degree of sulphonation of an acid dye (section 1.6.7) has a major influence on the profile of exhaustion values reached at various pH values on a specific substrate. At low pH in the absence of electrolyte all acid dyes show high exhaustion, irrespective of their sulpho group content. In neutral solution, on the other hand, multisulphonated dyes generally show much lower exhaustion than dye monosulphonates. Above the isoelectric point the fibre is negatively charged and the forces of electrostatic repulsion increase with the degree of sulphonation. Hydrophobic interaction permits adsorption of a dye monosulphonate onto the fibre surface in such a way that the charged group is directed outwards towards the dyebath phase.

The rate of dyeing of acid dyes of relatively small molecular size decreases with increasing degree of sulphonation. Simple monoazo monosulphonate types are rapidly absorbed but readily desorbed again. Thus they migrate easily but show extremely poor fastness to wet treatments. There are two main types of levelling acid dye:

(1) Disulphonated dyes of relative molecular mass (M_r) about 400–600 that are somewhat sensitive to dyeability differences in the substrate and show the lowest wet fastness of all dye classes used on wool

(2) Monosulphonated dyes of lower M_r (300–500) and slightly higher wet fastness that migrate more readily and cover dyeing faults (such as carbonising damage) more effectively.

In an early study of the dyeing of blends of normal and chlorinated wool with a series of naphthionic acid→2-naphthol dyes [75], the trisulphonated CI Acid Red 18 (3.68; $X = Y = SO_3Na$) showed the most marked contrast. Penetration of the hydrophobic epicuticle of normal wool by this hydrophilic dye was negligible in the initial stage of dyeing but chlorinated fibres were rapidly and deeply dyed. The monosulphonated Red 88 (3.68; $X = Y = H$), however, revealed relatively little contrast in dyeability between the two types of wool, whereas Red 13 (3.68; $X = SO_3Na$, $Y = H$) gave a degree of contrast intermediate between those of the other two dyes. Apparently the relatively hydrophobic 2-naphthol residue in CI Acid Red 88 is almost as effective a means of attachment to the epicuticle of normal wool as the negatively charged naphthionic acid residue is towards the hydrophilic surface of chlorinated wool.



3.68

There are three main subclasses of milling acid dyes:

(1) Monosulphonated dyes of M_r 500–600 are somewhat more hydrophobic than the monosulphonated levelling acid dyes. They also migrate and cover well but they are a little inferior to disulphonated milling dyes in wet fastness and thus have sometimes been described as 'half-milling' dyes;

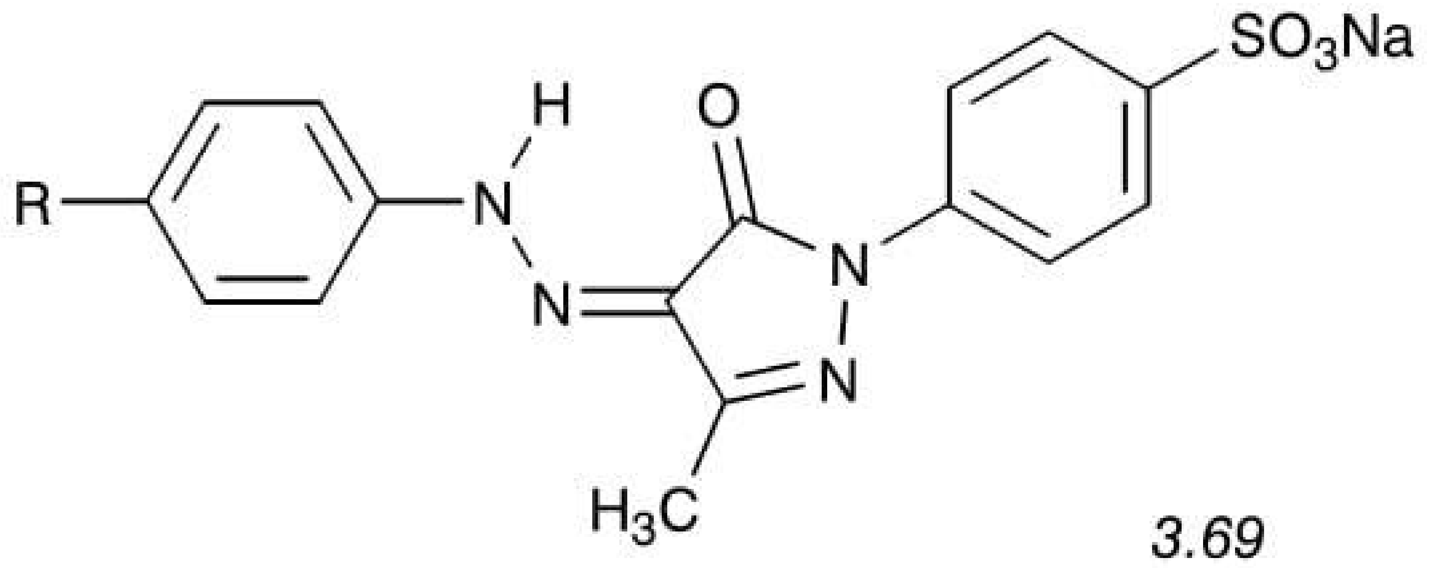
(2) Disulphonated dyes of M_r 600–900 diffuse much more slowly than typical levelling acid dyes. Thus they exhibit correspondingly higher wet fastness but their migration and coverage properties are inferior;

(3) Certain disulphonated milling acid dyes contain higher alkyl groups (such as butyl, octyl, dodecyl) to confer higher neutral dyeing affinity, better coverage of dyeability irregularities and exceptionally good wet fastness. They are sometimes described as 'super-milling' dyes to distinguish them from category (2), the largest of the three subclasses.

Direct evidence has been provided to demonstrate the contribution of hydrophobic interaction to the substantivity of milling dyes for wool [76]. In a series of monosulphonated phenylazopyrazolone dyes (Table 3.9), substantivity for wool increased with chain length in the alkyl series ($B \gg D > F$) but the increased polarisability of alkenyl groups almost completely negated this effect ($B \gg E$). Cyclisation of the saturated alkyl group produced maximum substantivity ($A > B$) and formation of an unsaturated aryl ring had a similar effect ($C \gg E$). Finally, a hydroxy substituent almost completely inhibited the hydrophobic interaction attributable to the ethyl group ($D > G$). It was evident from these results that coulombic interaction and hydrogen bonding played insignificant roles in these equilibria.

Table 3.9 Exhaustion of *p*-substituted phenylazopyrazolone dyes on wool [76]

Dye	Substituent (R) in 3.69	Exhaustion (%)
A	Cyclohexyl	85
B	n-Hexyl	65
C	Phenyl	59
D	Ethyl	17
E	Hexatrienyl	10
F	Hydrogen	8
G	2-Hydroxyethyl	3



3.69

Mordant dyes have always been important for the dyeing of wool. Chromium has become the only significant mordant because it yields exceptionally high fastness to light and wet treatments. Aftertreatment with dichromate is the only chroming process of any practical importance on wool. Chromic salts must be used on silk, however, which lacks the reducing power of wool to convert dichromate Cr(VI) anions to chromic Cr(III) cations. Despite the emergence of various ranges of metal-complex acid dyes and reactive dyes, chrome dyes still retain a market share at about one-third of all dyes for wool (Table 3.10).

Table 3.10 Estimated proportions of wool dyed worldwide in 1995 with different ranges of dyes [77]

Dye range	Proportion (%)
Chrome mordant dyes	29
1:2 Metal-complex acid dyes	29
Milling acid dyes	20
Levelling acid dyes	9
1:1 Metal-complex acid dyes	7
Reactive dyes for wool	6

The practical advantages of chrome dyes include economic build-up to full depths, good level-dyeing properties (M_r only 300–600) and excellent fastness after chromium-complex formation. Unfortunately, the marked change in colour of the dyeing during aftertreatment complicates the colour matching stage. Further drawbacks include the prolonged dyeing procedure, oxidative damage to the wool and the environmental hazards associated with chromium-containing effluent. All dyes requiring the use of chromium compounds have come under increasing pressure recently for ecological reasons. Hexavalent chromium in the form of dichromate salts is causing concern because of its toxic and mutagenic properties requiring special safety measures in handling [77].

The 1:1 metal-complex acid dyes are almost all monosulphonates of M_r 400–500. This gives them dyeing characteristics not unlike those of the monosulphonated levelling acid dyes, with good migration and coverage of damaged wool. In fabric dyeing it is usual to apply the 1:1 metal-complex dyes at pH 2, sacrificing optimum physical properties of the wool in favour of better migration and coverage. The 1:2 metal-complex dyes that were originally developed following the successful adoption of the 1:1 metal-complex types were symmetrical structures free from ionic solubilising groups and some were applied from aqueous dispersion. Most dyes of this type now used on wool or nylon are solubilised by one nonionised but polar group, such as sulphonamide ($-SO_2NH_2$), methylsulphonamide ($-SO_2NHCH_3$) or methylsulphone ($-SO_2CH_3$) on each of the dye ligand groups, which are often dissimilar. These are more expensive to manufacture than the traditional symmetrical structures, however, and share most of their drawbacks. They show high neutral-dyeing affinity and very good fastness to light, although they are significantly inferior to chrome dyes in fastness to the most severe wet treatments. Such hydrophobic structures favour coverage of dye-uptake variations in wool but their high affinity can cause rapid initial strike and they diffuse and migrate slowly (M_r 700–900).

Advances were made in developing dyeing methods and auxiliary products (sections 5.8.3 and 12.2) to improve the level-dyeing and coverage properties of sulphonated 1:2 metal-complex dyes, leading to the widespread adoption of the more economical of the monosulphonates in uses where unsulphonated dyes were previously considered essential. Sulphonated 1:2 metal-complex dyes may be divided into two subclasses:

(1) Unsymmetrical monosulphonated dyes of M_r 700–900. The presence of the ionic solubilising group reduces manufacturing costs and minimises the staining of adjacents in severe wet tests, but these dyes are more sensitive to dye-affinity differences than are the unsulphonated 1:2 metal-complex types.
(2) Disulphonated dyes of M_r 800–1000, many of them symmetrical in structure. Although often cheaper to manufacture than the unsymmetrical monosulphonates and the unsulphonated types, these slow-diffusing complexes have intrinsically poor levelling and migration properties.

Reactive dyes for wool are unmetallised acid dye structures that contain reactive groups capable of forming covalent bonds with nucleophilic sites in wool. Several types of reactive system have proved effective on wool, the most important being α-bromoacrylamide, 5-chloro-2,4-difluoropyrimidine and the *N*-methyltaurine precursor of vinylsulphone. Special amphoteric levelling agents were developed to minimise the inherent skittery dyeing properties of these relatively hydrophilic dyes (section 12.7.2).

Inherently more expensive than traditional dyes for wool, reactive dyes also require aftertreatment with ammonia to ensure optimum fixation and wet fastness. Consequently, their usage has been limited (Table 3.10) mainly to bright dyeings on machine-washable wool and other high-quality goods. Their moderate to good levelling and migration before fixation (M_r 500–900, usually two or three sulpho groups), together with excellent wet fastness make them highly suitable for dyeing shrink-resist wool, usually in slubbing or yarn form.

If the wool cuticle is damaged by local chemical attack, abrasion or exposure to light, more rapid strike of dye occurs on the exposed cortical cells. At low dyeing temperatures all anionic dyes are taken up preferentially by damaged fibres and fibre tips [78], but at temperatures close to the boil the more polar the dye the stronger is the preferential absorption by damaged fibres [79]. Dyes of low $M_{r,}$ particularly milling acid and sulphonated 1:2 metal-complex dyes, cover such differences well by subsequent migration away from the tip towards the undamaged root and good coverage can be promoted using cationic auxiliaries. These interact with anionic dyes to form hydrophobic complexes that are less sensitive to differences in fibre dyeability. Chrome dyes reveal a marked contrast between root and tip, since both the mordant and the dye are preferentially absorbed by the damaged tips and the reducing action of the cystine breakdown products resulting from wool damage accelerates the conversion of dichromate Cr(VI) to chromic Cr(III) ions. Most reactive dyes are highly sensitive to dye-affinity variations, especially on unchlorinated wool.

Normal nylon 6.6 fibres contain only about 35–45 milliequiv./kg of amine end groups and this limits the build-up attainable with the hydrophilic levelling acid dyes. Differential acid-dyeable nylon variant yarns can be made by modifying the amino-group content. Deep-dye (60–70 milliequiv./kg) and ultra-deep (>80 milliequiv./kg) variants are obtained by the inclusion of a primary aliphatic diamine containing a tertiary amino group, such as *N,N*-bis(2-aminoethyl)piperazine, in place of some of the hexamethylenediamine used in manufacture of the normal polymer. Pale-dye nylon (15–20 milliequiv./kg) is made by reacting a proportion of the amine end groups in the normal polymer with a suitable blocking reagent such as γ-butyrolactone. Basic-dyeable nylon is produced by replacing some of the adipic acid used in the polymerisation by a suitable tribasic acid, such as 5-sulphoisophthalic acid. The use of acid, basic and disperse dyes to achieve multicoloured effects on differential dyeing nylon has been described in detail elsewhere [80].

The distribution of an acid dye between the components of blends of acid-dyeable nylon variants depends on the dyeing conditions and the molecular structure of the dye, especially the degree of sulphonation. At a given pH in the neutral region, dyebath exhaustion of a series of dyes differing only in degree of sulphonation decreases as the number of sulpho groups in the molecule increases. These differences in substantivity become more marked as the content of basic groups in the fibre increases, so that the deeper-dyeable variants are more sensitive than the normal fibre to differences in degree of sulphonation within the series of dyes. Consequently, more highly sulphonated dyes give better differentiation between the variant yarns at a given pH than the less-sulphonated dyes with higher neutral-dyeing affinity.

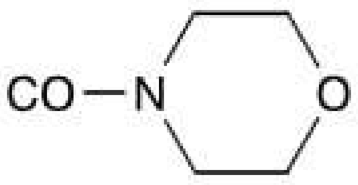
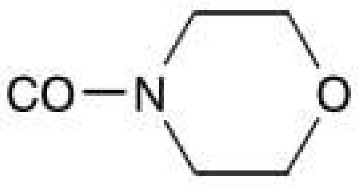
3.2.3 Dyeing of ester fibres with disperse dyes

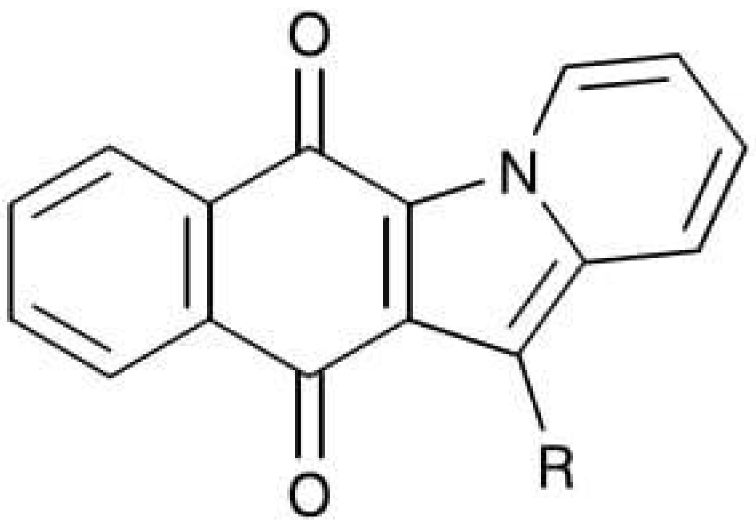
Since disperse dyes and ester fibres (cellulose esters and polyester) do not contain any ionic groups, dye-fibre attraction clearly depends on hydrogen bonding, dipole–dipole interaction and dispersion forces. Simple nonionised proton donors, such as phenol, are readily adsorbed by cellulose acetate and this has been taken as evidence of hydrogen bonding between the phenolic hydroxy groups and keto groups in the polymer. Most disperse dye structures contain proton-donating groups such as hydroxy and amino, as well as proton acceptors such as keto, methoxy, azo and dimethylamino groups. Refractometric studies have demonstrated that the α-keto hydrogen atoms in the acetate grouping $-OCOCH_3$ are sufficiently polarisable to take part in hydrogen bonding with proton acceptors [81]. Thus all the polar groups in a disperse dye molecule can contribute to its affinity for an ester fibre and not merely those with proton-donating character.

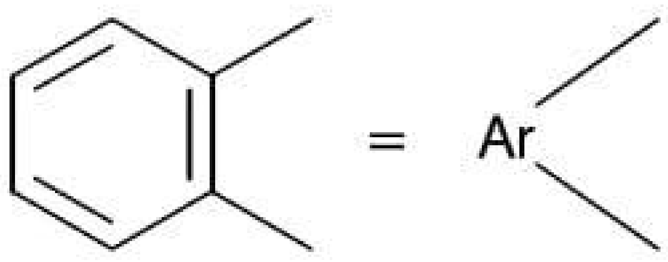
Monolayer experiments have indicated that face-to-face complexing occurs between azo disperse dye molecules and the hexa-acetylcellobiose units of cellulose triacetate, with the molecular segments lying parallel [82,83]. The relatively hydrophobic disperse dye molecule leaves the aqueous dyebath and penetrates between the polymer chains, entering a nonpolar environment where water molecules are unable to follow. New sites for adsorption become accessible as the dye molecule diffuses further into the amorphous regions of the fibre. The more numerous the substituents on the dye molecule that can interact with the polymer segments, the more it is able to break the interchain bonds of the fibre structure. Thus the greater the bonding capacity of a disperse dye molecule, the higher will be its saturation limit in the fibre.

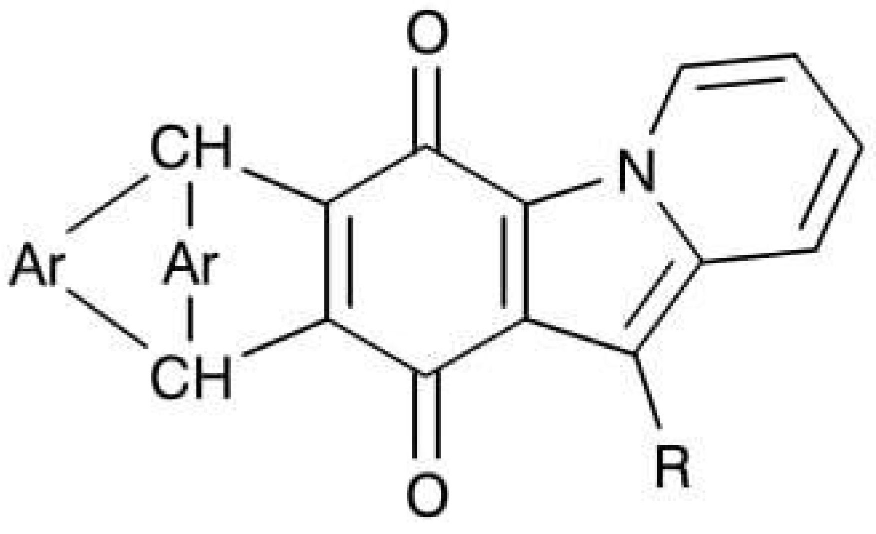
It is possible to account for the absorption of any disperse dye by cellulose acetate, triacetate or polyester in terms of the combined action of powerful hydrogen bonds and weak dispersion forces. The latter forces (*p*-bonding) between aryl rings in the dye and terephthalate residues make a more important contribution on polyester, but on polypropylene only weak aliphatic dispersion forces can operate [84]. Provided the dye molecule is planar and can lie flat against the cyclic segments of the ester polymer, all polar groups on the fringes of the rings have the potential to contribute to the overall strength of the dye-fibre multiple bonding. This accounts for the much higher affinity of planar disperse dye molecules compared with nonplanar analogues (Table 3.11). Partition coefficient in this table is defined as the ratio of the concentration (mol/kg) of dye in cellulose acetate to that (mol/l) in water.

Table 3.11 Partition coefficient and saturation value of disperse dyes on secondary cellulose acetate [85]

Dye structure	Substituent (R)	Partition coeff.	Satn. Value(mol/kg)
3.70	$COOCH_2CH_3$	998	0.218
3.71	$COOCH_2CH_3$	39	0.0319
3.70	$CONHCH_2CH_2OH$	194	0.135
3.71	$CONHCH_2CH_2OH$	2.6	0.0031
3.70		216	0.212
3.71		17	0.018







3.70 (planar)

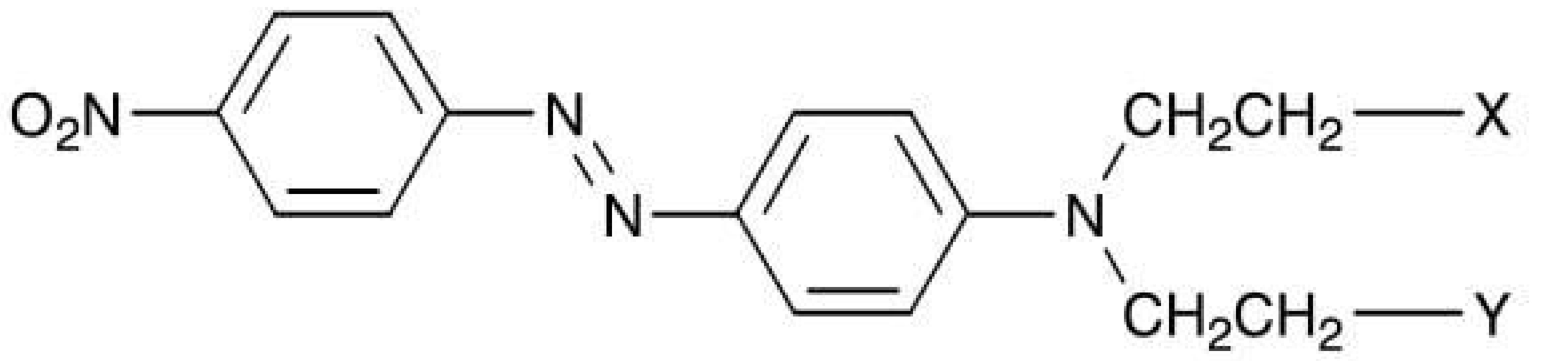
3.71 (non-planar)

Measurements of aqueous solubility and partition coefficient between cellulose acetate and water were compared for thirty disperse dyes and an approximate inverse relationship was postulated [60]. This can only be valid to a limited extent, however, because the partition ratio also depends on the saturation solubility of the dye in cellulose acetate. This property varies from dye to dye and is not directly related to aqueous solubility. The solubilities of four dyes in a range of solvents were compared with their saturation values on cellulose acetate. Solubilities in benzene showed no significant correlation. With the other solvents the degree of correlation increased in the order: ethanol < ethyl acetate < 20% aqueous diethylene glycol diacetate ($CH_3COOCH_2CH_2OCH_2CH_2OCOCH_3$). The last-named compound was suggested as a model with polar groups similar to those in cellulose acetate [86].

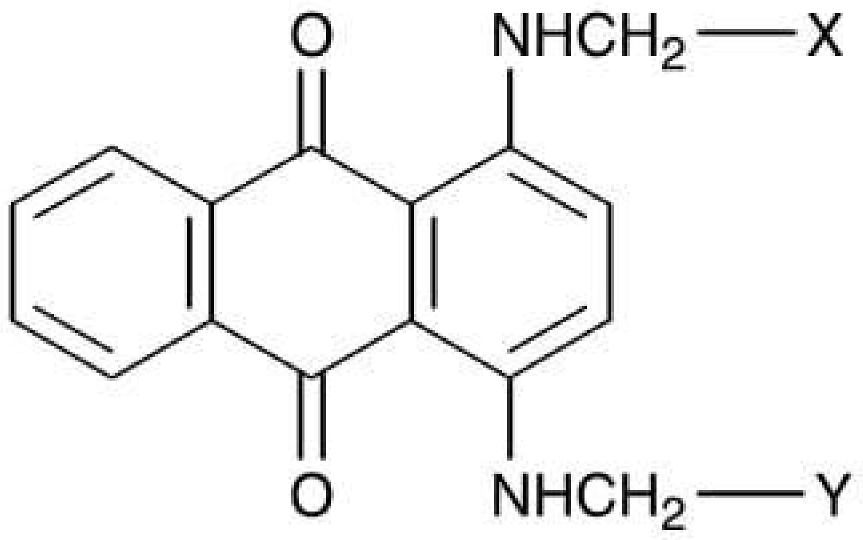
Dyes containing hydrophilic *N*-2-hydroxyethyl groups interact with unsubstituted hydroxy or keto groups in cellulose acetate by hydrogen bonding, whereas dyes with more hydrophobic *N*-alkyl substituents depend much more on nonpolar bonding. Hence dyes of the latter type have more affinity for cellulose triacetate or polyester than those of the former type, which are more suitable for acetate dyeing. Unsymmetrically disubstituted dyes often give higher absorption on secondary acetate than their symmetrical analogues (Table 3.12), presumably because they can readily participate in both types of dye–fibre bonding mechanism.

Table 3.12 Solubility of disubstituted dyes in secondary cellulose acetate [86]

Dye structure	X	Y	Solubility at 80 °C (g/kg)
3.72	H	H	ca 2.4
3.72	H	OH	18
3.72	OH	OH	14
3.73	H	H	ca 4.6
3.73	H	CH_2OH	22
3.73	CH_2OH	CH_2OH	6.6



3.72



3.73

In order to achieve efficient build-up to heavy depths when dyeing cellulose acetate at 80 °C it is customary, particularly for navy blues, to use a mixture of two or more components of similar hue. If these behave independently, each will give its saturation solubility in the fibre. In practice, certain mixtures of dyes with closely related structures are 20–50% less soluble in cellulose acetate than predicted from the sum of their individual solubilities [87]. Dyes of this kind form mixed crystals in which the components are able to replace one another in the crystal lattice. The melting point depends on composition, varying gradually between those of the components, and the mixed crystals exhibit lower solubility than the sum of solubilities of the component dyes [88]. Dyes of dissimilar molecular shape do not form mixed crystals, the melting point curve of the mixture shows a eutectic point and they behave additively in mixtures with respect to solubility in water and in the fibre.

Quite small variations in disperse dye structure can markedly modify substantivity for polyester [89]. This is evident from Figure 3.4, where the two blue dye structures differ only in the 3-acylamino substituent of the diethylaniline coupling component. Replacing acetylamino by propionylamino in dye 3.74 increases the colour yield by at least 30% for a 1.5% depth applied to polyester fibre for 45 minutes at 130 °C. An even more striking example is provided in Figure 3.5, illustrating two isomeric greenish blue dyes applied to polyester under the conditions already specified. In this case, replacement of the *N*-n-hexyl group in dye 3.75 by *N*-1-methylpentyl increases the colour yield at 0.5% depth by about 25%.

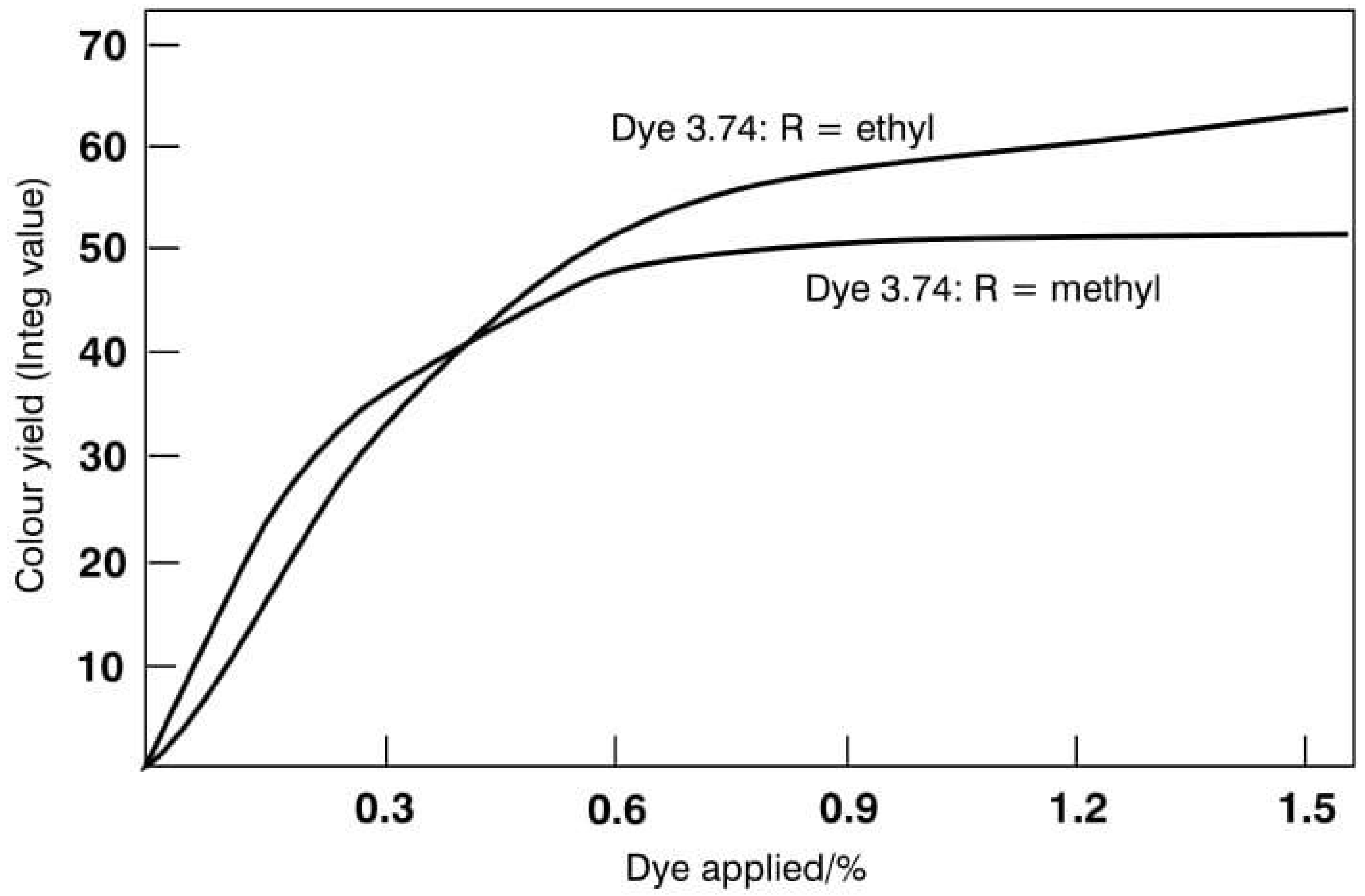


Figure 3.4 Colour yield of acylamino-substituted blue monoazo disperse dyes [89]

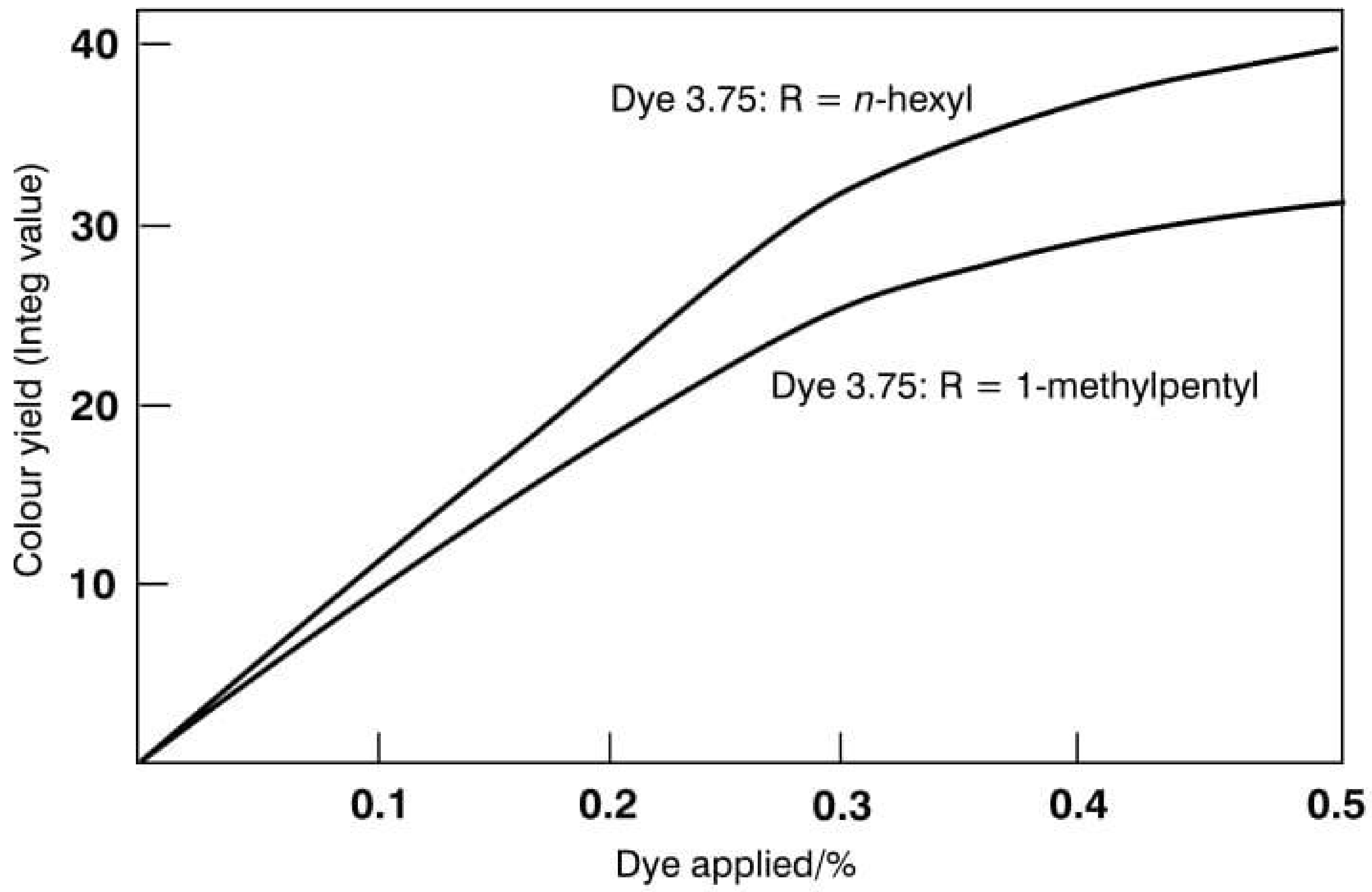
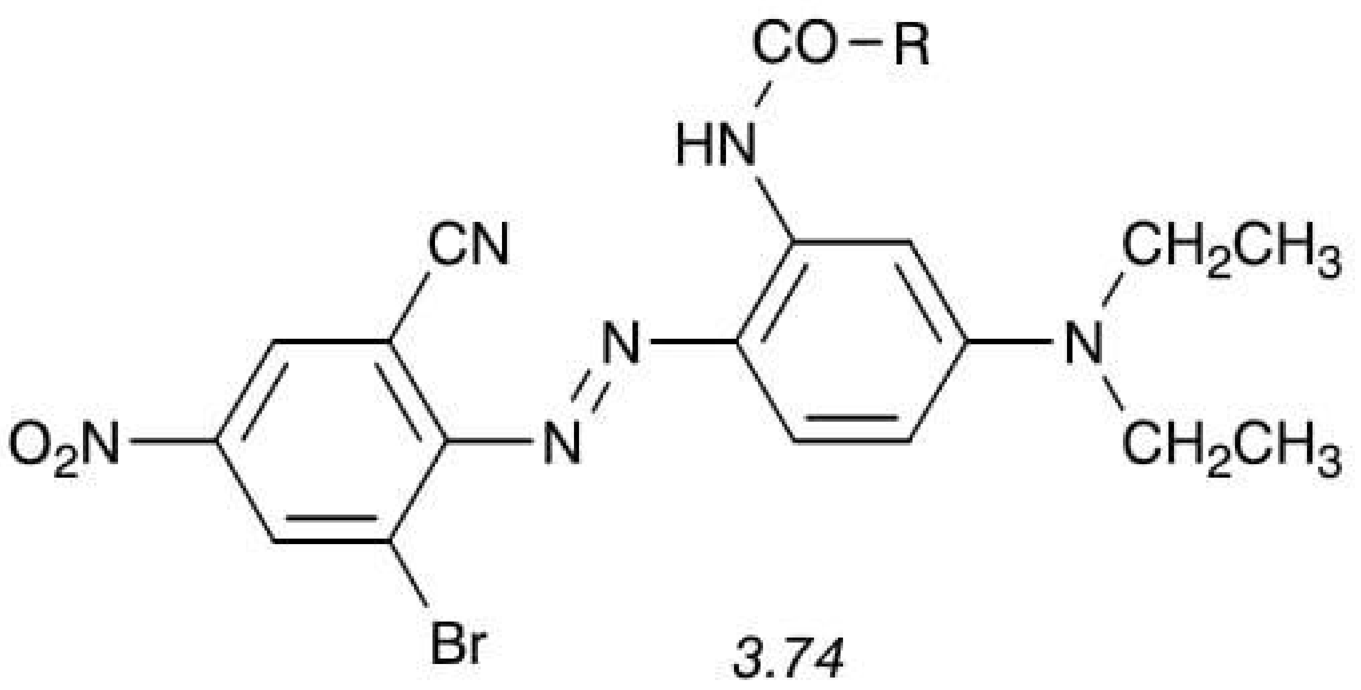
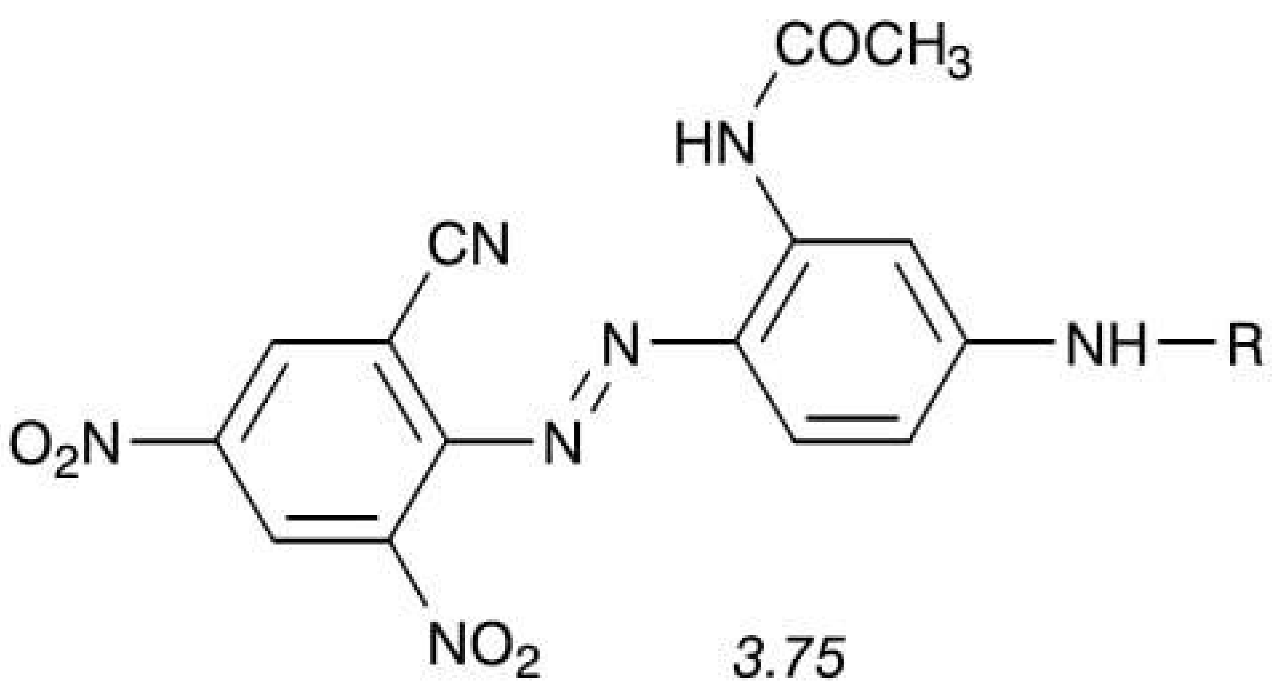


Figure 3.5 Colour yield of N-alkylated greenish blue monoazo disperse dyes [89]

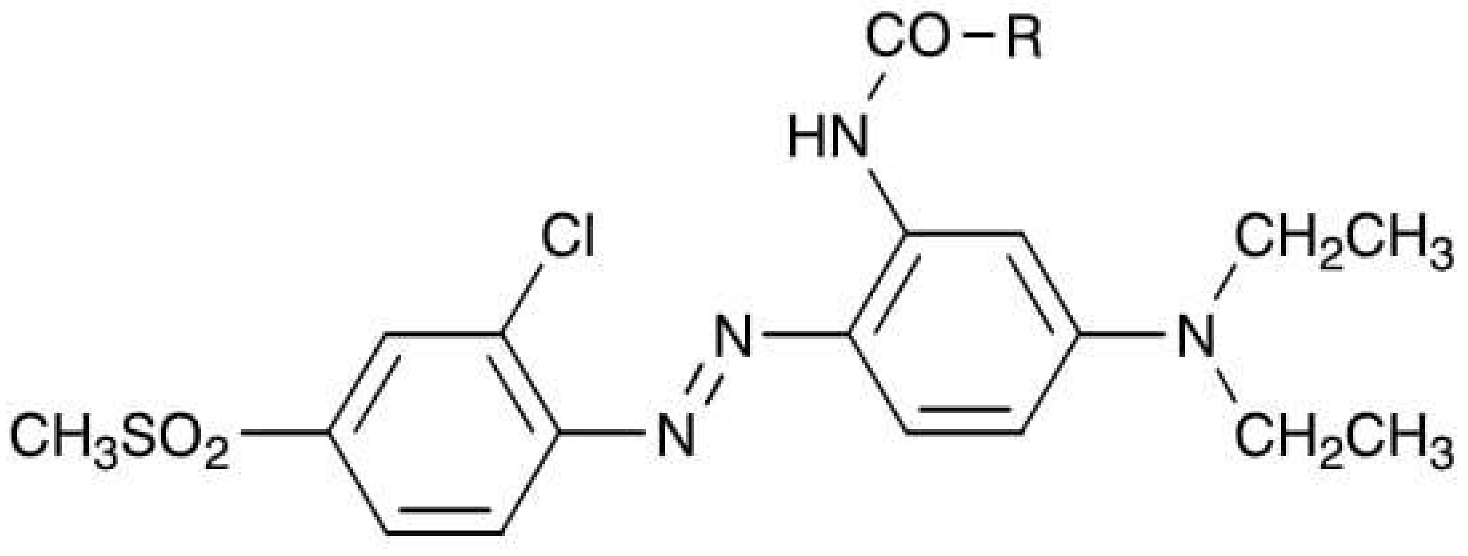


3.74



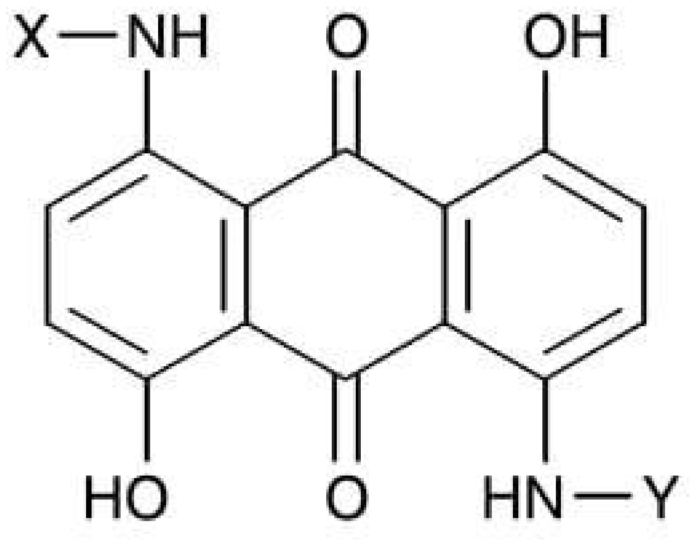
3.75

One of the criteria that determine the substantivity of disperse dyes for ester fibres is that the solubility parameter of the dye must be within one unit $(cal/cm^3)^{½}$ of that of the fibre [90]. Thus the 3-acetylamino dye (3.76; R = CH_3) with a solubility parameter(s) of 11.3 has much higher substantivity for polyester (s = 10.8) than has the 3-propionylamino analogue (3.76; R = CH_2CH_3, s = 13.0). The effects of dyeing auxiliaries on the exhaust dyeing process can also be interpreted by reference to the solubility parameters of fibre, dye and auxiliary [91]. The solubilities of six azo disperse dyes in water and polyester were determined and the thermodynamic parameters influencing solubility were calculated. Water solubility is governed by the mixing enthalpy but this does not play a role in the polyester environment and cannot be predicted satisfactorily from solubility parameters [92].



3.76

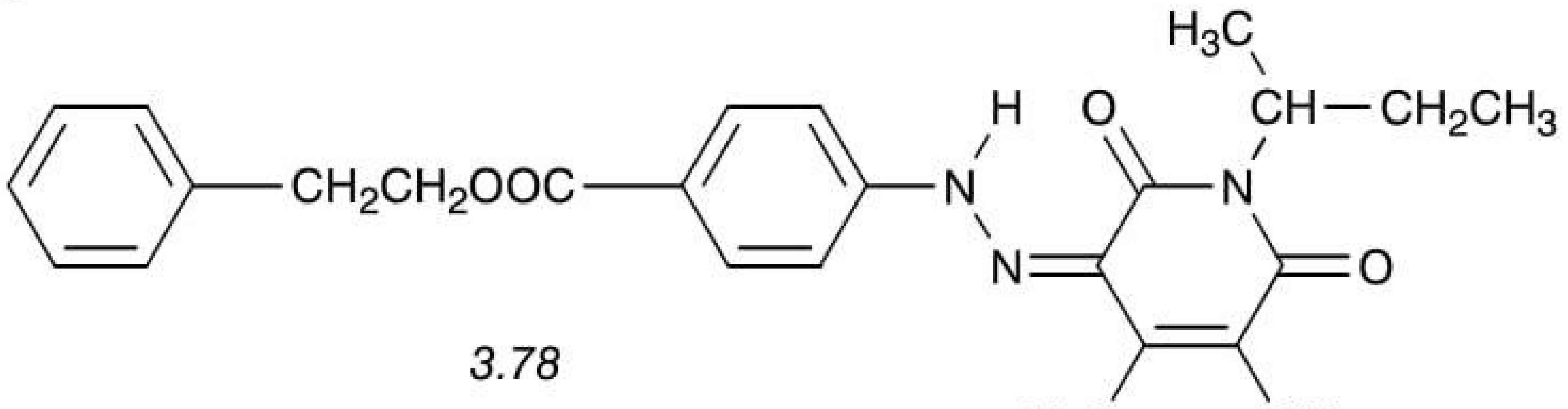
Derivatives of diaminoanthrarufin (3.77; X = Y = H) and its 1,8-dihydroxy-4,5-diamino isomer (diaminochrysazin) have been among the most widely used anthraquinone dyes for ester fibres. For example, methylation of diaminoanthrarufin gives CI Disperse Blue 26, a mixture of several components. Study of the pure *N*-alkylated derivatives from the base confirmed that monosubstitution (3.77; X = H, Y = alkyl) gives mid-blue dyes with excellent dyeing properties and acceptable fastness on polyester, but the bis-alkyl dyes (3.77; X = Y = alkyl) are greener and inferior in application properties. Mixtures of the unsubstituted base with alkylated components, as obtained industrially, were especially advantageous for build-up to heavy depths, however [93].



3.77

The effects of disperse dye-substrate interaction on the tensile properties of coloured poly(ethylene terephthalate) film was examined recently [94]. Incorporation of various hydroxy derivatives of anthracene and anthraquinone into the polymer gave indications that aggregation of dye molecules within voids was favoured when their affinity for the substrate was inadequate. Lowering of the glass-transition temperature (T_g) of polymers was investigated recently by incorporating various concentrations of a series of yellow or orange disperse dyes of increasing M_r, namely *p*-nitroaniline, *p*-nitrophenylazoaniline (CI Disperse Orange 3), *p*-nitrophenylazodiphenylamine (CI Disperse Orange 1) and the azopyridone CI Disperse Yellow 231 (3.78). As expected, the T_g values were lowered with increasing concentrations of dye in the polymer and on poly(vinyl butyral) the degree of lowering of T_g

increased in the order of increasing M_r of the dye present. On a copolymer of vinyl chloride and vinyl acetate, however, the degree of lowering of T_g with Yellow 231 was less than with Orange 1 or Orange 3, suggesting that Yellow 231 interacts in different ways with these two polymers [95].



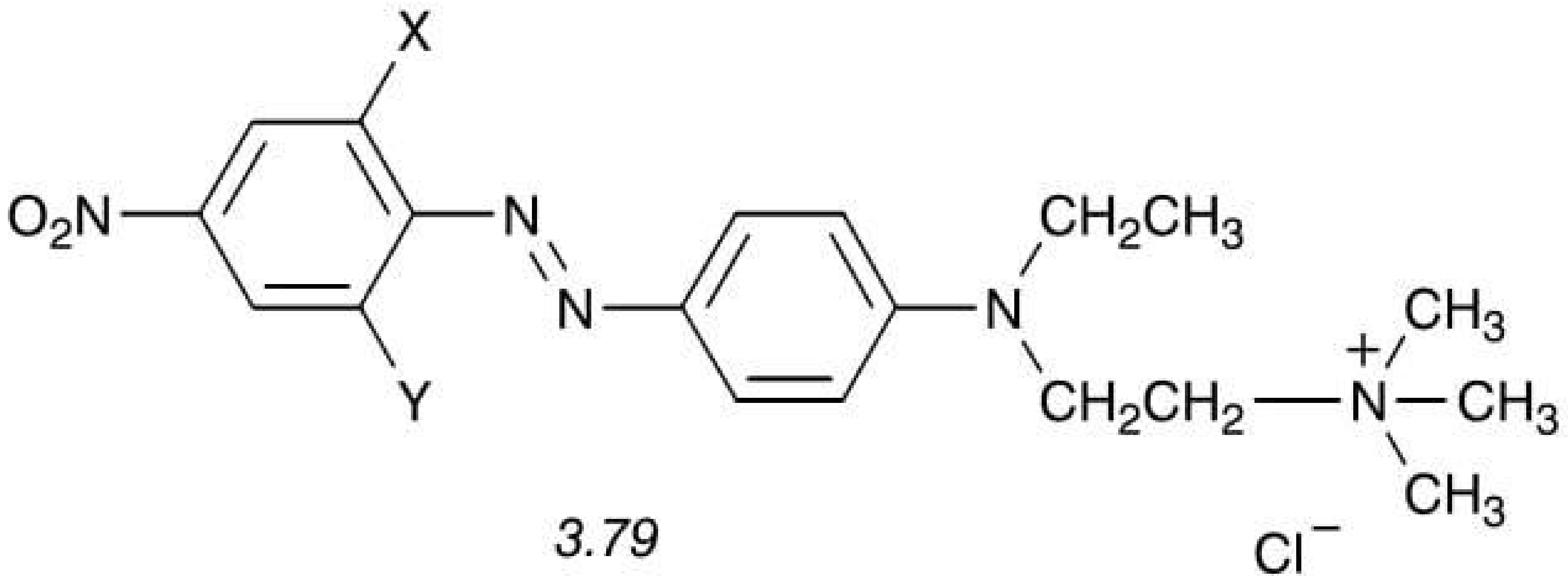
3.78

CI Disperse Yellow 231

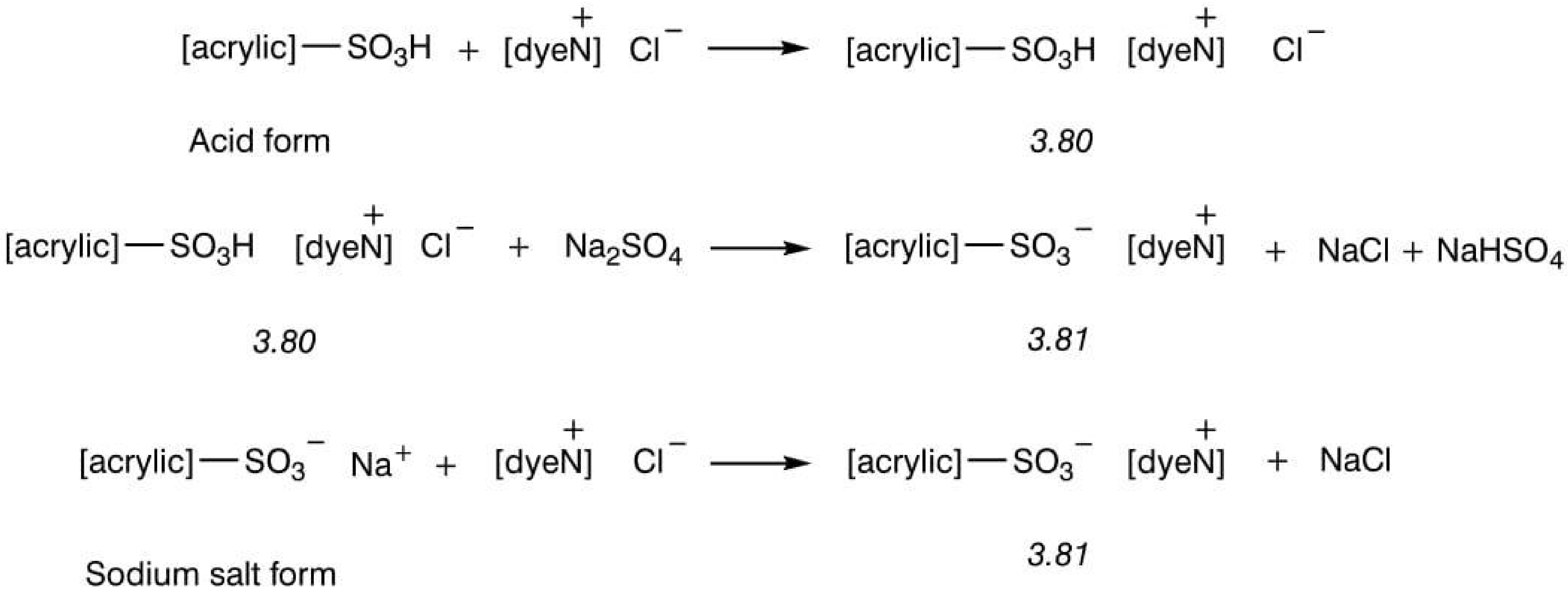
3.2.4 Dyeing of acrylic fibres with basic dyes

Most acrylic copolymer fibres contain sulphate and sulphonate groups on the polymer chains, derived from the inorganic redox catalysts (potassium persulphate and sodium bisulphite) that initiate the polymerisation reaction. The adsorption of basic dyes at low pH occurs mainly on these strongly acidic groups [96–99]. Carboxylic groups are sometimes present, however, if benzoyl peroxide has been used as initiator, resulting in dyeing behaviour that varies considerably more with dyebath pH [100]. The concentration of strongly acidic sites for dye adsorption in an acrylic fibre, as determined by sulphur analysis or by non-aqueous titration with a suitable base, agrees extremely well with saturation values derived from Langmuir isotherms defining the uptake of basic dyes [97,101]. This correspondence provides excellent confirmation that the dyeing mechanism is essentially a process of ion exchange.

In commercial acrylic fibres the strongly acidic groups are normally stabilised in sodium salt form. If this is transformed into the acid form during preparation, anomalous colour changes (halochromism) may take place in the subsequent dyeing stage. Thus when an acrylic fibre prepared in the free acid form was dyed at 80 °C with CI Basic Orange 33 (3.79; X = Y = H) the dyeing became increasingly much redder than normal, only reverting slowly to the usual orange hue after prolonged dyeing for 1.5 hours or more. A control dyeing on the same fibre prepared as the sodium salt showed no hue change, building up to the normal orange hue. Chloro-substitution in the diazo component inhibited the effect, since with CI Basic Red 18 (3.79; X = Cl, Y = H) and especially CI Basic Brown 30 (3.79; X = Y = Cl) the hue changes were much less marked [102]. This halochromic change is attributed to transient formation of the redder associated complex 3.80 on the acid-treated fibre, followed by reversion to the usual ion-exchange product 3.81 that is formed by conventional dyeing (Scheme 3.14). Addition of a neutral electrolyte such as sodium sulphate suppresses the protonation of the strongly acidic groups in the fibre.



3.79



$$\text{[acrylic]—SO}_3\text{H} + [\text{dye}\overset{+}{\text{N}}]\ \text{Cl}^- \longrightarrow \text{[acrylic]—SO}_3\text{H}\ [\text{dye}\overset{+}{\text{N}}]\ \text{Cl}^-$$

$$\text{[acrylic]—SO}_3\text{H}\ [\text{dye}\overset{+}{\text{N}}]\ \text{Cl}^- + \text{Na}_2\text{SO}_4 \longrightarrow \text{[acrylic]—SO}_3^-\ [\text{dye}\overset{+}{\text{N}}] + \text{NaCl} + \text{NaHSO}_4$$

$$\text{[acrylic]—SO}_3^-\ \text{Na}^+ + [\text{dye}\overset{+}{\text{N}}]\ \text{Cl}^- \longrightarrow \text{[acrylic]—SO}_3^-\ [\text{dye}\overset{+}{\text{N}}] + \text{NaCl}$$

Scheme 3.14

The rate of dyeing of basic dyes on acrylic fibres is highly sensitive to temperature. This originates in the response of the segmental mobility of the polymer chains to changes in temperature. At or near the glass-transition temperature (T_g), the rate of diffusion of dye into the polymer structure increases markedly owing to the onset of enhanced mobility of the chain segments. Water acts as a plasticising agent for this process, by lowering the T_g of the acrylic polymer by 30–35 °C [103]. This acceleration of the rate of dyeing as soon as T_g is exceeded, together with the virtual irreversibility of the electrostatic interaction between the dye cation and the anionic dyeing site (3.81) in an otherwise nonpolar local environment, means that careful control of application conditions is essential if level dyeing is to be achieved.

Difficulties of incompatibility can arise with mixtures of basic dyes on acrylic fibres because of competition for the limited number of dyeing sites available and the differences between dyes in terms of affinity and rate of diffusion. The rate of uptake of each dye when applied in admixture with another is invariably slower than when the dye is applied alone at the same concentration. Competition effects of this kind can lead to serious practical problems unless the dyes are carefully designed and selected to have similar dyeing characteristics [97,98,104,105]. Dyes with exceptionally low affinity and rapid rates of diffusion have been developed, offering improved migration on acrylic fibres [106]. These dyes have migration properties not unlike those of monosulphonated acid dyes on nylon.

With the majority of basic dyes for acrylic fibres, however, levelling by migration is extremely limited because of their high affinity. A slow rate of increase of dyeing temperature (0.5 °C/min or even less) over the range within which the diffusion rate is increasing rapidly gives an improved degree of control. Colourless cationic retarding agents provide temporary competition for the available anionic sites in the early stage of adsorption of the dye. The amount of retarder applied is adjusted according to the proportion of unoccupied sites remaining when the dyeing equilibrium is attained, in order to minimise the risk of undesirable restraining. Since dye uptake is related to the number of unoccupied sites remaining, the temporary blocking action of the retarder effectively slows the rate of dyeing [107].

3.3 APPLICATION PROPERTIES AND CHEMICAL STRUCTURE

The choice of dyes for a required colour on a given substrate almost always involves compromise between conflicting requirements. Similarly there is seldom an ‘ideal’ dye structure of a desired hue that embodies all possible attractive features with regard to application and fastness properties. Many bright azo dyes have only moderate fastness to light. The incorporation of a metal atom to form a complex of higher fastness often entails a significant loss in brightness. The gain in aqueous solubility provided by an extra sulpho group in a direct or reactive dye often has to be paid for by a decrease in affinity for cellulose. An increase in the hydrophobic character of an acid dye for wool or nylon may improve the neutral dyeing affinity at the expense of impaired level-dyeing properties. Likewise, the migration behaviour of a disperse dye is often affected adversely by an increase in molecular size intended to confer higher wet fastness on cellulose acetate or improved sublimation fastness on polyester. Further examples of such conflicting requirements will emerge in the remainder of this chapter.

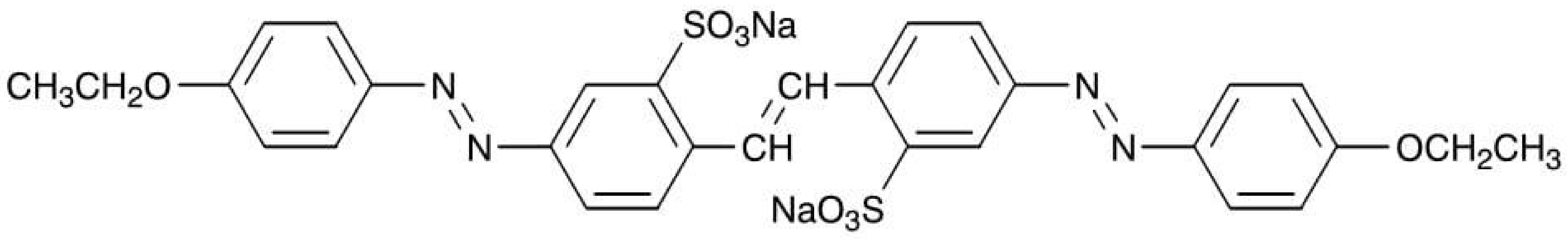
3.3.1 Dyeing kinetics and dye structure

The rates of uptake of direct dyes by cellulose vary extremely widely, as indicated by the data in Table 3.13. The time of ‘half-dyeing’ (the time to reach an exhaustion level half of that attained at equilibrium) on viscose for the highly substantive disazo J acid derivative CI Direct Red 23 is approximately 400 times that for the rapidly diffusing azostilbene dye CI Direct Yellow 12 [108]. Coefficients of diffusion for five of these dyes have been measured in cellophane film [109] and these values do account for some of the differences in dyeing rate, although the inverse relationship is only approximate. There is a tendency for smaller molecules to diffuse more quickly, in that structures 3.82 to 3.84 contain only four or five aryl nuclei and one or two sulpho groups, whereas structures 3.88 to 3.90 have six to eight aryl rings and two to four solubilising groups.

A much more decisive factor in determining the rates of dyeing of many direct dyes from aqueous salt solutions is their tendency to aggregate (section 3.1.2), since this greatly retards their diffusion into the water-swollen voids of the substrate. Ureido-linked J acid residues

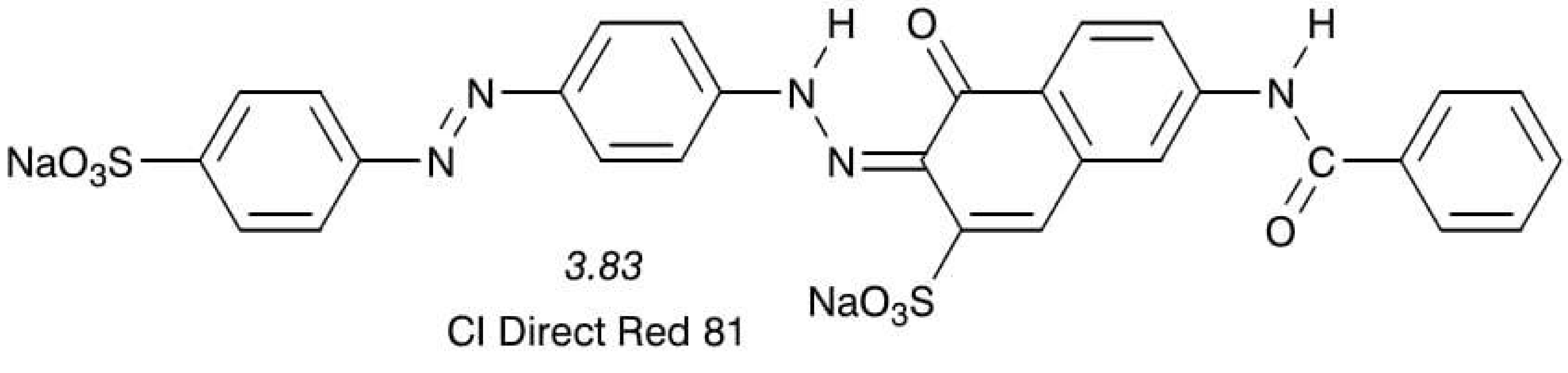
Table 3.13 Times of half-dyeing on viscose [108] and diffusion coefficients in cellophane film [109] for direct dyes at 90 °C

CI Direct	Structure	Diffusion coeff. in cellophane film × 10^{14} (m^2/s)	Time of half-dyeing on viscose yarn (min)
Yellow 12	3.82	150	0.26
Red 81	3.83	50	0.84
Yellow 59	3.84		1.0
Red 31	3.85	25.3	1.7
Red 2	3.86	7.7	8.9
Blue 1	3.87	13.3	15.9
Red 26	3.88		43.8
Black 22	3.89		43.8
Red 23	3.90		100



3.82

CI Direct Yellow 12



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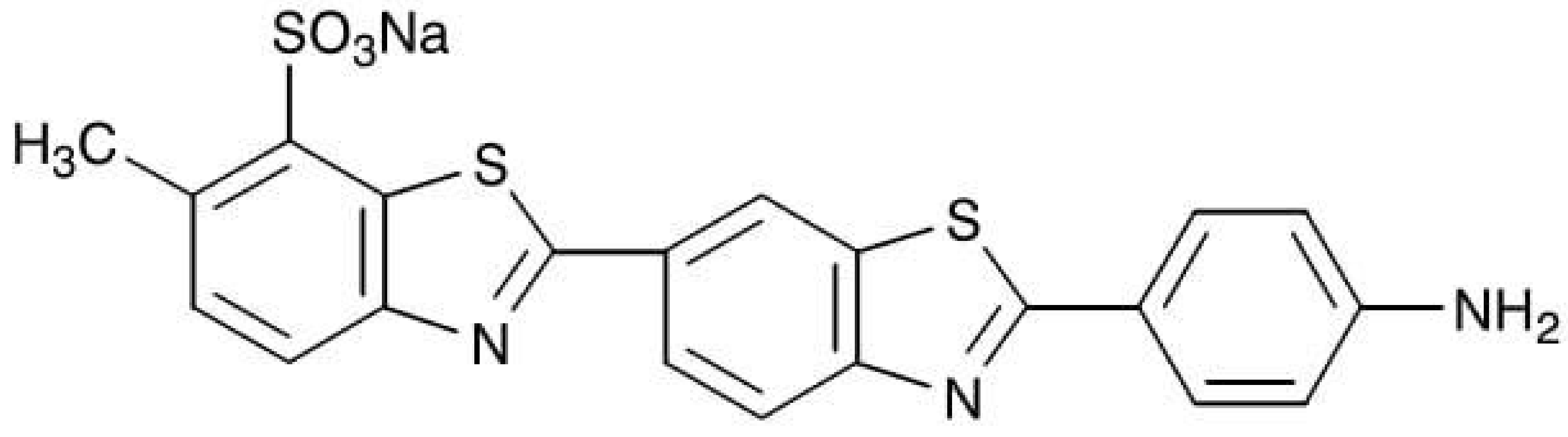
CI Direct Red 81



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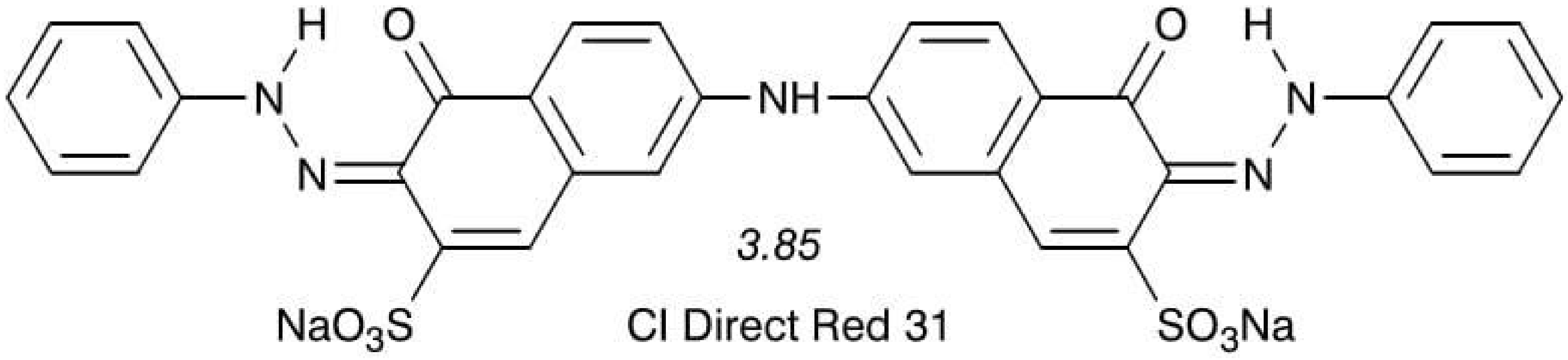
CI Direct Yellow 59



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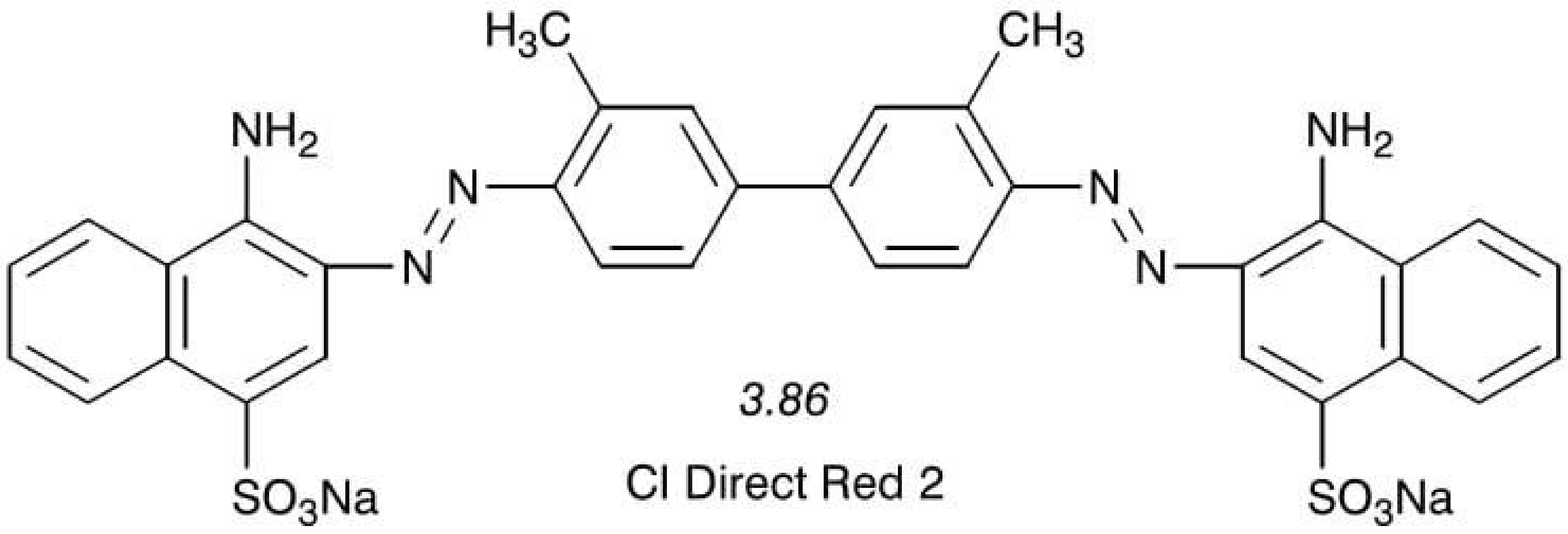
CI Direct Red 31



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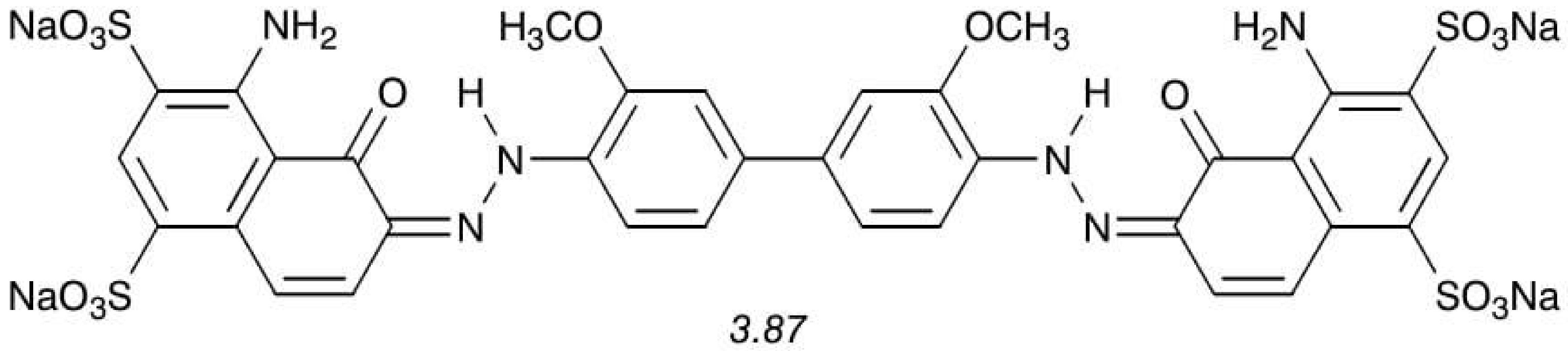
CI Direct Red 2



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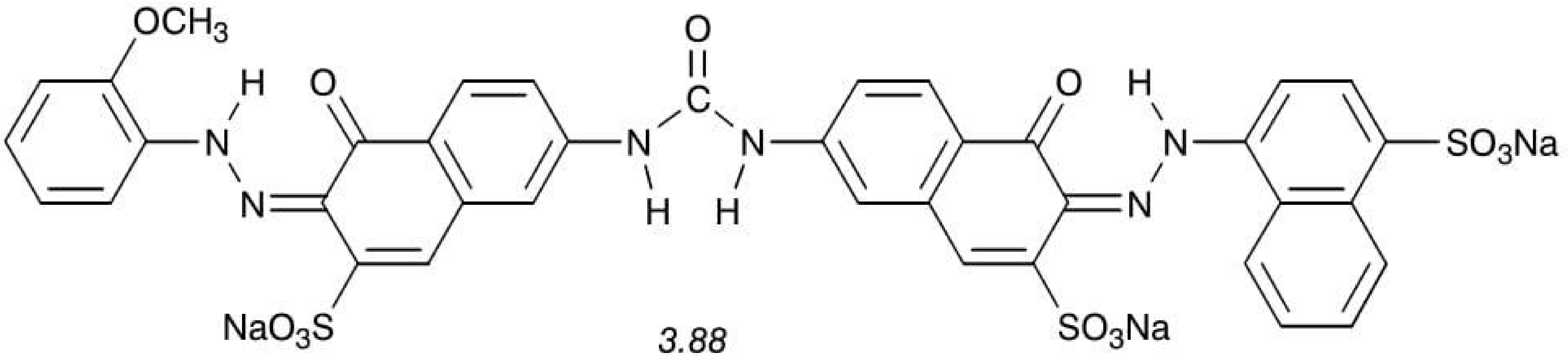
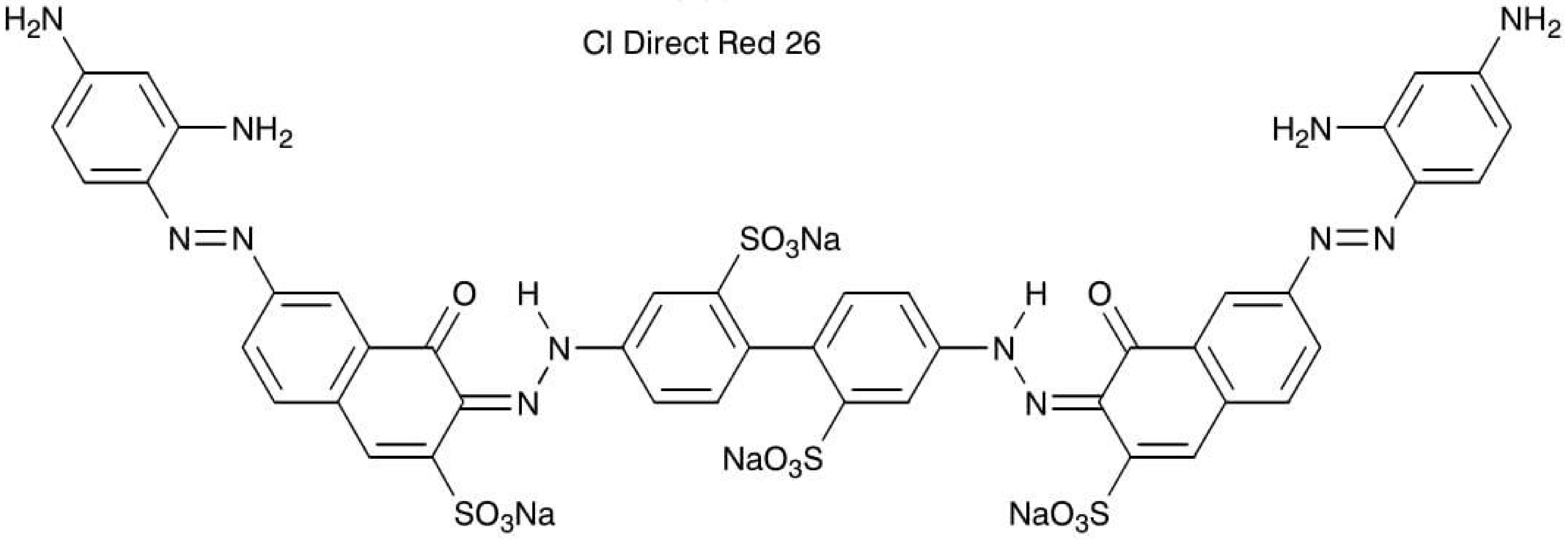
CI Direct Blue 1



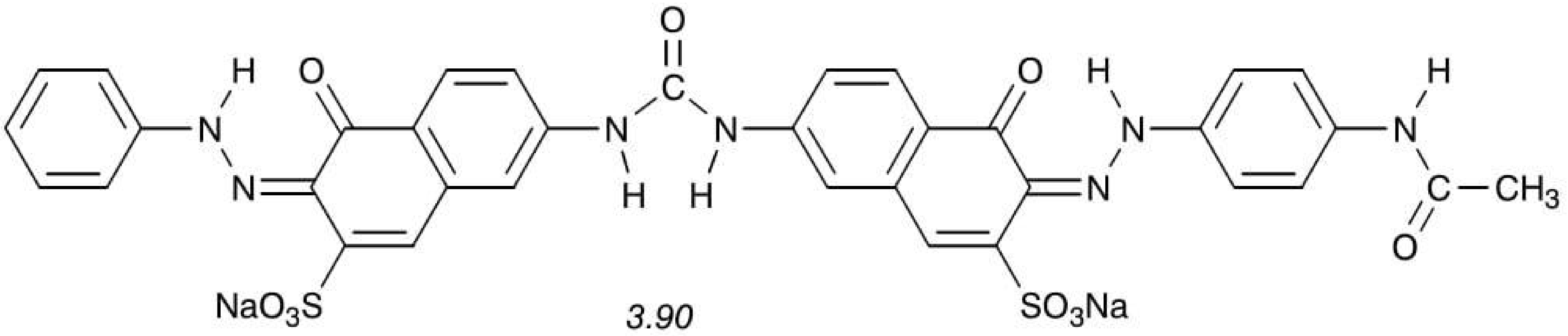
3.88

CI Direct Red 26



3.89

CI Direct Black 22

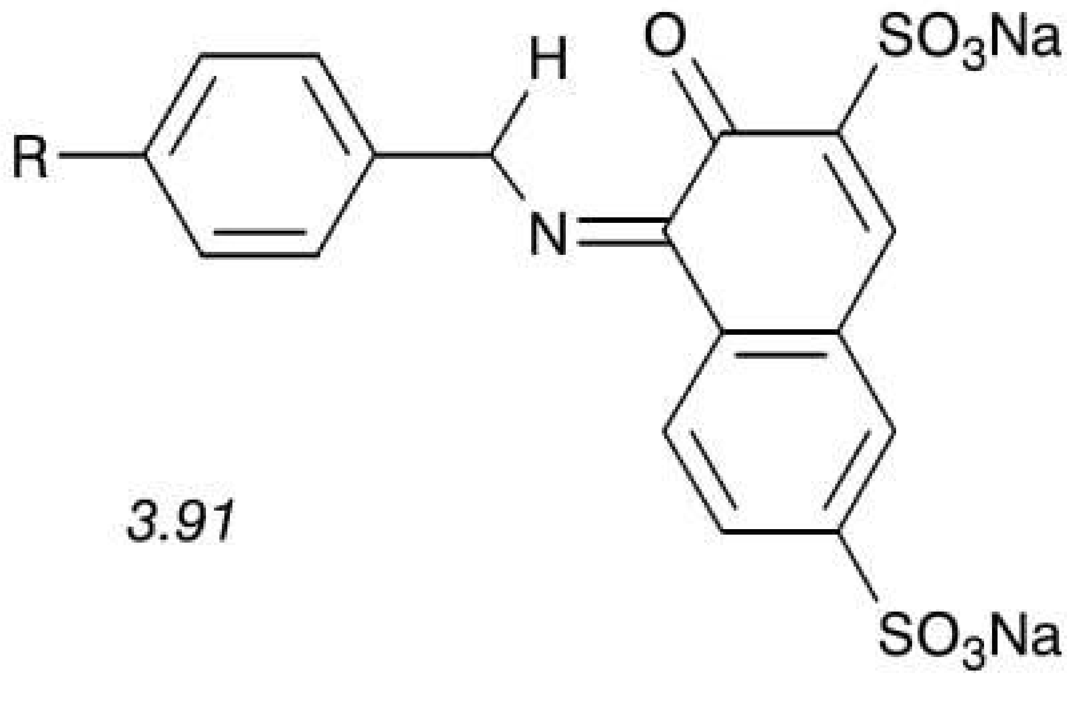


3.90

CI Direct Red 23

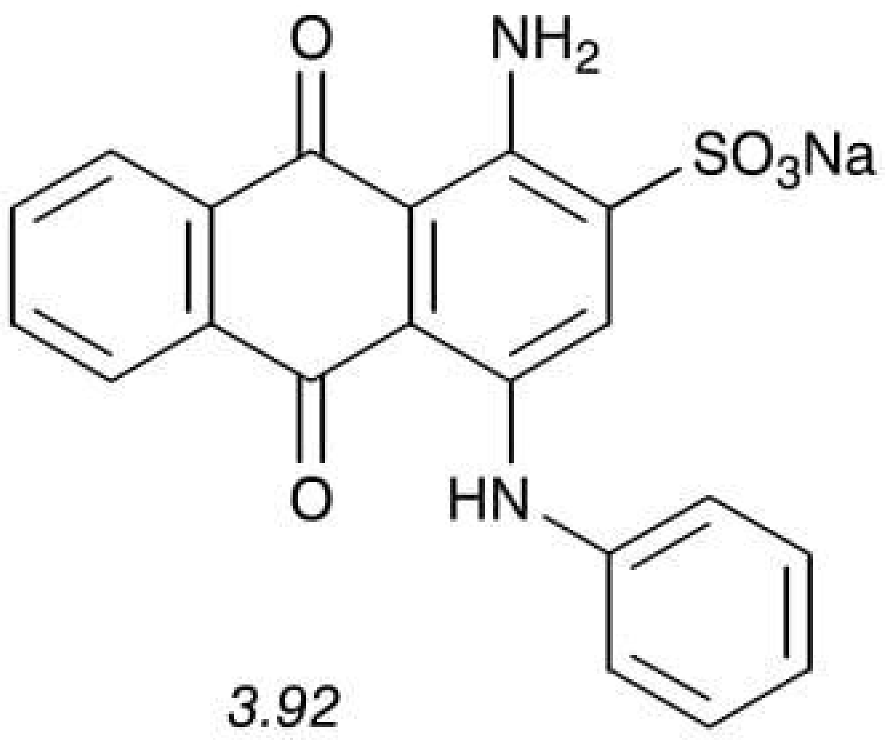
(CI Direct Reds 23 and 26), especially with an acetanilide residue elsewhere in the molecule (as in Red 23), provide opportunities for hydrogen-bond stabilisation of the weaker *p*-bonding attraction between aryl rings in neighbouring component molecules of an aggregate.

The kinetic behaviour of anionic dyes on amide fibres tends to be much more closely related to molecular size and hydrophilic-lipophilic balance. Thus within a related series of dye structures it is possible to discern more specific relationships. For example, in the series of *p*-substituted aniline→R acid dyes (3.91; R = H, methyl, n-butyl or n-dodecyl) the logarithm of the rate of dyeing on wool is inversely proportional to the molecular volume [110].



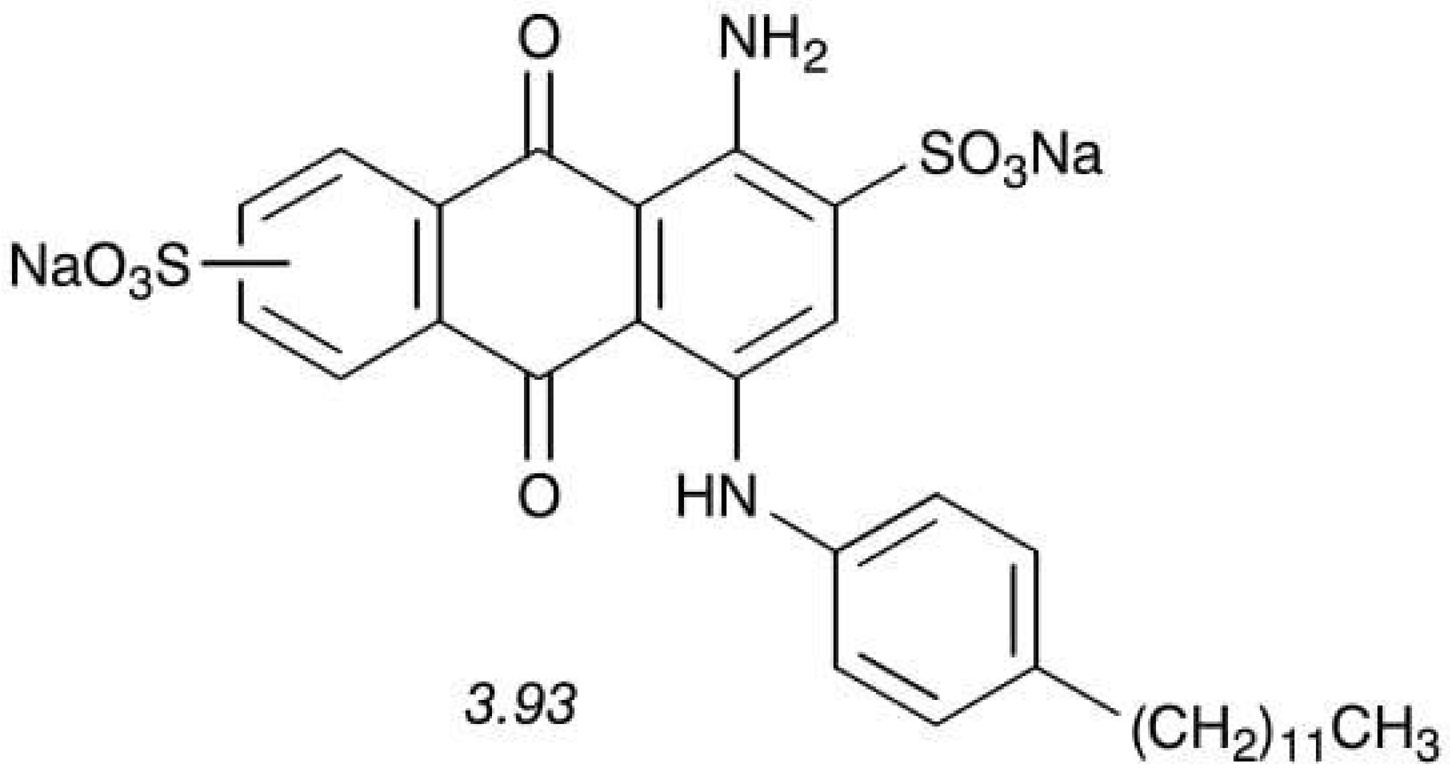
3.91

A somewhat similar inverse relationship between dyeing rate and molecular size was invoked to interpret the relative degree of penetration of three anthraquinone blue dyes into nylon fibres after dyeing under various conditions [111]. After only 5–10 minutes at 90 °C, CI Acid Blue 25 (3.92) had penetrated the nylon almost completely, with no evidence of ring dyeing. CI Acid Blue 138, a disulphonated analogue with an additional dodecyl group on the aniline ring (3.93), showed a marked difference in degree of penetration after dyeing for one hour (40% at 90 °C, compared with 100% at 100 °C). The extremely slow-diffusing disulphonated dye CI Acid Blue 175 (3.94), with seven interlinked rings able to form a coplanar arrangement, attained only 40–50% penetration of the substrate even after dyeing for two hours at 100 °C.



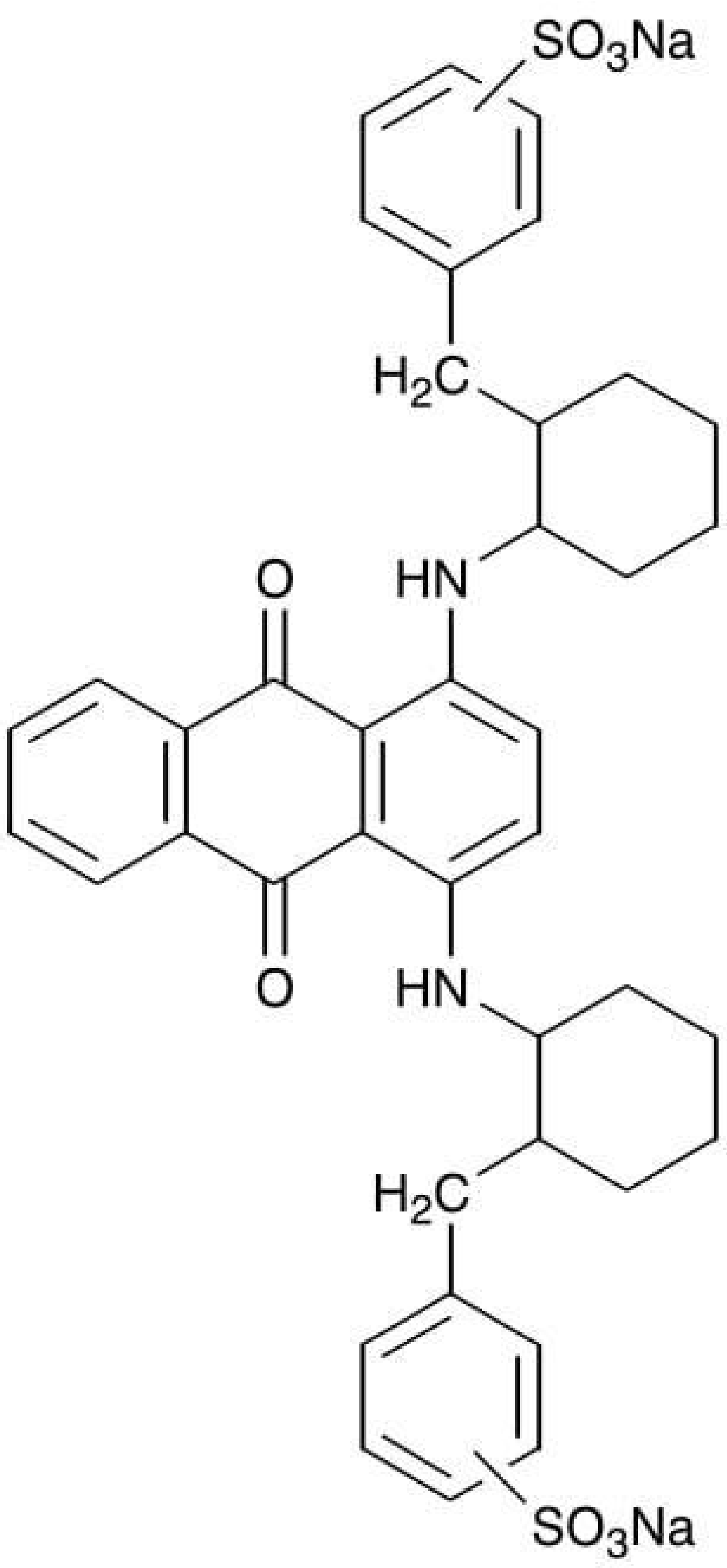
3.92

CI Acid Blue 25



3.93

CI Acid Blue 138



3.94

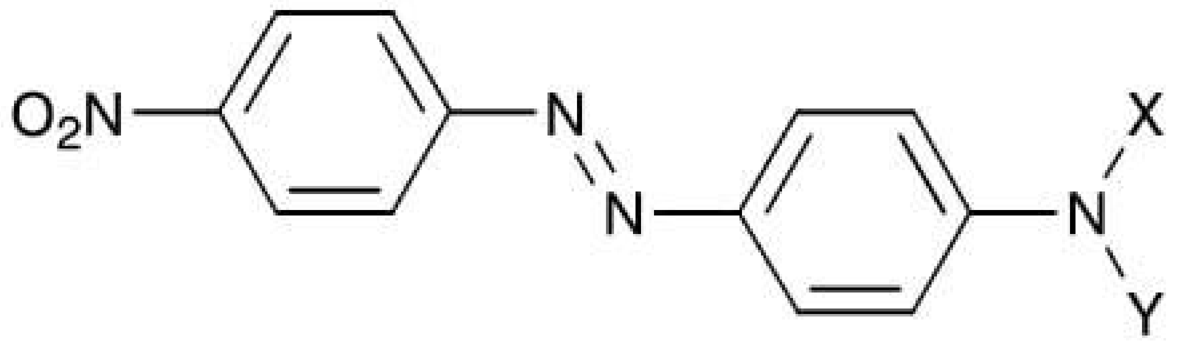
CI Acid Blue 175

The relative rates of diffusion of disperse dyes in hydrophobic fibres tend to exhibit an approximately inverse relationship to molecular size, although here again the overall trend is somewhat obscured by specific forces of interaction between hydrogen-bonding substituents in the dye and polymer chain segments. CI Disperse Orange 3 (M_r 242) diffuses about five times more quickly than CI Disperse Blue 24 (M_r 328) in nylon and polyester but only about 1.5 times in cellulose acetate [112]. These differences (Table 3.14) suggest that the orange azo dye interacts more strongly than the blue anthraquinone dye with the acetate fibre, possibly by hydrogen bonding of the terminal primary amino group in Orange 3 with an acetyl group in cellulose acetate.

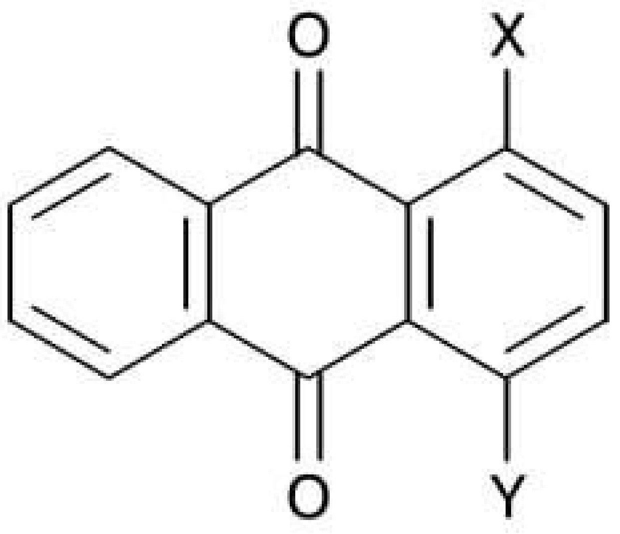
The relative rates of diffusion of CI Disperse Orange 3 on nylon, acetate and polyester indicated in Table 3.14 are reasonably consistent with those measured independently in the early days of polyester dyeing [113], as shown in Table 3.15. These figures, for three disperse

Table 3.14 Diffusion coefficients of disperse dyes in hydrophobic fibres [112]

		Diffusion coefficient at 100°C × 10^{15} (m^2/s)		
CI Disperse	Structure	Nylon	Acetate	Polyester
Orange 3	3.95; $X = Y = H$	23.1	15.1	1.3
Blue 24	3.96; $X = NHCH_3$, $Y = NHPh$	4.2	10.6	0.3



3.95



3.96

dyes of almost equal M_r also emphasise a marked increase in diffusion rate on polyester between 85 and 100 °C, that is much less evident on nylon or cellulose acetate. Disperse dyes tend to diffuse more rapidly in polypropylene than in other hydrophobic fibres but to give relatively low saturation values indicative of poor affinity for this fibre. Table 3.16 illustrates these differences for 1-anilinoanthraquinone (3.96; $X = NHPh$, $Y = H$) on cellulose acetate and polypropylene [84].

Table 3.15 Relative diffusion coefficients of disperse dyes [113]

			Relative diffusion coefficient			
			Nylon	Acetate	Polyester	
CI Disperse	Structure	Rel. mol. mass (M_r)	85°C	85°C	85°C	100°C
Orange 3	3.95; $X = Y = H$	242	680	460	1	48
Red 15	3.96; $X = NH_2$, $Y = OH$	239	1000	286	1	34
Violet 1	3.96; $X = Y = NH_2$	238	450	452	1	31

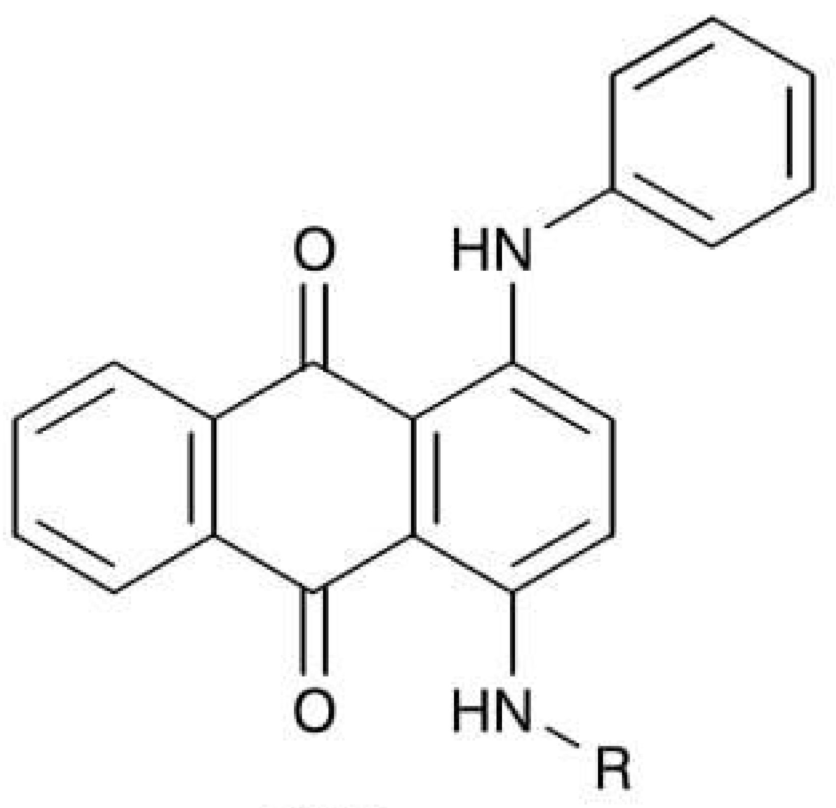
Table 3.16 Saturation values and diffusion coefficients of 1-anilinoanthraquinone [84]

Dyed at 80°C	Saturation value (g/kg)	Diffusion coeff. × 10^{14} (m^2/s)
Polypropylene	3.2	6.74
Cellulose acetate	6.0	1.12

There is a roughly inverse relationship for a series of structurally related dyes between the time of half-dyeing and the saturation solubility in an appropriate substrate, as illustrated for several 4-alkylamino derivatives of 1-anilinoanthraquinone on cellulose acetate (Table 3.17). It is interesting that methylamino and 2-hydroxyethylamino substituents confer good solubility in this substrate, but ethylamino groups are even less effective than isobutylamino groups in this respect [114].

Table 3.17 Times of half-dyeing and solubilities of disperse dyes in cellulose acetate at 85°C [114]

Substituent (R) in 3.97	Time of half-dyeing (min)	Solubility (g/kg)
Methyl	30	8.8
2-Hydroxyethyl	35	4.2
Isobutyl		4.1
Ethyl	37	1.5



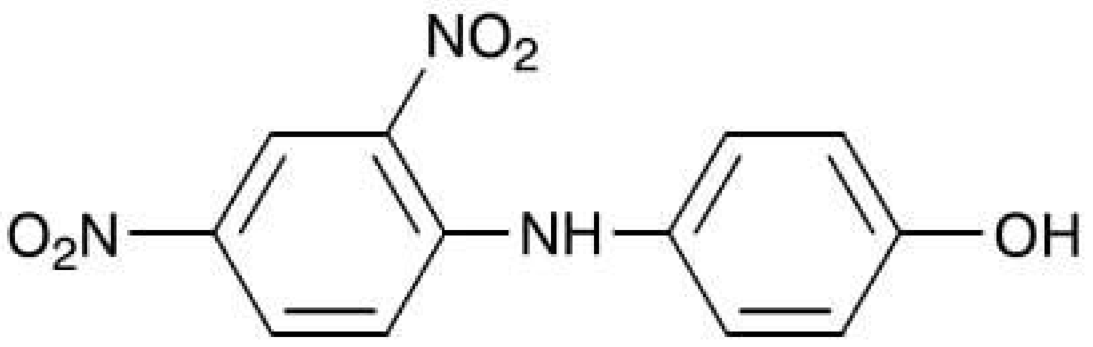
3.97

The times of half-dyeing on cellulose acetate listed in Table 3.18 give some significant pointers to the relationship between disperse dye structure and dyeing rate on this fibre. The most mobile molecular structure shown is the dinitrodiphenylamine dye CI Disperse Yellow 1, closely followed by the unsubstituted *p*-nitrophenylazoaniline Orange 3. The introduction of one *N*-phenyl group into the latter structure (to form Orange 1) has a much more pronounced effect than two ethyl or 2-hydroxyethyl groups (Red 1 or Red 19). In the series of 1,4-diaminoanthraquinone (3.96) derivatives, the unsymmetrically substituted types (Red 15, Violet 4 and Blue 3) are absorbed much more rapidly than is the symmetrical analogue with two methylamino groups (Blue 14). This dye is greatly retarded in comparison with the unmethylated dye (Violet 1). In a similar way, Blue 26:1 containing mono- and dimethylated diaminoanthrarufin is absorbed several times more slowly than Blue 26, a mixture of the monomethyl and unmethylated derivatives. Possibly the presence of methylamino substituents favours aggregation of these anthraquinone dyes.

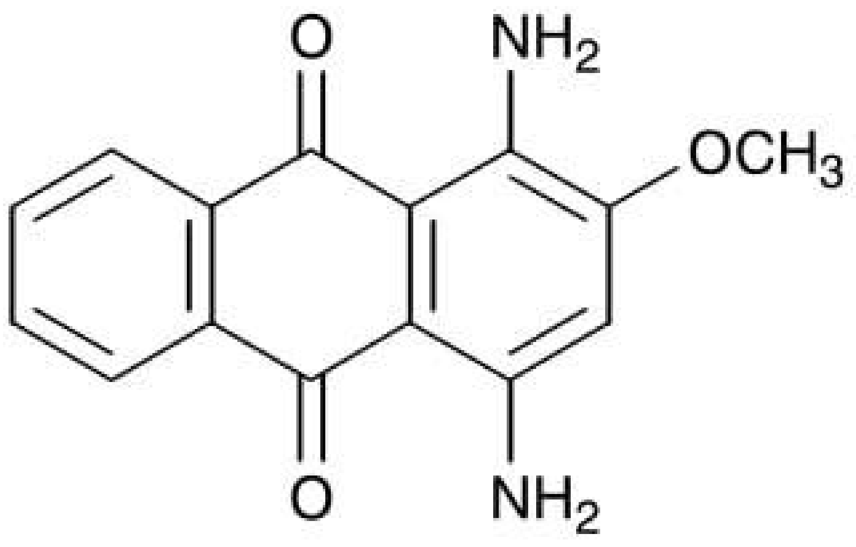
Diffusion coefficients [115] and dyeing rate constants [116] for the same fifteen dyes on nylon are given in Table 3.19, confirming many of the trends already noted above. Yellow 1, Orange 3 and Violet 4 are again the three most rapidly absorbed dyes, in the same order. The diffusion coefficients place the first two dyes in reverse order, however, suggesting that the terminal phenolic group in Yellow 1 interacts more effectively with proton-acceptor sites

Table 3.18 Times of half-dyeing of disperse dyes on cellulose acetate at 85 °C [115]

CI Disperse	Structure	Time of half-dyeing (min)
Yellow 1	3.98	0.75
Orange 3	3.95; X = Y = H	0.8
Violet 4	3.96; X = NH_2, Y = $NHCH_3$	1.6
Red 15	3.96; X = NH_2, Y = OH	2.4
Blue 3	3.96; X = $NHCH_3$, Y = $NHCH_2CH_2OH$	2.5
Violet 1	3.96; X = Y = NH_2	3.0
Red 19	3.95; X = Y = CH_2CH_2OH	3.3
Red 1	3.95; X = CH_2CH_3, Y = CH_2CH_2OH	4.0
Red 11	3.99	4.8
Blue 26	3.100; X = H	6.5
Orange 1	3.95; X = H, Y = Ph	14.0
Red 13	3.101	16.5
Blue 14	3.96; X = Y = $NHCH_3$	16.5
Orange 13	3.102	19.0
Blue 26:1	3.100; X = CH_3	28.5


3.98

CI Disperse Yellow 1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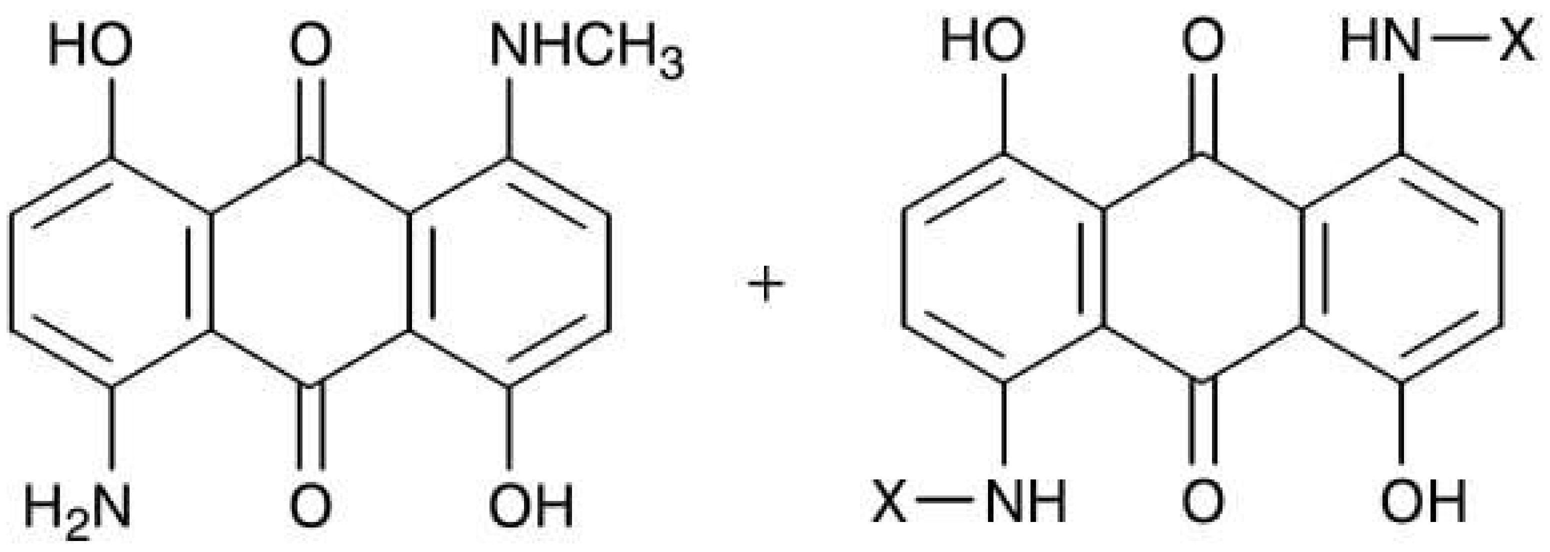
CI Disperse Red 11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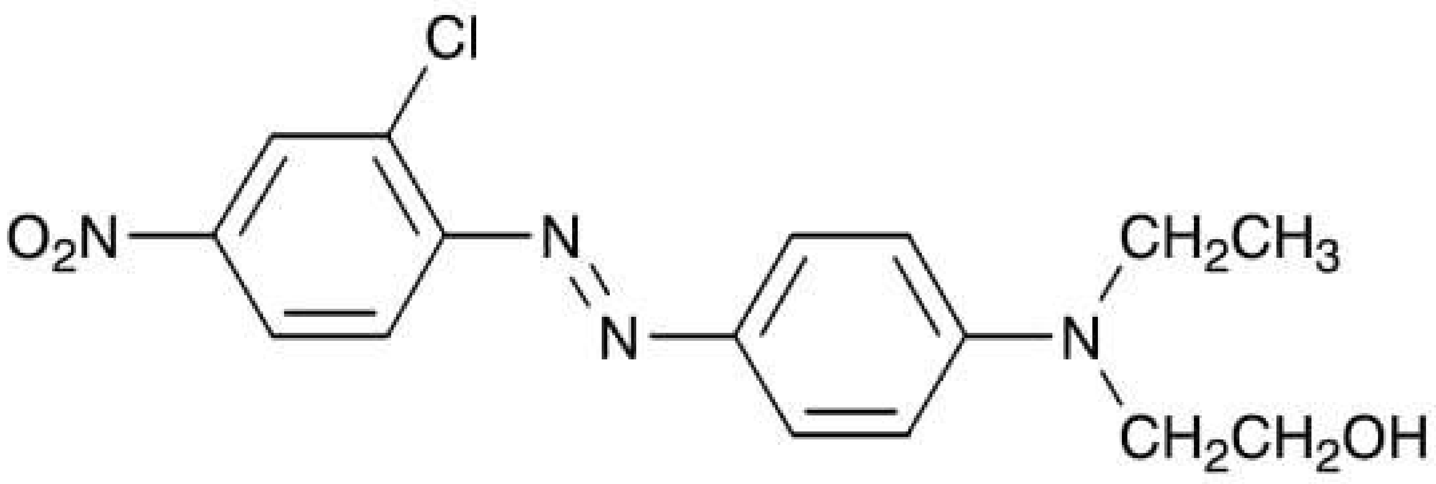
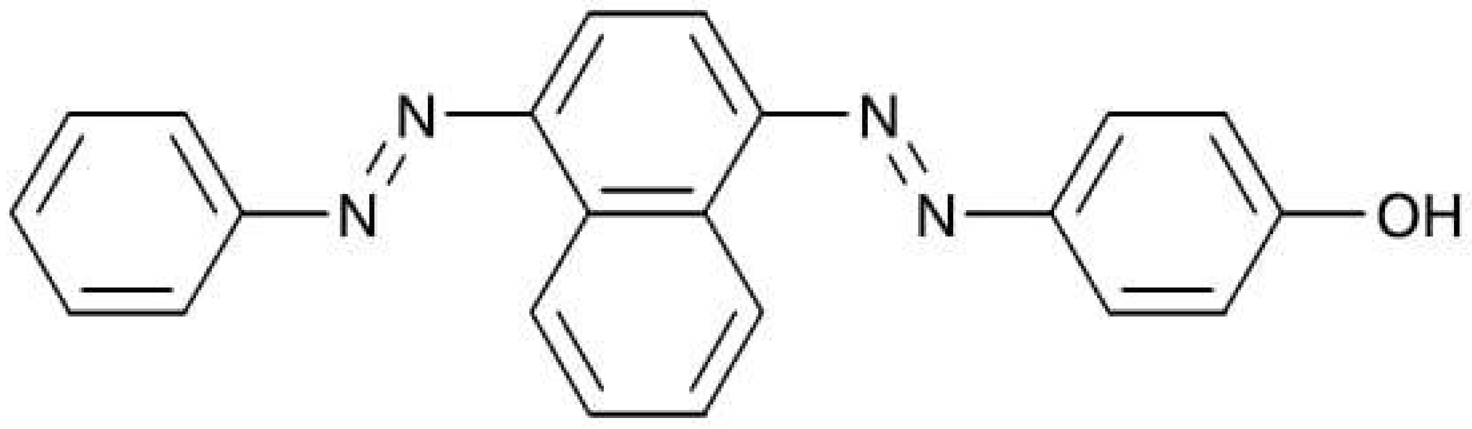

3.101

CI Disperse Red 13


3.102

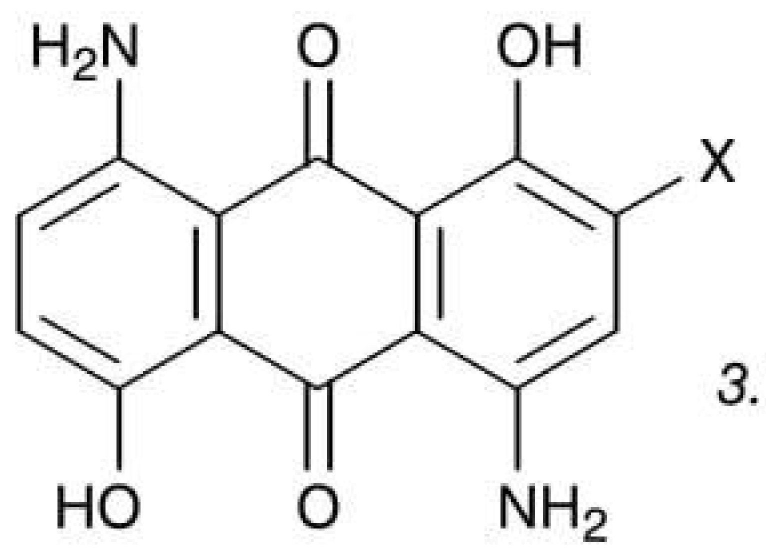
CI Disperse Orange 13

in nylon than the primary amino terminal group in Orange 3. As before, an *N*-phenyl substituent (Orange 1) exerts a markedly greater retarding influence than *N*-ethyl-*N*-2-hydroxyethyl (Red 1) or *N*,*N*-bis(2-hydroxyethyl) (Red 19) substitution of the parent structure (Orange 3). Once again in the 1,4-disubstituted anthraquinone series, the rate constants for the unsymmetrical structures (Red 15, Violet 4 and Blue 3) are much higher than that for the symmetrical bis-methylamino analogue (Blue 14). The rates for the two mixed diaminoanthrarufin derivatives, however, are much closer on nylon than on cellulose acetate. The diffusion coefficients of these dyes do differ markedly, perhaps because the unmethylated component of Blue 26 interacts more strongly with proton-acceptor sites in nylon than does the more fully methylated mixture Blue 26:1.

Table 3.19 Diffusion coefficients [115] and dyeing rate constants [116] for disperse dyes on nylon at 80 °C

CI Disperse	Structure	Diffusion coeff. × 10^{15} (m^2/s)	Rate constant
Yellow 1	3.98	11	1820
Orange 3	3.95; X = Y = H	23	940
Violet 4	3.96; X = NH_2,Y = $NHCH_3$		840
Blue 3	3.96; X = $NHCH_3$,Y = $NHCH_2CH_2OH$		570
Red 19	3.95; X = Y = CH_2CH_2OH		450
Violet 1	3.96; X = Y = NH_2	11	350
Red 15	3.96; X = NH_2,Y = OH		280
Red 1	3.95; X = CH_2CH_3,Y = CH_2CH_2OH	3	200
Orange 13	3.102	1	160
Red 13	3.101		130
Blue 14	3.96; X = Y = $NHCH_3$	11	120
Red 11	3.99	15	80
Blue 26	3.100; X = H	5	80
Blue 26:1	3.100; X = CH_3	17	68
Orange 1	3.95; X = H,Y = Ph	3	56

The study of the degree of penetration of blue acid dyes in nylon mentioned earlier also included a further series of measurements for two blue disperse dyes on polyester [111]. A fully penetrated dyeing with CI Disperse Blue 56 (3.103; X = Br) was achieved after 90 minutes at 120 °C, but with the Blue 83 mixture (3.103; X = $PhOCOCH_3$ or PhOCOPh) complete penetration within this time of dyeing could only be attained at 140 °C. In practice, the dyeing of polyester fibres is often restricted to 30–60 minutes at 125–130 °C in order to minimise the release of oligomer into the dyebath or to preserve desirable fabric properties. When applying high-energy dyes of the Blue 83 type these conditions can produce dyeings that are only 30–40% penetrated.

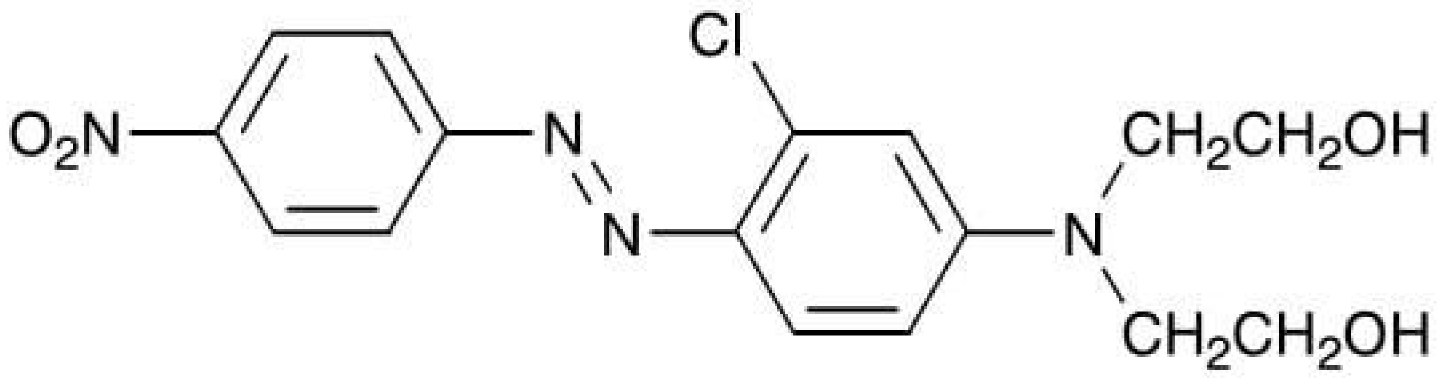


3.103

Diffusion coefficients for five disperse dyes on polyester are compared in Table 3.20. Four of these structures were included in the corresponding data for the nylon and cellulose acetate systems. As before, the unsymmetrical 1,4-diaminoanthraquinone derivative (CI Disperse Blue 3) diffuses significantly more rapidly than the symmetrical bis-dimethylamino analogue (Blue 14). It is interesting that the disazo dye Orange 13 with a terminal *p*-hydroxy group shows a higher diffusion coefficient on polyester than the two monoazo dyes with a terminal p-nitro group (Reds 7 and 13).

Table 3.20 Diffusion coefficients of disperse dyes on unset polyester at 100 °C [61]

CI Disperse	Structure	Diffusion coeff. $\times 10^{14}$ (m^2/s)
Blue 3	3.96; $X = NHCH_3$, $Y = NHCH_2CH_2OH$	1.6
Orange 13	3.102	1.4
Red 7	3.104	1.25
Blue 14	3.96; $X = Y = NHCH_3$	1.0
Red 13	3.101	0.9



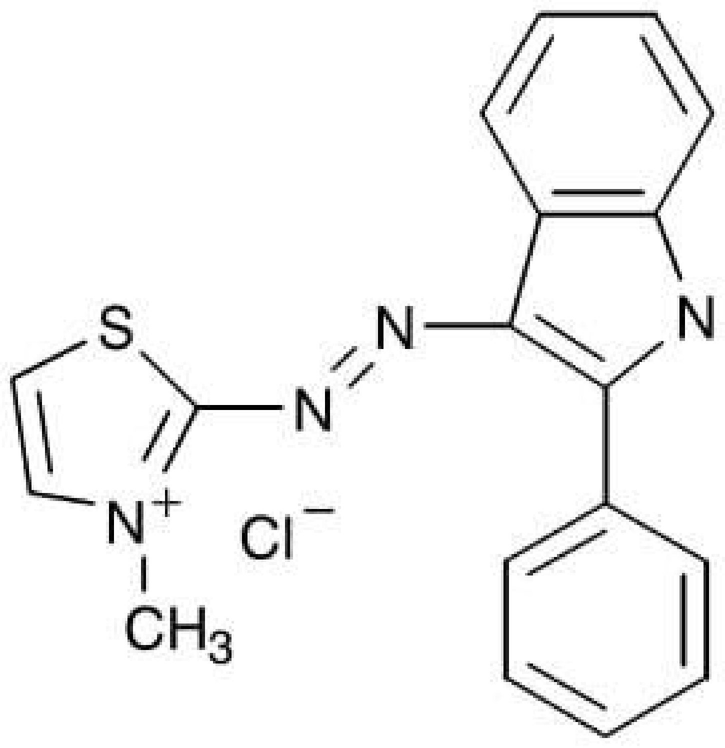
3.104

CI Disperse Red 7

As in the case of disperse dyes on polyester, the coefficients of diffusion of basic dyes in acrylic fibres tend to decrease as molecular size increases. Most basic dyes have a single cationic centre surrounded by a relatively compact hydrophobic system containing three or four aryl rings. Five typical structures are compared in Table 3.21 in terms of their relative diffusion coefficients in an acrylic fibre and in a basic-dyeable polyester variant in the presence and absence of a diphenyl-type carrier [117]. Individual substituents exert only minor effects on the overall rate of diffusion. Thus the *N*-ethyl-*N*-2-hydroxyethyl substitution pattern in CI Basic Blue 41 produces only slightly lower diffusion coefficients than the dimethylamino analogue (Blue 54) and even the dimethyltriazole diazo component in Yellow 25 has a minor retarding effect relative to the monomethylthiazole group in Red 29.

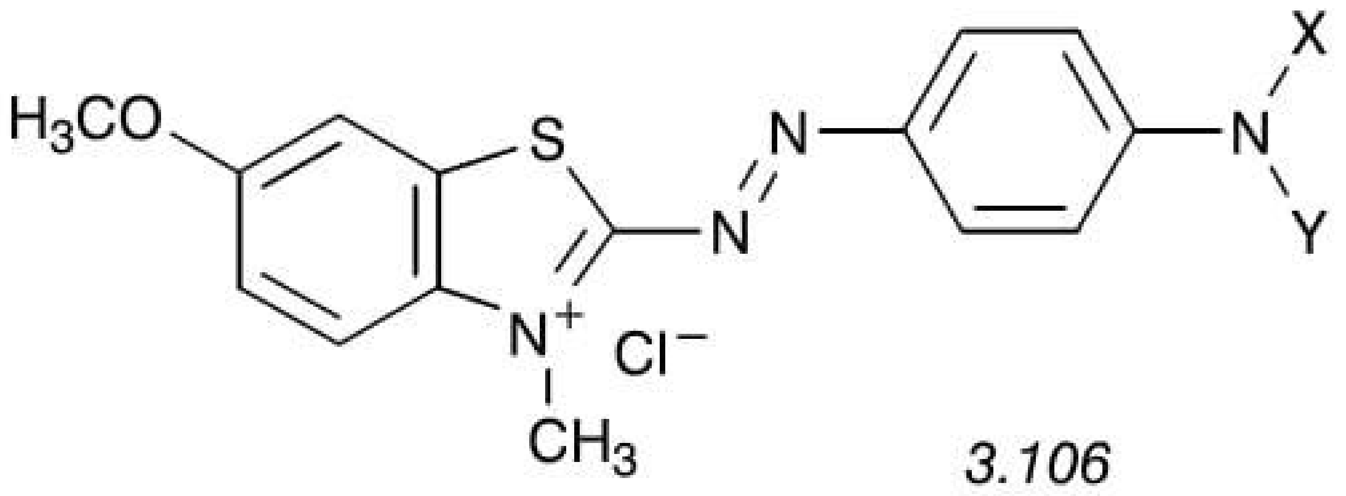
Table 3.21 Relative diffusion coefficients of basic dyes on basic-dyeable polyester and acrylic fibres at 100 °C [117]

		Basic-dyeable polyester		
CI Basic	Structure	No carrier	Carrier	Acrylic fibre
Red 29	3.105	1.1	1.9	3.6
Blue 54	3.106; $X = CH_3$, $Y = CH_3$	1.1	1.8	3.4
Blue 41	3.106; $X = CH_2CH_3$, $Y = CH_2CH_2OH$	1.0	1.8	3.1
Yellow 25	3.107	1.0	1.7	2.8
Yellow 11	3.108	0.7	1.6	2.6

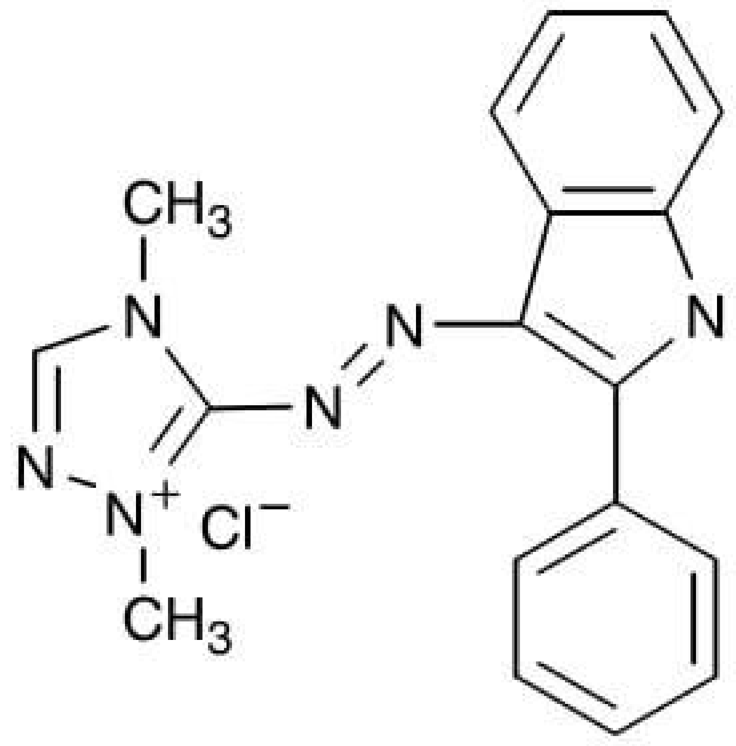


3.105

CI Basic Red 29

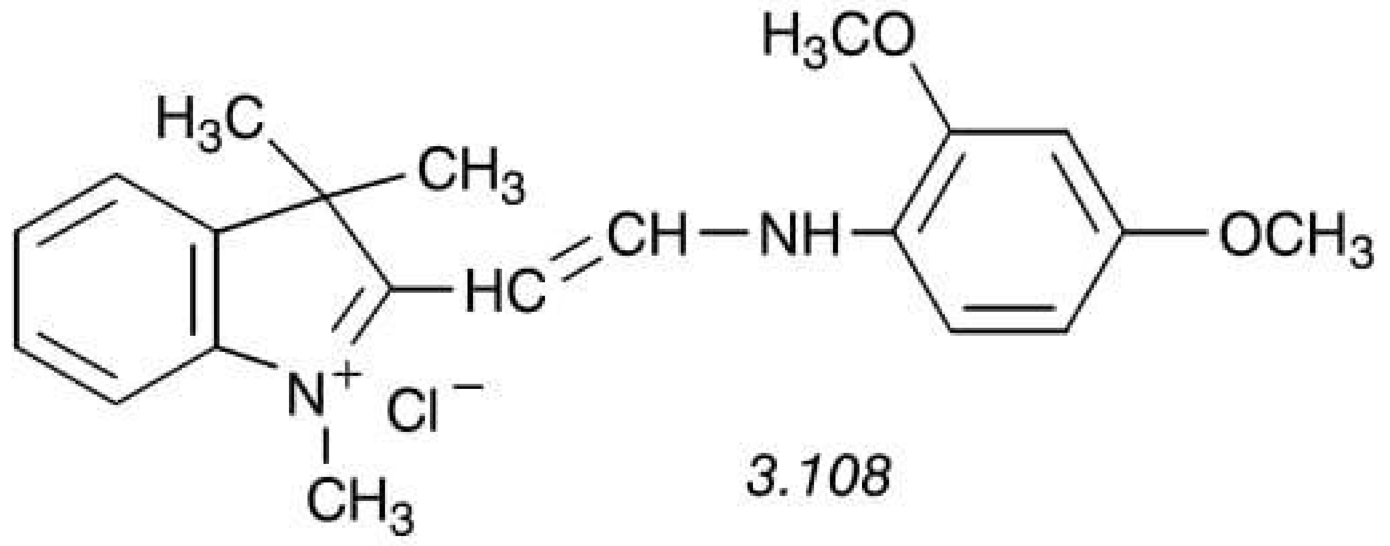


3.106



3.107

CI Basic Yellow 25



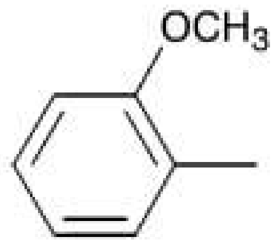
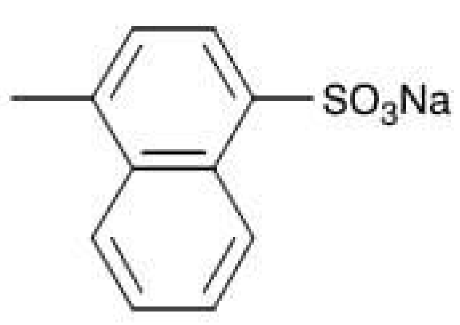
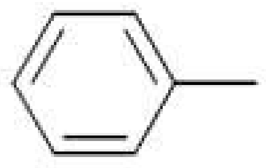
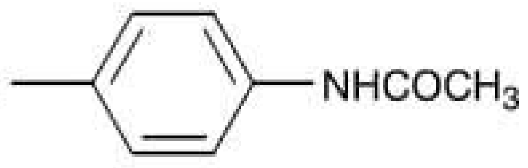
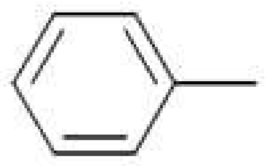
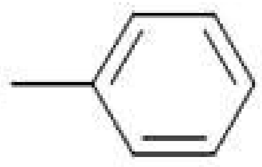
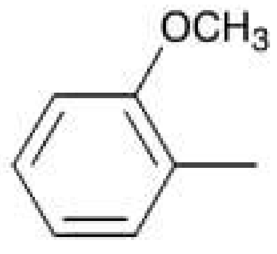
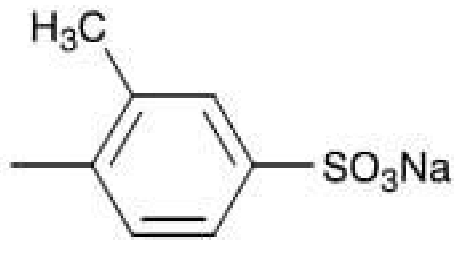
3.108

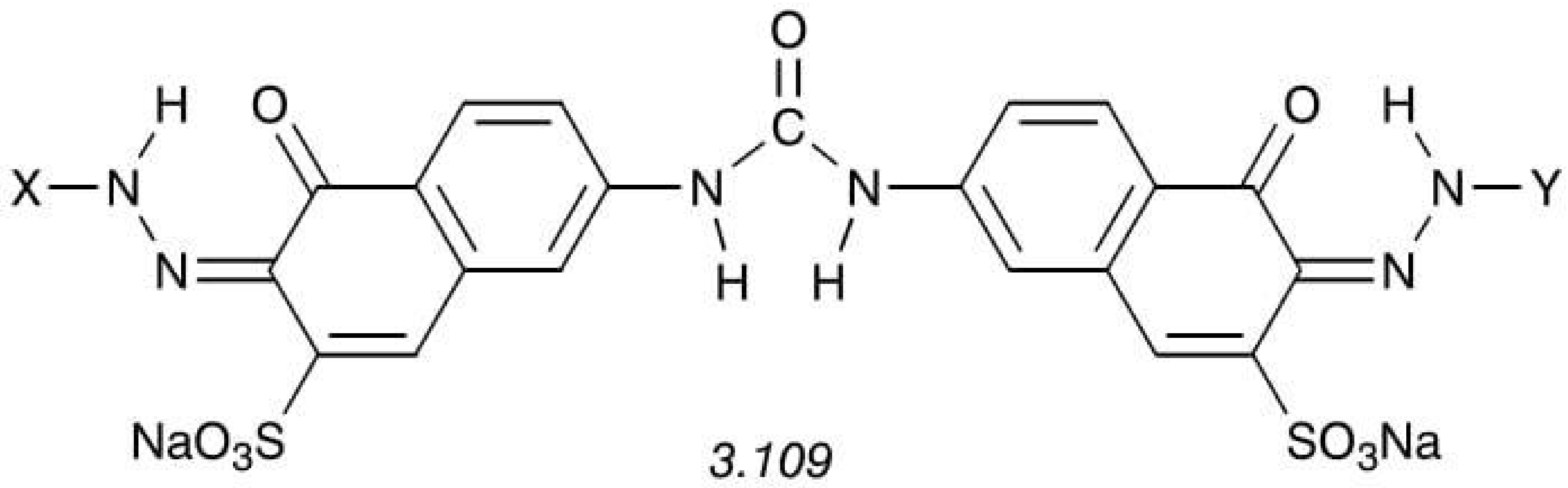
CI Basic Yellow 11

3.3.2 Dye structure and affinity for the fibre

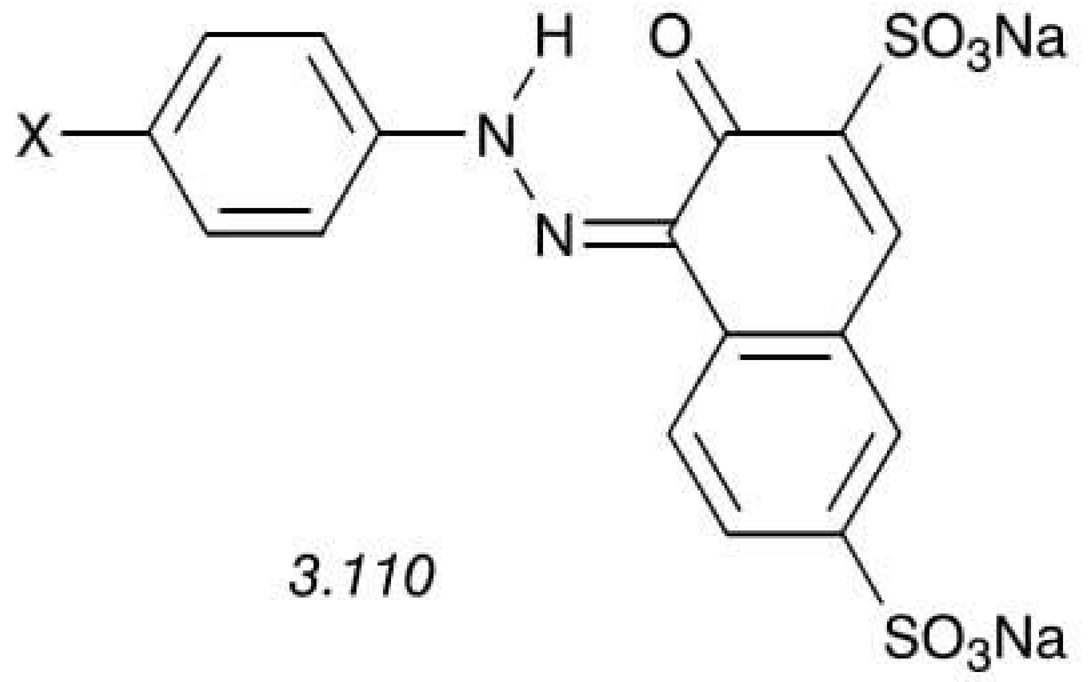
As already noted in relation to kinetic behaviour, minor changes in direct dye structure can have marked effects on dyeing properties. Within the closely related series of J acid disazo dyes in Table 3.22, insertion of an acetylamino group in CI Direct Orange 26 to form Red 23 gives a significant boost to the affinity as well as a bathochromic influence on the colour. Comparing the other two members of this series, an additional aryl ring (Red 26) has a much greater effect on the overall affinity of the molecule than a simple methyl group (Red 24).

Table 3.22 Affinity of direct dyes for viscose at 60 °C [67]

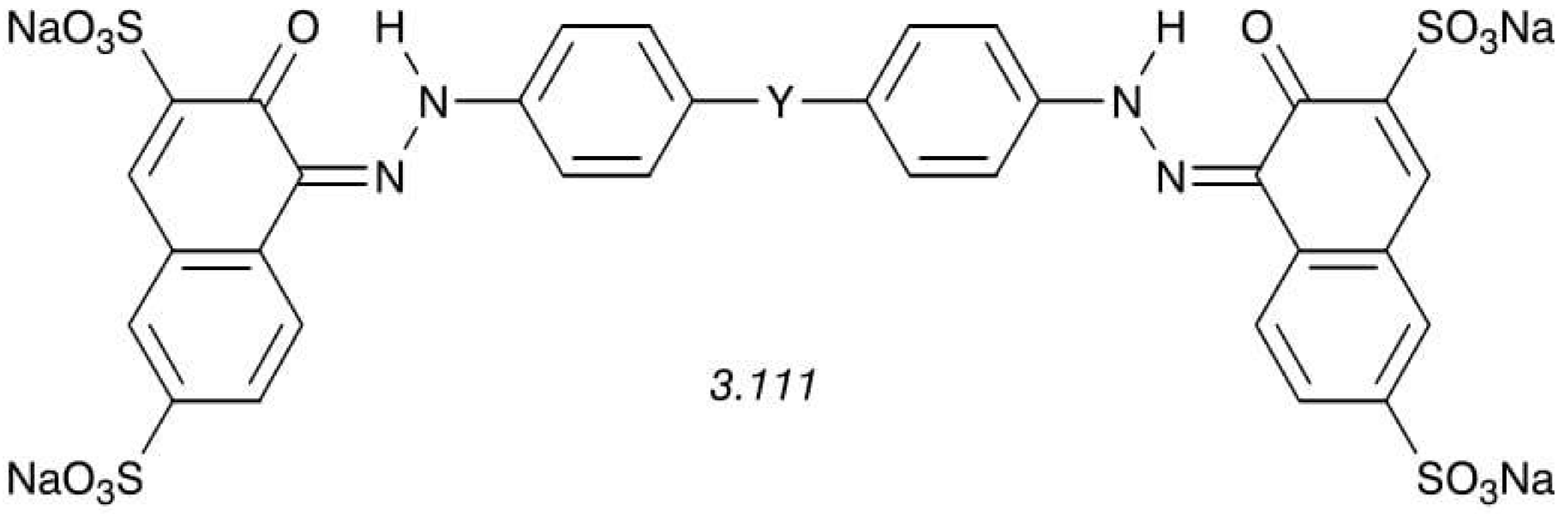
CI Direct	Substituents in structure 3.109		Affinity(kJ/mol)
Red 26	X = 	Y = 	−23.8
Red 23	X = 	Y = 	−21.3
Orange 26	X = 	Y = 	−20.1
Red 24	X = 	Y = 	−18.4



3.109



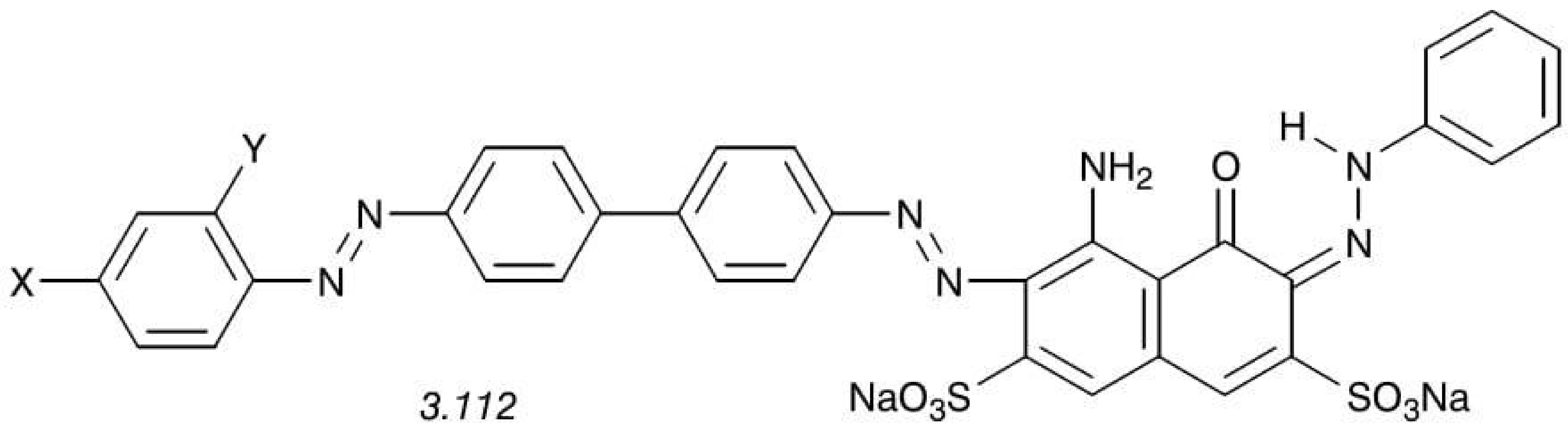
3.110



3.111

The important contribution of hydrogen bonding to the substantivity of direct dyes was explored by the synthesis of red (3.110; X = CHO) and violet (3.110; X = $PhNHCSNH_2$) monoazo derivatives of R acid. The existence of hydrogen bonding between the X group and hydroxy groups in cellulose was demonstrated. This research was followed up by a more comprehensive survey of various disazo R acid dyes derived from a range of diamines (3.111; Y = O, NH, CH_2, CO, SO_2, CH=CH, CONH, NH.CO.NH, NH.CS.NH, CO.NH.NH.CO, NH.CO.CO.NH, NH.CO.CH_2.CO.NH, NH.C=NH.NH and CO.NH.C=NH.NH.CO). The significance of such central functional groups with scope for hydrogen bonding or dipolar interaction with hydroxy groups in cellulose was clearly evident [118].

Numerous linear diamines, such as many of those in the survey mentioned above, have been evaluated as potential replacements for benzidine, an inexpensive and highly versatile intermediate that was banned in the 1970s because it posed a carcinogenic threat. Two trisazo dyes have been synthesised recently using 4,4′-diaminodiphenyl thioether instead of the benzidine component of CI Direct Black 38 (3.112; X = Y = NH_2) and CI Direct Green 1 (3.112; X = OH, Y = H). These new dyes exhibited higher substantivity and fastness to washing than the two traditional products on cellulosic fibres [119].



3.112

Affinity values of the symmetrical disazo dyes CI Direct Yellow 12 (3.6), Red 2 (3.8; X = CH_3, Y = H) and Blue 1 (3.2) on cellophane have been measured recently under hydrostatic pressures up to 600 Mpa [120]. The affinity of Yellow 12 increased slightly but values for the other two dyes decreased considerably with increasing hydrostatic pressure (Table 3.23). The sulpho groups on the central stilbene nuclei of the Yellow 12 molecule tend to inhibit aggregation, whereas Red 2 and Blue 1 aggregate much more readily. The small increase in the affinity observed with Yellow 12 may indicate that isomerisation from the *cis* to the more stable *trans* form may occur as the hydrostatic pressure is increased.

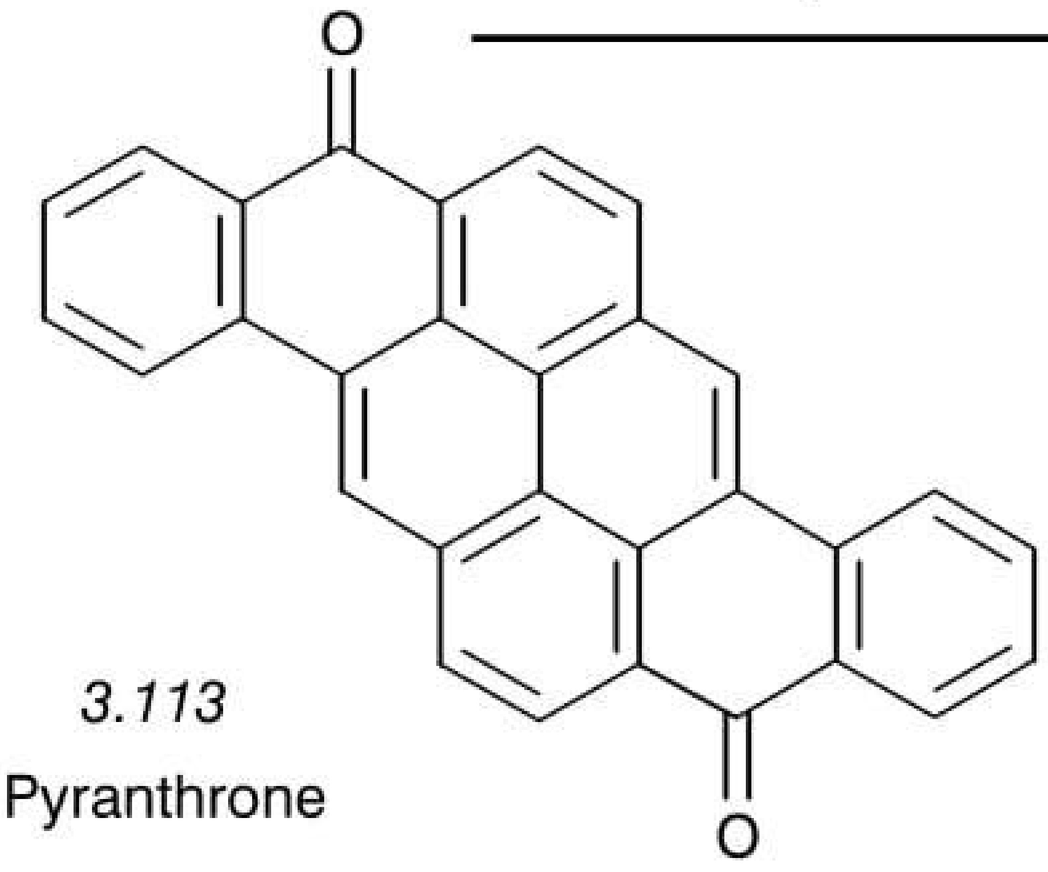
Table 3.23 Affinity of direct dyes for cellophane at 55 °C [120]

	Affinity (kJ/mol)		
Hydrostatic pressure (MPa)	CI Direct Yellow 12	CI Direct Red 2	CI Direct Blue 1
0.1	–18.2	–20.9	–31.0
100	–18.2	–17.5	–28.3
200	–18.8	–16.2	–25.3
400	–19.3	–14.9	–22.7
600	–19.8	–14.1	–21.6

The attraction between cellulose and the leuco form of a simple polycyclic vat dye is believed to be mainly attributable to dispersion forces. Not surprisingly therefore, affinity tends to increase with relative molecular mass in the series shown in Table 3.24. This is not the only factor, however, because the eight-ring pyranthrone (3.113) has a higher affinity than the nine-ring violanthrone isomers (3.114 and 3.115). The configuration of the rings and the location of the keto groups are also significant, since violanthrone is more substantive than isoviolanthrone.

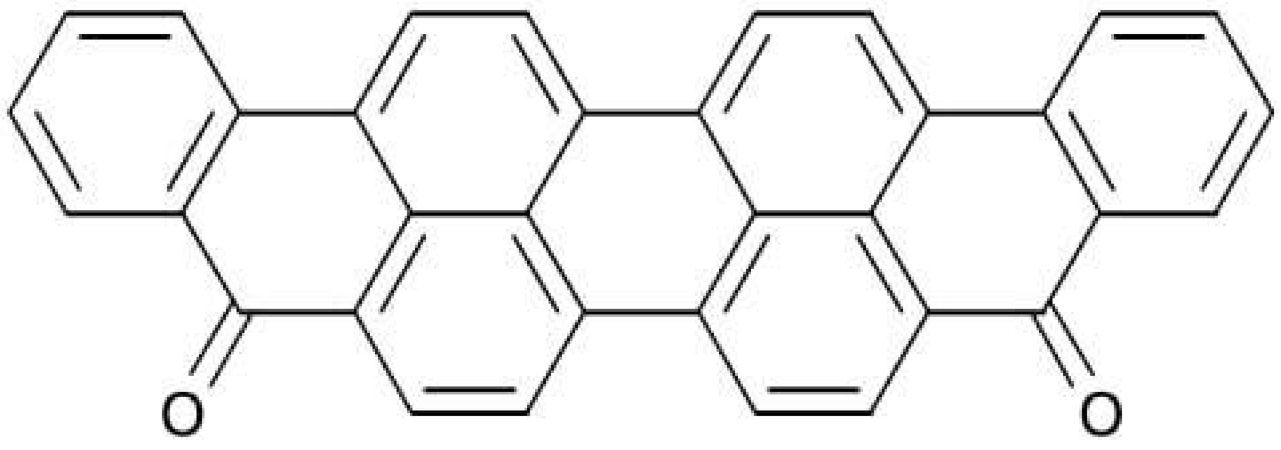
Table 3.24 Affinity of polycyclic vat dyes for cotton at 40 °C [115,121]

Polycyclic vat dye	Structure	M_r	Affinity (kJ/mol)
Pyranthrone	3.113	406	–23.2
Violanthrone	3.114	456	–22.8
Isoviolanthrone	3.115	456	–19.9
Dibenzopyrenequinone	3.116	332	–15.7
Anthanthrone	3.117	306	–12.0
Benzanthraquinone	3.118	258	–4.9



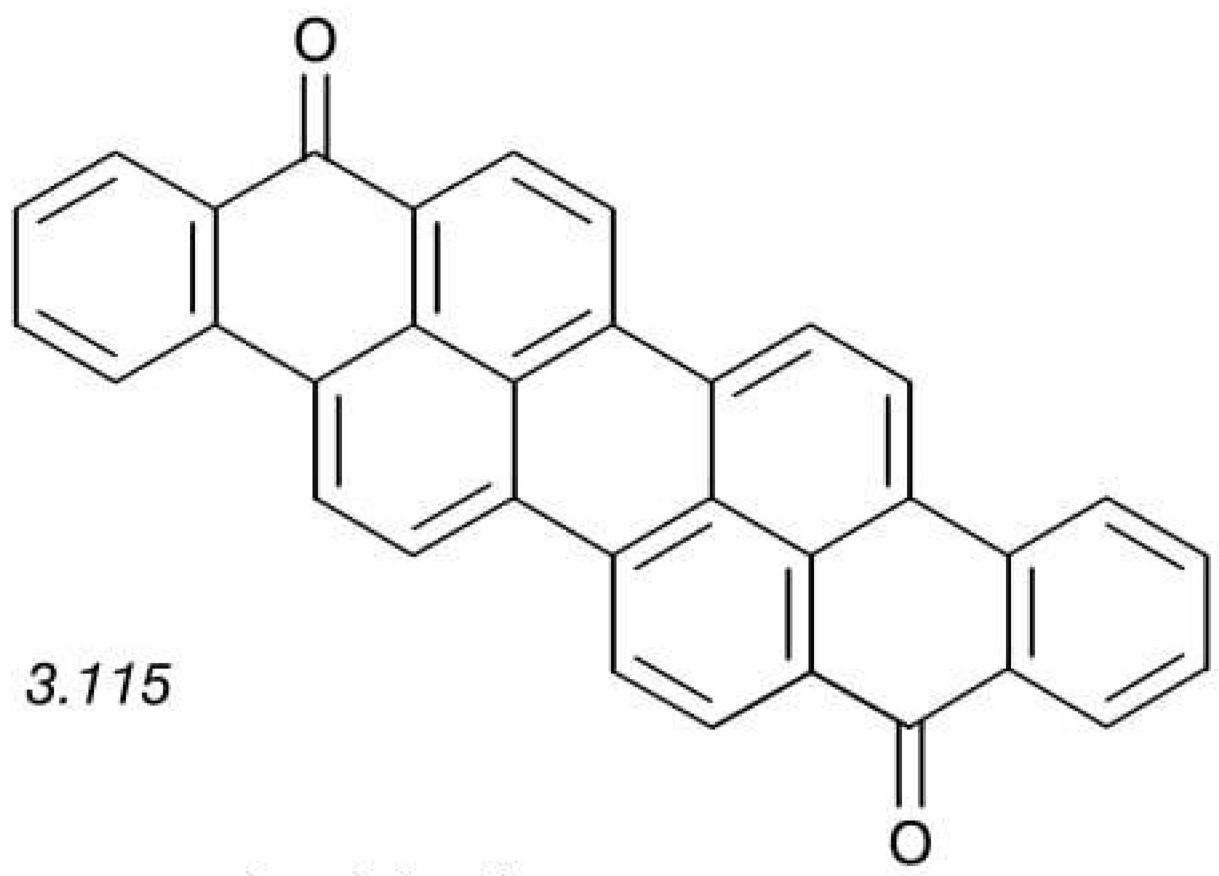
3.113

Pyranthrone



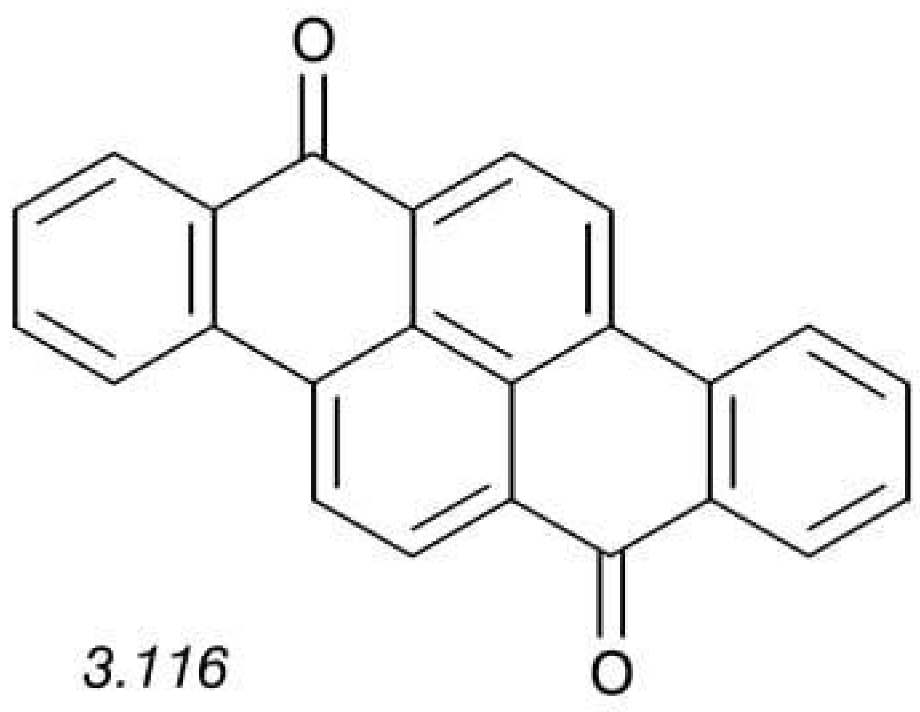
3.114

Violanthrone



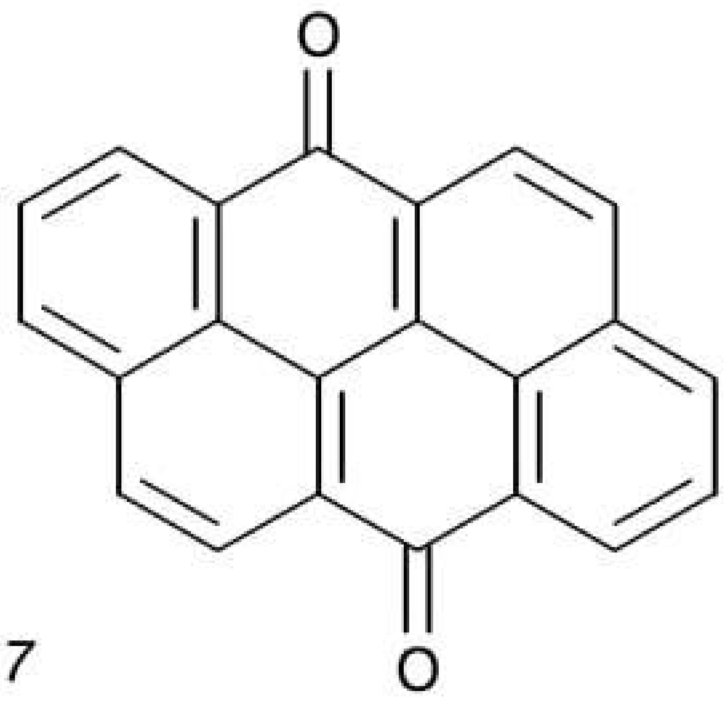
3.115

Isoviolanthrone



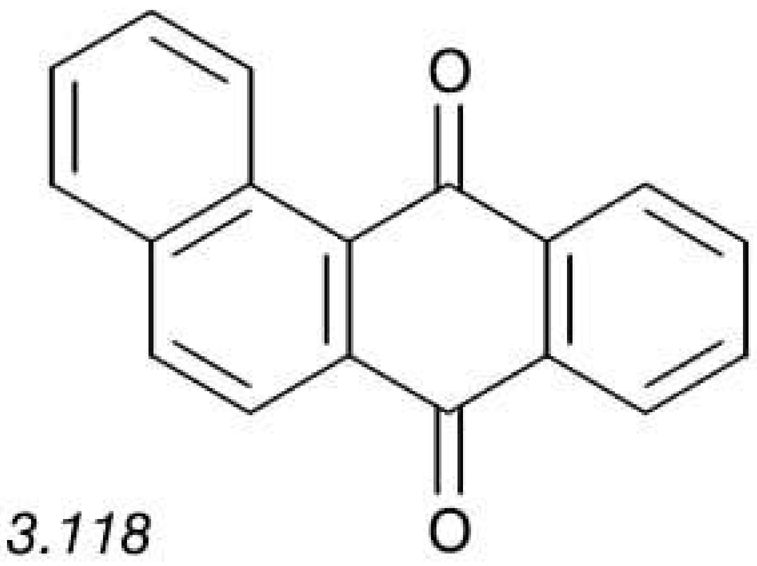
3.116

Dibenzopyrenequinone



3.117

Anthanthrone

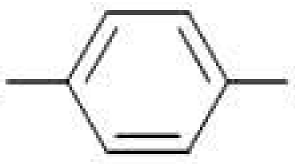
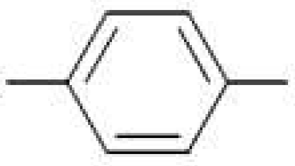
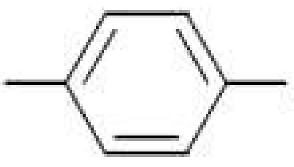


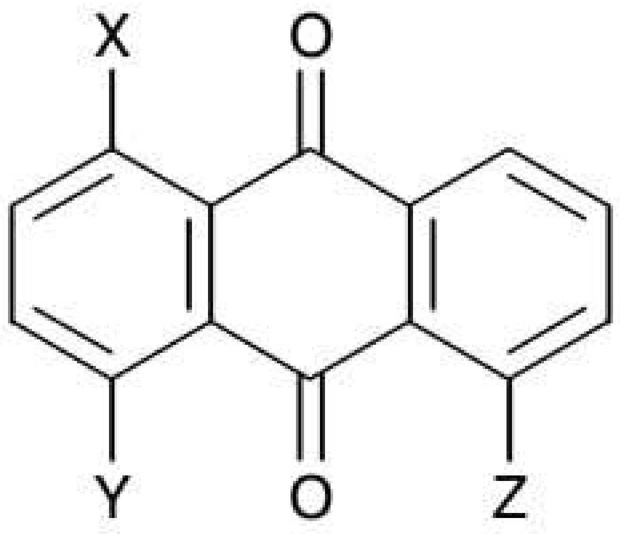
3.118

Benzanthraquinone

Hydrogen bonding is believed to strongly influence the substantivity of benzoylaminoanthraquinone vat dyes, as detailed studies have shown (Table 3.25). Introduction of a second benzoylamino group into 1-benzoylaminoanthraquinone approximately doubles the affinity, 1-4-disubstitution having a greater effect than 1,5-disubstitution. The enhanced affinity conferred by the *p*-R-substituted benzoylamino group increases with the dipole moment of the C–R bond (Table 3.25). Such substituents are almost equally effective in either *m*- or *p*-positions, but *o*-R-substituted analogues are much less substantive because coplanarity of the aryl rings with the plane of the anthraquinone nucleus is inhibited.

Table 3.25 Affinity of benzoylaminoanthraquinone vat dyes on cotton at 40 °C [115]

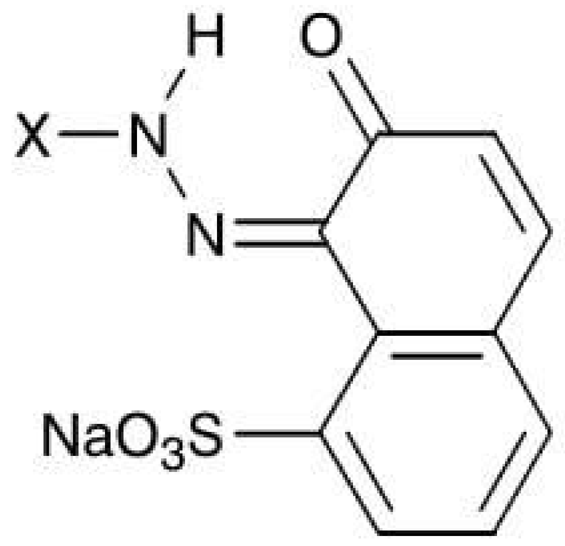
	Affinity(kJ/mol)			
Substituent (R) Dipole moment (C-R)	H	CH_3 0.41	CH_3O 1.16	Cl 1.56
Structure 3.119				
X = Y = R–  –CONH, Z = H	–15.3	–16.6	–16.0	–19.6
X = Z = R–  –CONH, Y = H	–12.0	–12.8	–14.5	–15.6
X = R–  –CONH, Y = Z = H	–6.9	–8.2	–9.1	–9.6



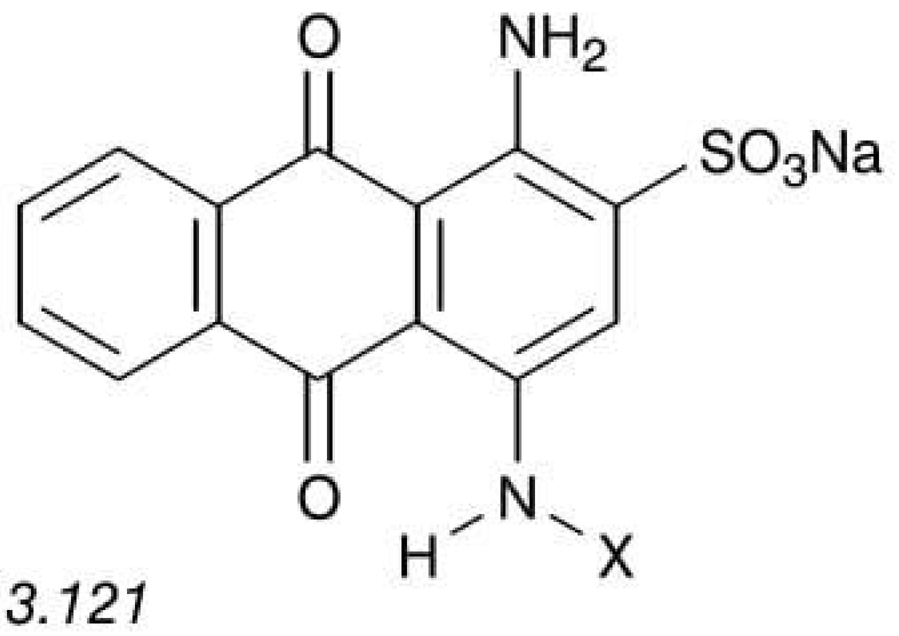
3.119

Early studies of the affinity of acid dyes for wool revealed noteworthy correlations with dye structure. For example, in four pairs of monoazo dyes differing only by replacement of a benzene by a naphthalene nucleus, the affinity increase in each pair was consistently within the range -4.6 to -6.3 kJ/mol. In three related pairs of dyes, an additional sulpho group reduced the affinity by about -4 kJ/mol. In a series of alkylsulphuric acids (ethyl, octyl, dodecyl) and in two series of monoazo dyes containing alkyl chains of increasing length, the increment per methylene group was consistently about -1.66 kJ/mol. A close correlation between affinity and M_r was also obtained for a series of substituted phenylazo-1-naphthol-4-sulphonic acid dyes [115].

Two further interesting series of systematic changes in structure have shed light on the relative effects of alkyl and aryl groupings in conferring enhanced affinity for wool. The phenylazo member (3.120; X = Ph) of the series shown in Table 3.26 has an affinity of -16.7 kJ/mol and the introduction of a 4-n-butyl substituent has almost as great an effect as the additional aryl ring when the phenylazo is replaced by a naphthylazo grouping. Likewise, in the three anthraquinone derivatives shown in Table 3.27, replacing the 4-methylamino by an n-butylamino group in structure 3.121 boosts the affinity by about 10%, but the effect of an anilino residue represents almost a 15% increase.



3.120



3.121

Table 3.26 Affinity of monoazo acid dyes for wool at 70 °C [122]

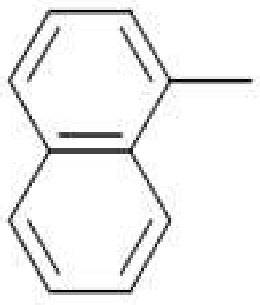
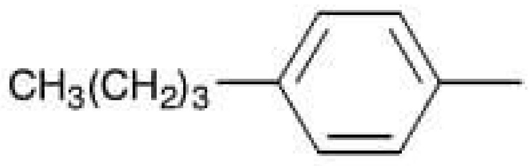
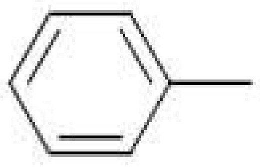
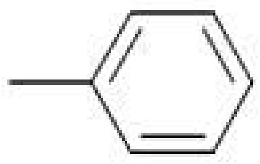
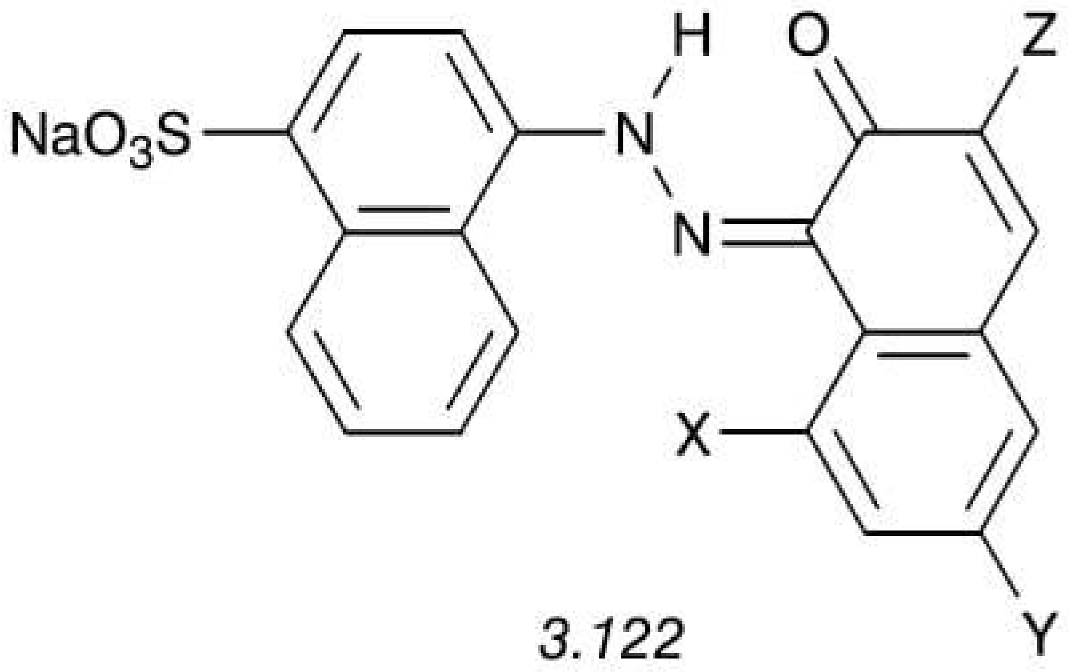
Substituent (X) in 3.120	Affinity (kJ/mol)
	−22.6
	−22.2
	−16.7

Table 3.27 Affinity of anthraquinone acid dyes for wool at 50° C and pH 4.6 [123]

Substituent (X) in 3.121	Affinity (kJ/mol)
	−25.1
$-(CH_2)_3CH_3$	−24.2
$-CH_3$	−22.2

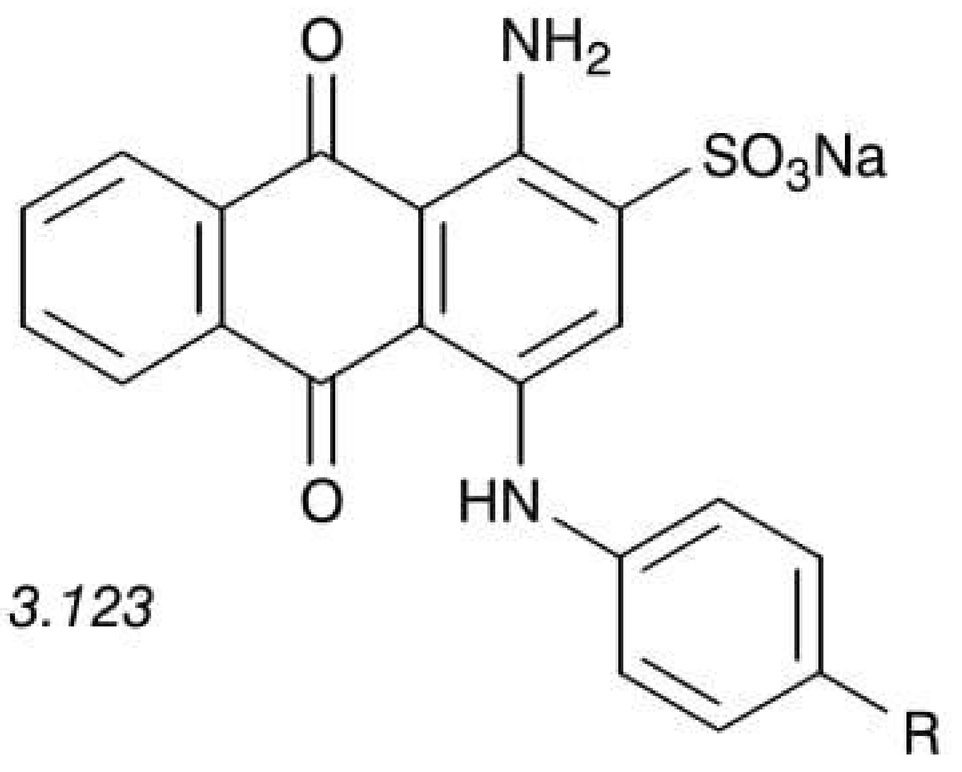
Careful measurements have been made of the affinity of many levelling and milling acid dyes for nylon using various experimental techniques. Radio tracer analysis was used to follow the uptake of a series of 1-naphthylazo-2-naphthol dyes (3.122) on nylon 6.6 film. The highest neutral-dyeing affinity was shown by the monosulphonate CI Acid Red 88 (3.122; X = Y = Z = H), which exhibited the greatest degree of overdyeing in excess of the amine end group content of the nylon. The disulphonate Red 13 (3.122; Y = SO_3Na, X=Z=H) and the trisulphonate Red 18 (3.122; X=Y=SO_3Na, Z=H) gave progressively lower neutral-dyeing affinity and overdyeing, whilst the tetrasulphonate Red 41 (3.122; X = Y = Z = SO_3Na) showed no tendency to overdye [124].



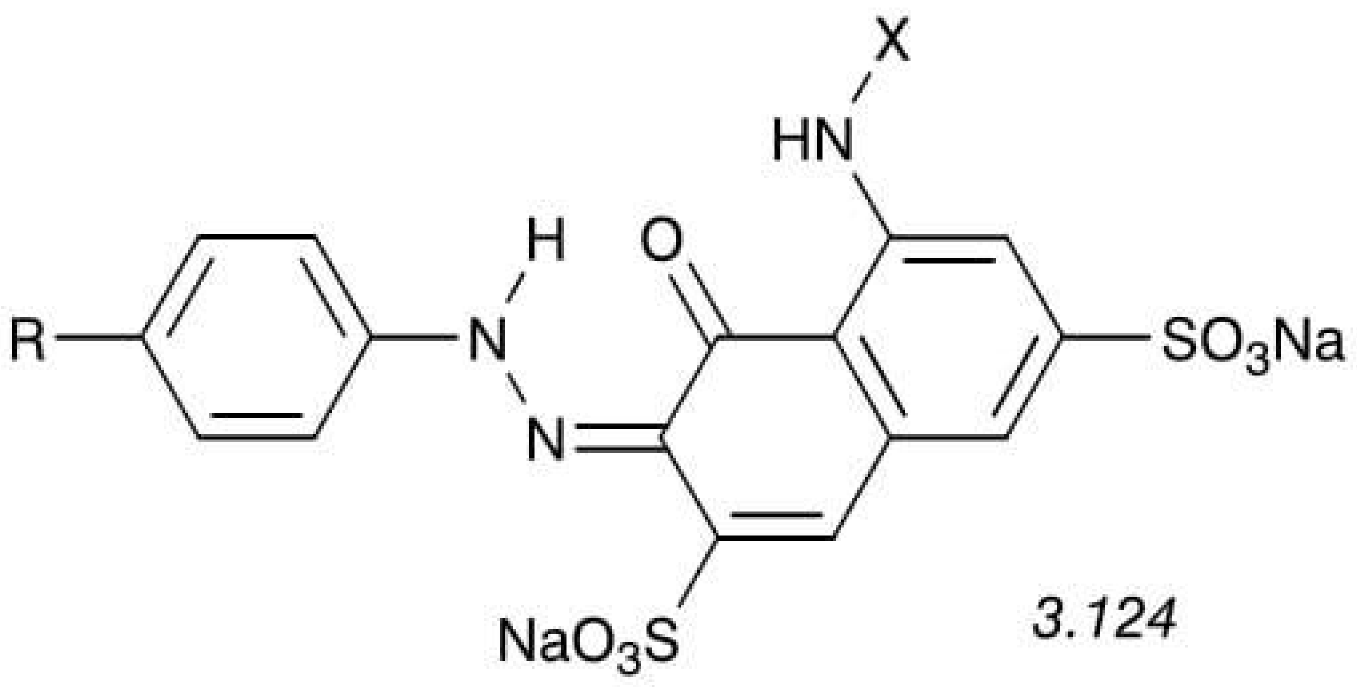
3.122

In a recent study of the series of acid dyes obtained by diazotisation of *p*-alkylanilines and coupling with 1- or 2-naphtholsulphonic acids [125], the substantivity, wet fastness and water repellency characteristics of these dyes on nylon were found to increase progressively with alkyl chain length, provided the dyes were dissolved completely in the dyebath. Aggregation to form multimers and ultimately micelle stabilisation complicates the behaviour of alkylated dye monosulphonates of this kind (section 3.1.2). This research was followed up more recently in a detailed evaluation of anthraquinone blues (3.123) prepared by condensation of bromamine acid with a series of *p*-n-alkylanilines (R = H, butyl, octyl, dodecyl or hexadecyl). Related series of monoazo dyes were synthesised using the same *p*-n-alkylanilines as diazo components with various couplers such as H acid (as in structure 3.124), γ acid, M acid, NW acid or R acid [126]. In some cases (as in 3.124; X = H or $COCF_2CF_2CF_3$) the effects of inserting a perfluorobutyroylamino substituent in the coupling component were also assessed [127]. Although the perfluoro group and the long-chain alkyl groups adversely affected substantivity for nylon 6, they did enhance wet fastness and water repellency as expected. The perfluorobutyroyl grouping was particularly effective in conferring water repellency [126].

Affinity values have been used to interpret the important practical problem of mutual blocking effects in mixture recipes on nylon [128]. Typical values for some commercially

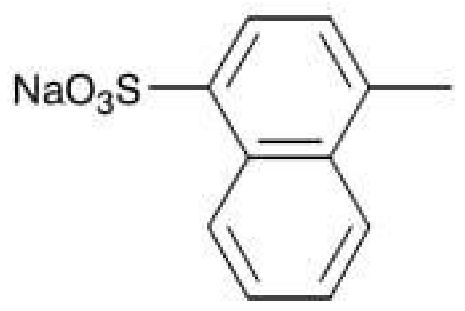
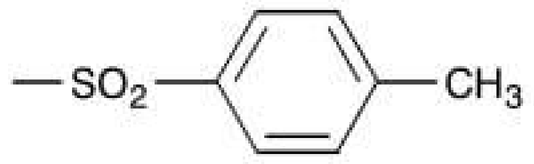
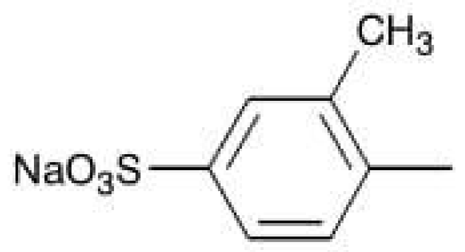
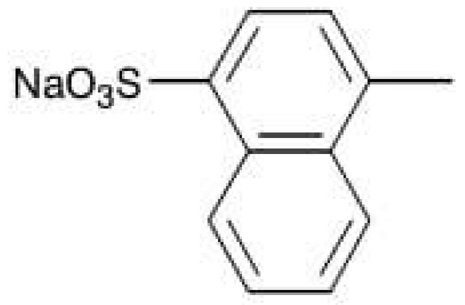
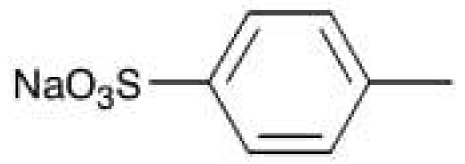
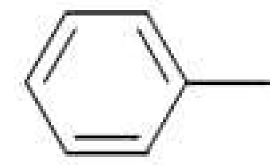


3.123

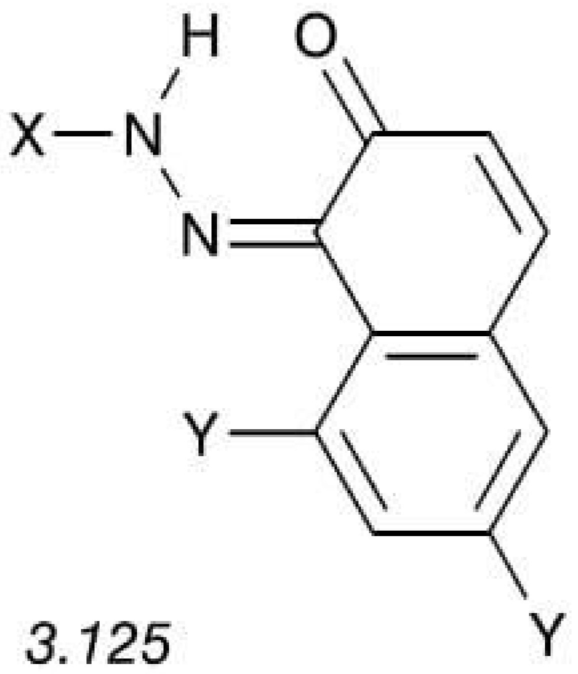


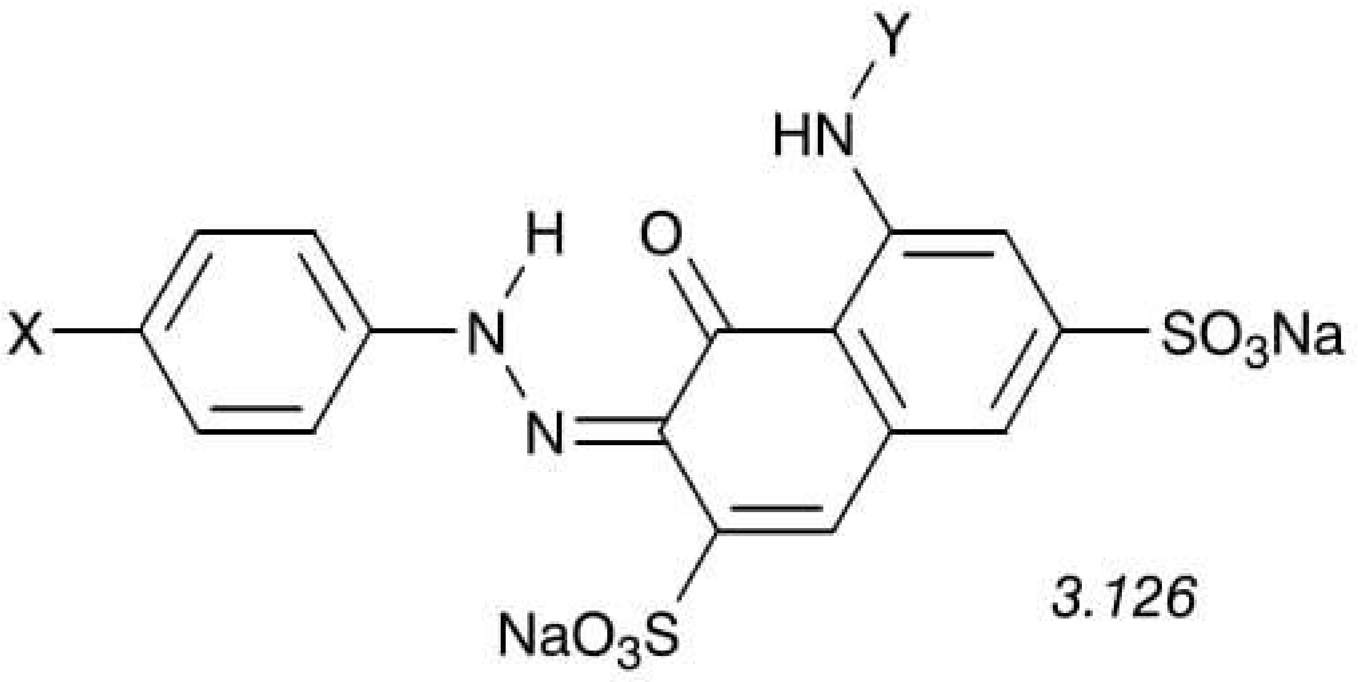
3.124

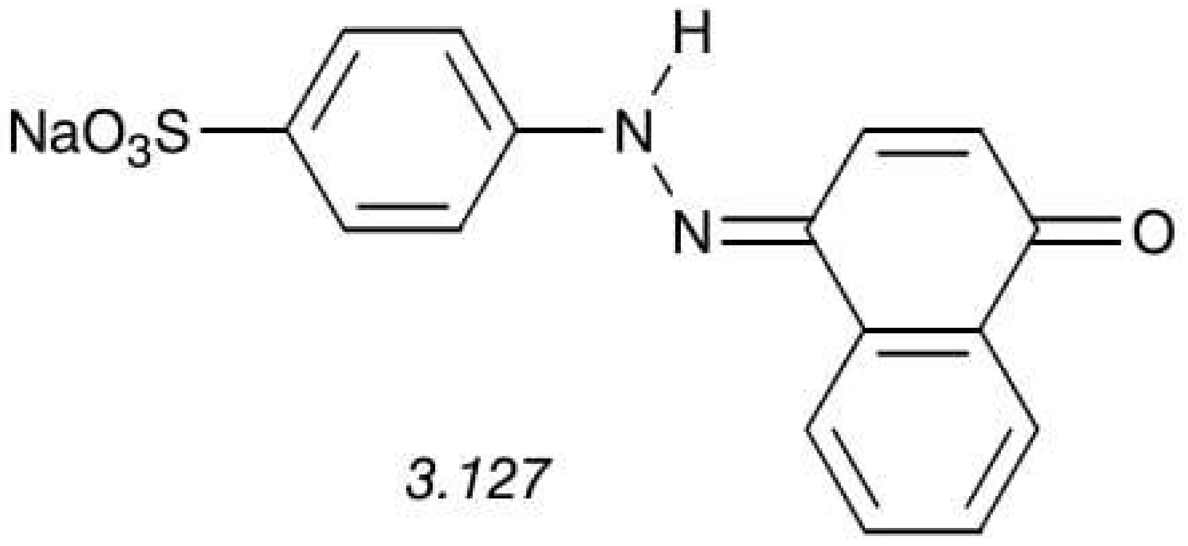
Table 3.28 Affinity of acid dyes for nylon 6.6 by chloride desorption at 75 °C [128]

CI Acid	Structure		Affinity (kJ/mol)
Red 88	3.125; X = 	Y = H	–32.0
Violet 5	3.126; X = CH_3CONH	Y = 	–27.7
Orange 20	3.127		–25.8
Orange 8	3.125; X = 	Y = H	–25.2
Red 18	3.125; X = 	Y = SO_3Na	–24.6
Orange 7	3.125; X = 	Y = H	–24.3
Violet 7	3.126; X = CH_3CONH	Y = $COCH_3$	–22.4
Yellow 17	3.128; X = CH_3	Y = Cl	–22.2
Red 1	3.126; X = H	Y = $COCH_3$	–21.4
Yellow 23	3.128; X = COOH	Y = H	–20.9
Orange 10	3.125; X = 	Y = SO_3Na	–20.9

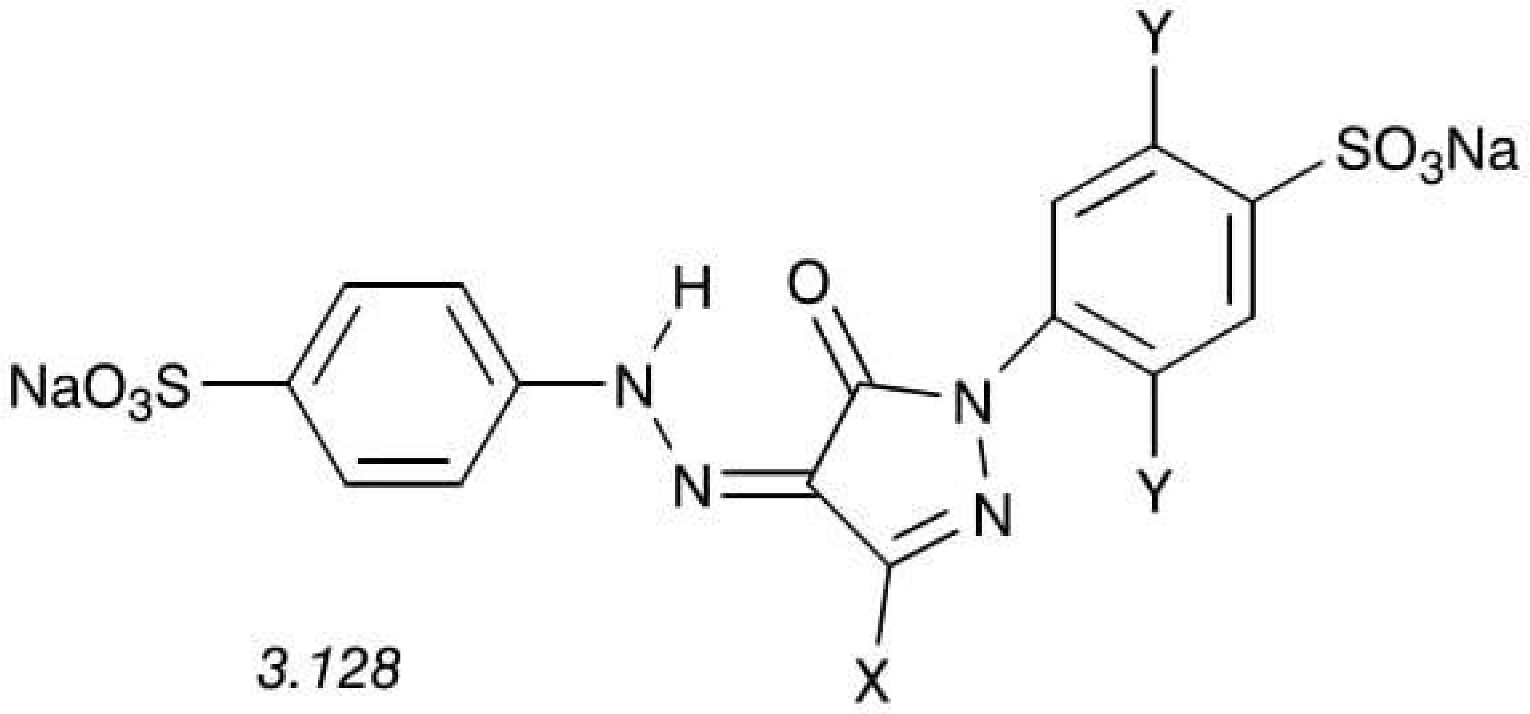
important monoazo acid dyes are given in Table 3.28. CI Acid Orange 7 is the *ortho* isomer of Orange 20 (3.127). The latter has a significantly higher affinity, probably because hydrogen bonding of the keto group with proton-donor sites in nylon is favoured. Orange 7 and Orange 10 have the same 1-phenylazo-2-naphthol chromogenic system but the additional sulpho group in Orange 10 lowers the affinity by about -3.4 kJ/mol. Similarly, the two extra sulpho groups in Red 18 reduce the affinity by about -7.4 kJ/mol compared with the analogous Red 88, the most substantive of the dyes listed in Table 3.28. Orange 8 differs from Orange 7 only in having an additional methyl substituent *ortho* to the azo linkage. This only raises the affinity by about -0.9 kJ/mol, but the bathochromic change from phenylazo to naphthylazo in going from Orange 7 to Red 88 gives an increase of approximately -7.7 kJ/mol, virtually the same magnitude as the lowering effect of two sulpho groups.


3.125


3.126


3.127

CI Acid Orange 20


3.128

In the series of three *N*-acylated phenylazo H acid dyes (3.126), the additional *p*-acetylamino group in Violet 7 enhances the affinity above that of Red 1 by about –1.0 kJ/mol, as well as producing a marked bathochromic shift in hue. Replacing the *N*-acetylamino group in the H acid residue by *N*-*p*-tosylamino (Violet 5) has less effect on hue but raises the affinity by about –5.3 kJ/mol. Somewhat surprisingly, replacing the carboxyl group in the azopyrazolone chromogen (3.128) of Yellow 23 by a methyl group and introducing two chloro substituents into the *N*-phenyl ring only increases the overall affinity by about –1.3 kJ/mol.

The yield of disperse dyes on polyester is limited by their slow rate of diffusion into the fibre rather than by inherently low substantivity. If dyeing times are sufficiently long, saturation values on polyester approach those on cellulose acetate and often exceed those on nylon (Table 3.29; for structures of these dyes see Tables 3.14 and 3.18).

Some early measurements of the partition of various aminoanthraquinone derivatives between cellulose acetate and ethanol (Table 3.30) dramatically illustrate the value of primary amino groups in conferring affinity for cellulose acetate. Indeed, the introduction of

Table 3.29 Saturation values of disperse dyes on hydrophobic fibres at 85 °C [113]

		Saturation value (% o.w.f.)		
CI Disperse	Structure	Acetate	Nylon	Polyester
Yellow 1	3.98	16.0	5.0	7.1
Red 15	3.96; X = NH_2, Y = OH	11.2	4.4	12.0
Violet 1	3.96; X = Y = NH_2	8.3	4.9	4.4
Orange 3	3.95; X = Y = H	5.1	2.0	4.1

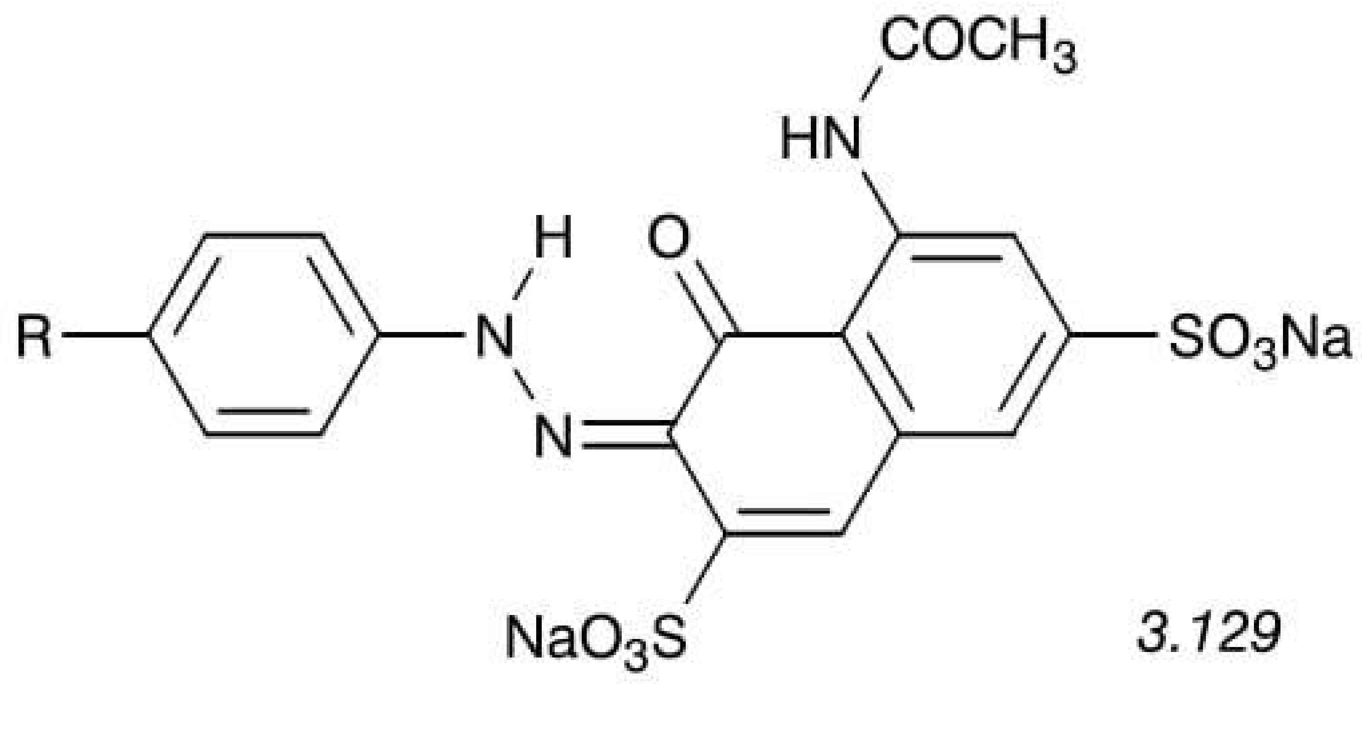
Table 3.30 Partition coefficients of aminoanthraquinone derivatives between cellulose acetate and ethanol at 60 °C [129]

Anthraquinone derivative	Partition coefficient
1,4,5,8-Tetra-amino	8.77
1,5-Diamino	6.64
1,8-Diamino	5.73
1,4-Diamino	2.80
1-Amino-2-methyl	2.67
1-Methylamino	2.38
1-Amino	1.79
1-Amino-4-hydroxy	1.59

a 4-hydroxy group into 1-aminoanthraquinone actually lowers the affinity for the fibre slightly, perhaps by favouring intermolecular hydrogen bonding and thus greater aggregation in the ethanolic phase. Methylation of the 1-amino group promotes affinity, but introduction of a 2-methyl substituent into 1-aminoanthraquinone has a greater effect. The most impressive increases, however, are caused by further amino substitution. The partition coefficients of the 1,4-, the 1,8- and the 1,5-isomers are respectively about twice, three times and four times that of the monoamino analogue. Further amino substitution has a less marked effect, the 1,4,5,8-tetra-substituted derivative having a partition coefficient about five times that of 1-aminoanthraquinone.

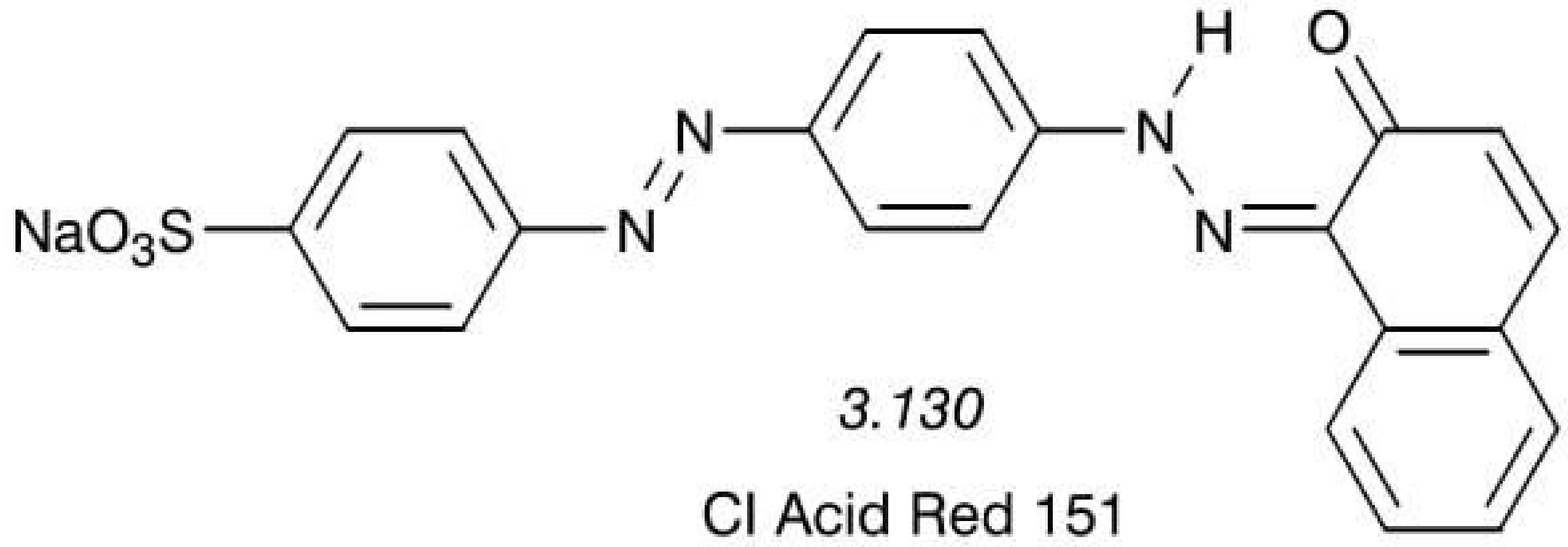
3.3.3 Effect of dye structure on migration and levelling

Early investigators of the skittery dyeing of wool concluded that the differences in dyeability between individual fibres are attributable to the variations in extent of degradation that they have undergone in the fleece and during preparation [130,131]. The responses of levelling and milling acid dyes to such differences were studied in detail [132]. With typical levelling acid dyes such as CI Acid Red 1 (3.129; R = H) the proportion of ring-dyed fibres present gradually increases with dyeing temperature up to a maximum at about 70 °C. As dyeing continues above this temperature the content of ring-dyed fibres gradually falls again and uniformly penetrated fibres begin to predominate. Eventually the migration process ensures that a level and fully penetrated dyeing is achieved.



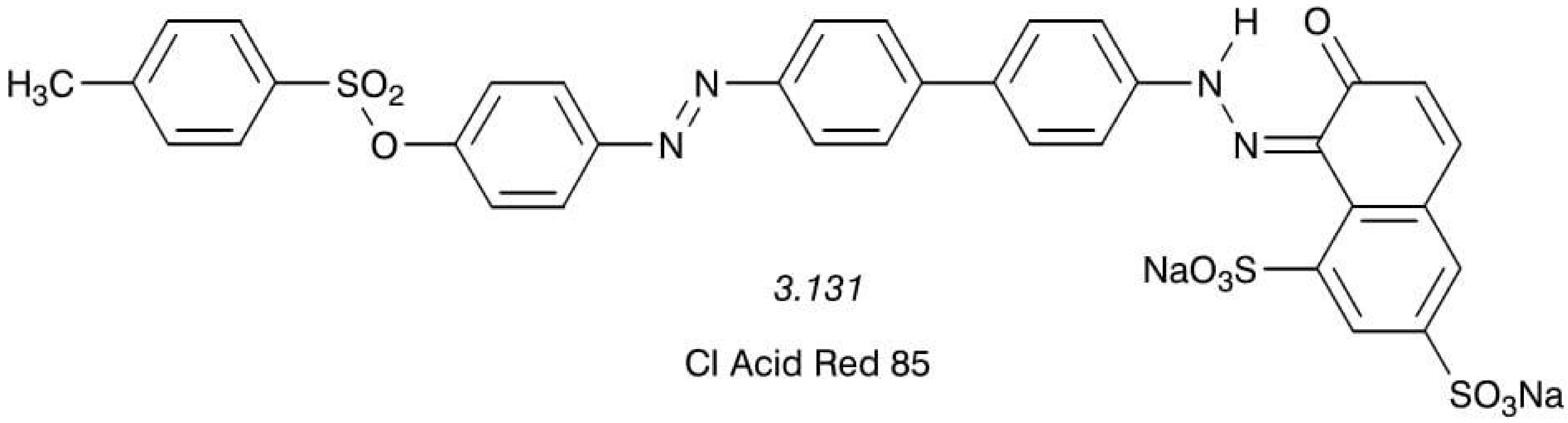
3.129

Milling acid dyes behave in a more individual way. The disazo monosulphonate CI Acid Red 151 (3.130) is absorbed extremely rapidly at low temperature, all fibres becoming ring-dyed. Little further uptake takes place until the temperature approaches 90 °C. Diffusion into the fibre then accelerates markedly, the proportion of ring-dyed fibres rapidly falling to zero and soon all fibres present become deeply and uniformly dyed. The disazo disulphonate CI Acid Red 85 (3.131), however, shows virtually no uptake at all below 70 °C and ring dyeing is at a maximum in the range 80–90 °C. Only after boiling for about 30 minutes does the proportion of fully penetrated fibres exceed that of ring-dyed ones. A level dyeing of satisfactory fastness requires at least an hour at the boil. More hydrophobic 'super-milling' dyes such as CI Acid Red 138 (3.129; R = n-dodecyl), the *p*-alkylated analogue of Red 1, give ring dyeings at 70 °C and above. Even after prolonged boiling, it is difficult to attain more than a small proportion of fully penetrated fibres. Such dyes tend to be especially sensitive to skitteriness and to root-tip differences of dyeability in weathered wool.



3.130

CI Acid Red 151



3.131

CI Acid Red 85

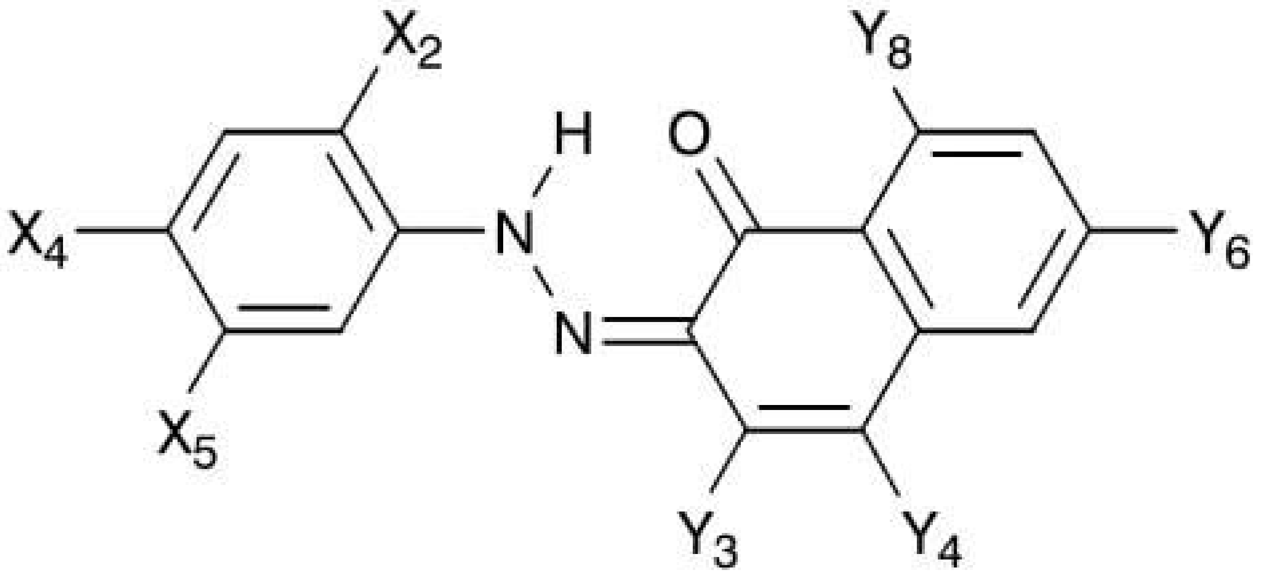
As already indicated in section 3.3.2, the introduction of a further sulpho group into an acid dye tends to lower the affinity by about –4 kJ/mol. The results in Table 3.31 for two series of phenylazo-l-naphthol dyes with varying degrees of sulphonation clearly demonstrate that the increase in hydrophilic character brought about in this way significantly impairs their migration behaviour. Thus the monosulphonated levelling acid dye sulphanilic acid→1-naphthol has excellent migration properties, but the pentasulphonated analogue aniline-2,5-disulphonic acid→oxy-Koch acid migrates only with great difficulty.

Systematic studies of the relationship between disperse dye structure and levelling properties on the ester fibres have shown that in general levelling tends to decrease as molecular size increases. Thus an inverse linear correlation was found between the molar volume of a series of disperse dyes and their barriness rating on polyester [90]. As molecular size increased, migration became less effective in covering dye affinity variation in a textured polyester fabric prone to show barriness. Molecular size is not the only relevant factor, however, because disperse dyes with significant aqueous solubility show better migration properties than less soluble dyes of similar molecular size.

Disperse dyes containing n-alkyl substituents within the range butyl to octadecyl showed only 20-40% exhaustion on polypropylene fabric. Exhaustion and washing fastness increased but levelling decreased with increasing alkyl chain length. Dyeing with 1,4-bis(octylamino)anthraquinone in the presence of an ethoxylated octadecanol surfactant,

Table 3.31 Migration properties of phenylazonaphthol acid dyes on wool [115]

Structure (3.132; unspecified X and Y = H)	Basicity	Migration
$Y_4 = SO_3Na$	1	5
$X_4 = Y_4 = SO_3Na$	2	4
$X_2 = X_5 = Y_4 = SO_3Na$	3	3–4
$X_4 = SO_3Na$	1	5
$X_4 = Y_4 = SO_3Na$	2	4
$X_4 = Y_6 = Y_8 = SO_3Na$	3	3–4
$X_4 = Y_3 = Y_6 = Y_8 = SO_3Na$	4	3
$X_2 = X_5 = Y_3 = Y_6 = Y_8 = SO_3Na$	5	2



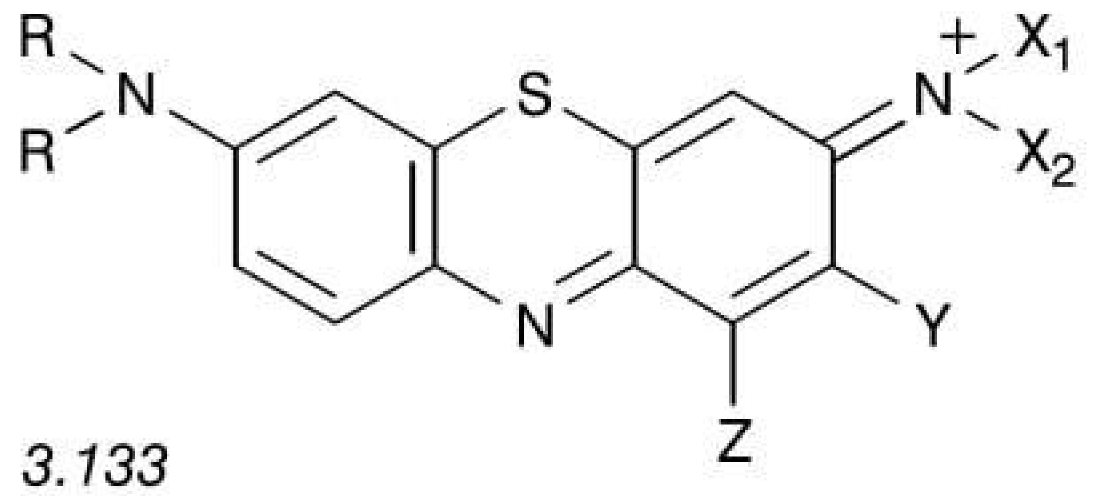
3.132

however, gave 70-90% exhaustion and markedly improved levelling. Exhaustion increased progressively with the degree of ethoxylation of the nonionic levelling agent [133].

An interesting comparison of the migration behaviour of a related series of alkylaminothiazine basic dyes on an acrylic fibre is outlined in Table 3.32. Methylene blue (CI Basic Blue 9), the best known of these, is the tetra-*N*-methylated derivative with a migration rating of 2–3. Insertion of a nitro group *meta* to one of the dimethylamino groups slightly impairs migration. As might be expected, the completely unmethylated diaminothiazine structure shows excellent migration, whereas the tetra-*N*-ethyl analogue of methylene blue migrates only with great difficulty. Surprisingly, removal of one of the *N*-methyl groups from the methylene blue structure reduces migration slightly, but the isomeric trimethylated derivative with one of the methyl groups *ortho* to the unmethylated amino group has a migration rating almost as good as the parent unmethylated diaminothiazine.

Table 3.32 Migration properties of thiazine basic dyes on acrylic fibre [134]

Structure (3.133)	Migration
R = X = Y = Z = H	5
$R = Y = CH_3$, X = Z = H	4
$R = X_1 = CH_3$, $X_2 = Y = Z = H$	2
$R = X = CH_3$, Y = Z = H	2–3
$R = X = CH_3$, Y = H, $Z = NO_2$	2
$R = X = CH_2CH_3$, Y = Z = H	1



3.133

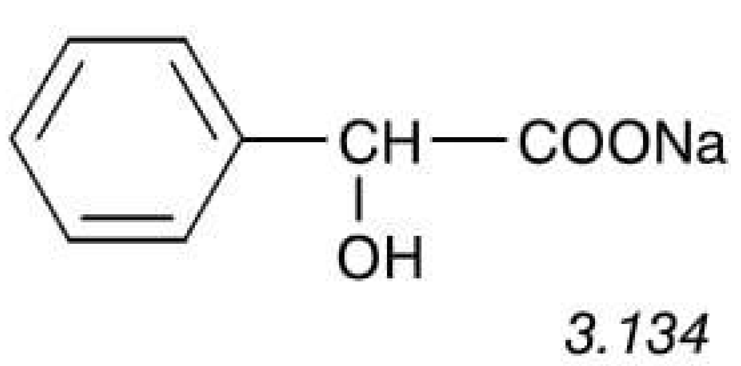
3.3.4 Dye structure and light fastness

The fastness to light of a dyed fibre depends on many factors. These include the inherent stability of the dye chromogen when exposed to photochemical attack and the way in which this interaction is modified by the polymer substrate and the conditions of exposure. General reviews of the mechanisms of fading reactions and the influence of dye structure and aggregation behaviour on these processes are available [135–140]. Kinetic evidence indicates that the light fastness of direct dyes on cotton is markedly dependent on the formation of aggregates within the fibre. This can sometimes lead to apparently anomalous differences in fastness rating for the same dye applied and aftertreated in various ways. Hence the light fastness of direct dyeings is determined more by their state of aggregation than by structural features of the dye chromogen [141–145].

Interesting pointers to the reasons for the limited light fastness of monoazo red and disazo blue reactive dyes on cellulosic fibres, particularly those derived from H acid coupling components, have emerged in recent years. Experimental evidence for free-radical formation has been presented and the important role of radical reactions in the fading mechanisms of reactive dyes has been defined [146]. The environmental effects of atmospheric oxygen on the fading behaviour of aminochlorotriazine reactive dyes on dry cotton fabric have been investigated. Most of the dyes were degraded in two stages, a rapid initial fade followed by a slower and incomplete process. Oxygen accelerated the major fading step for almost all dyes, but a phthalocyanine derivative was more sensitive in a nitrogen atmosphere. In some instances the mechanism of fading in air was initially oxidative but became reductive in the second stage [147].

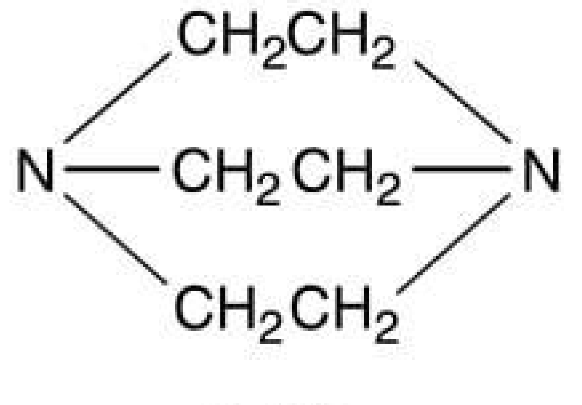
Accelerated fading in the wet state is characteristic of many azo reactive dyeings. If cellulose dyed with such dyes is exposed to light in aerated water the fading mechanism is an oxidative one. The rate of fading depends on dye structure, pH and oxygen concentration present [148]. Photoreduction can take place on exposure in deaerated water, however, especially in the presence of sodium mandelate (3.134) under a nitrogen atmosphere. Catalytic wet fading of certain azopyrazolone yellow reactive dyes in mixture dyeings with phthalocyanine or triphenodioxazine blues has long been recognised as an important problem of reactive dye selection. The effect is very slight in the dry state and is almost completely suppressed in the absence of oxygen. Considerable protection of the azopyrazolone component is achieved by adding the singlet oxygen quencher 1,4-diazabicyclo[2,2,2]octane (3.135). Oxidative destruction of the azopyrazolone chromogen does not rupture the ether bond formed in the dye-cellulose fixation process [148].

Complaints of accelerated or anomalous fading of reactive dyeings often implicate azo dyes derived from H acid and may involve wetting of the affected textile by perspiration during sunlight exposure. The mechanism of fading by light and perspiration simultaneously is not always the same as fading by light alone. In the dry state, dyes of the H acid type generally fade by a reductive mechanism but in the presence of aerated water the



3.134

Sodium mandelate



3.135

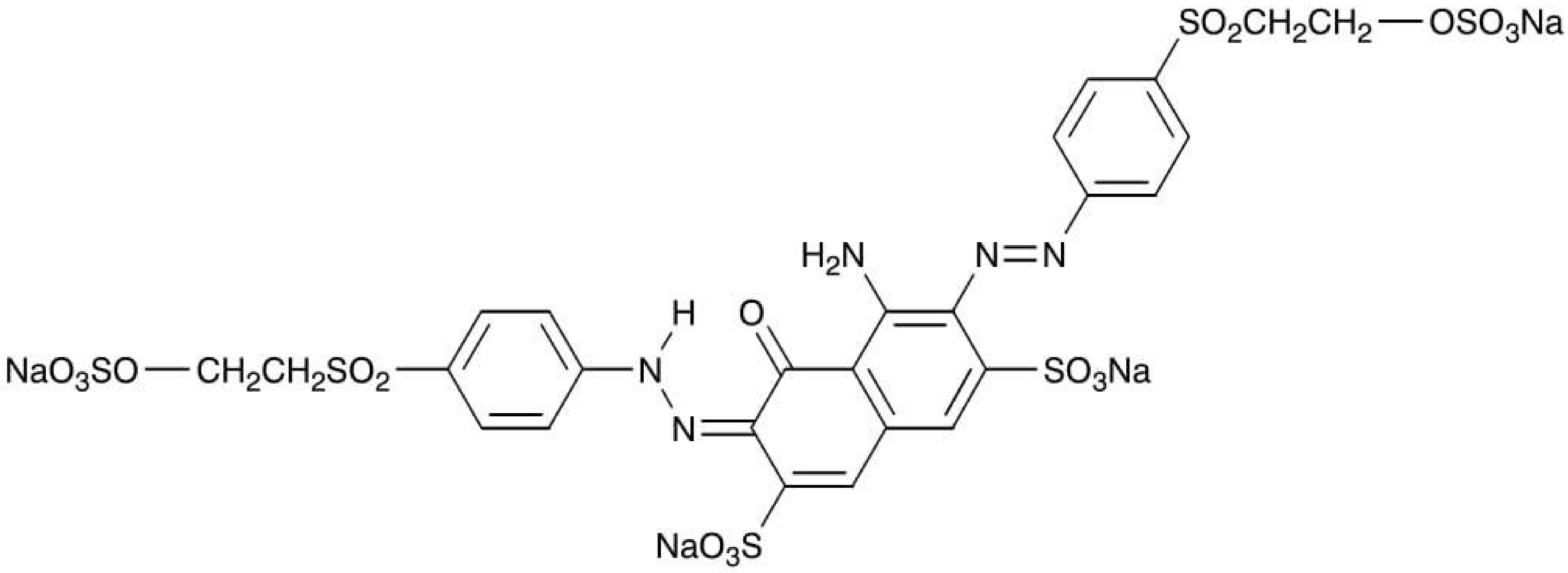
DABCO

degradation reaction becomes oxidative. Dyes containing strongly electron-donating substituents tend to fade oxidatively, whereas those with strongly electron-withdrawing groups are more vulnerable to reductive attack. The reductive fading mechanism is greatly enhanced when the exposed dyeing is wetted with acidic or alkaline perspiration [149].

In a recent study of the combined effects of perspiration and light, garments dyed with five typical reactive dyes of various chromogenic types (Table 3.33) were worn by tennis players in bright sunlight. The fastness ratings showed good agreement with results from the Japanese ATTS test on these dyeings. The sensitivity to this problem shown by the commercially predominant disazo CI Reactive Black 5 (3.136) derived from H acid was confirmed, compared with the much more stable anthraquinone derivative CI Reactive Blue 19 (3.137).

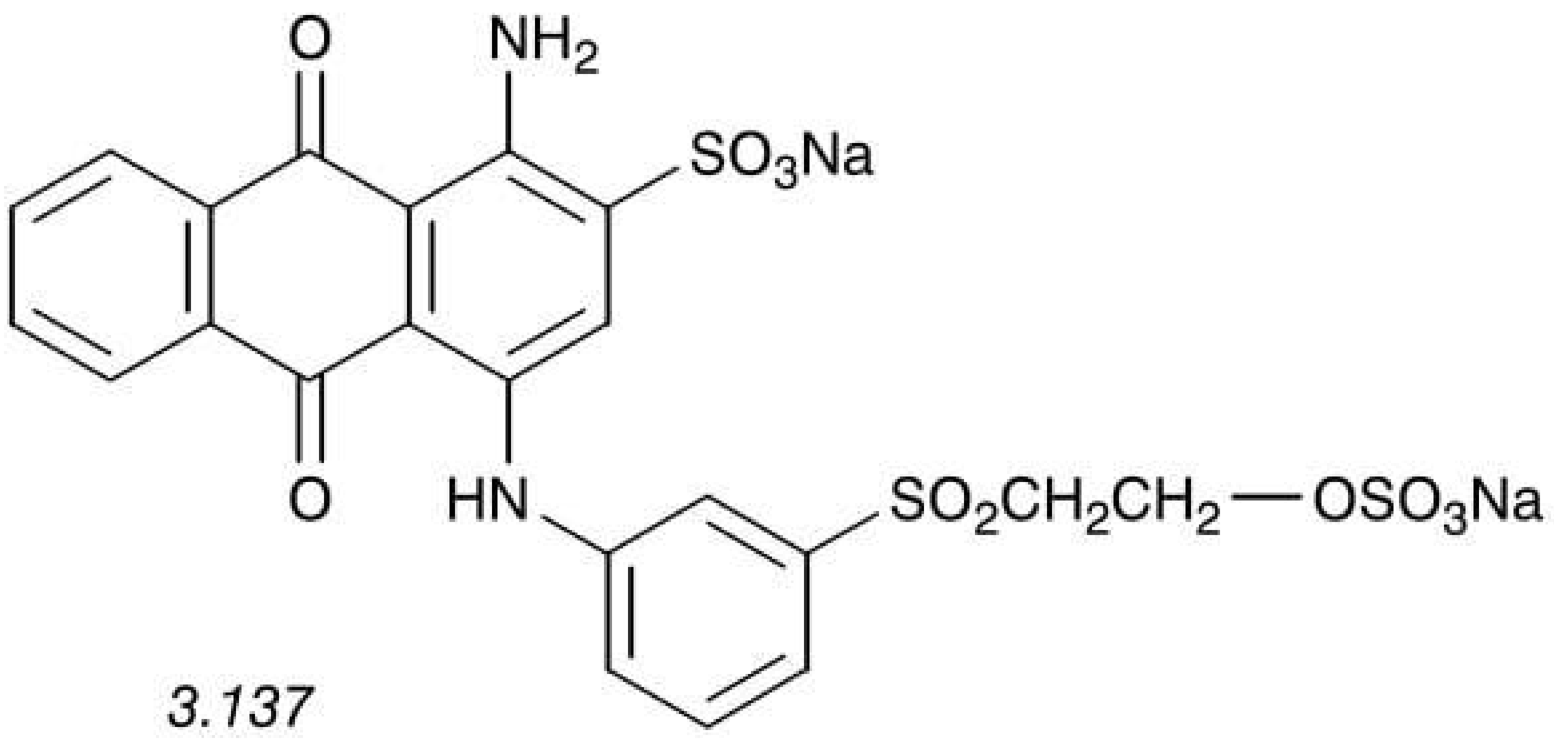
Table 3.33 Wearer trial and fastness tests on dyeings representing various chromogens [150]

CI Reactive	Chromogen	Wearer trial	Perspiration (acid)/light ATTS test	Light Xenon arc
Blue 19	Anthraquinone	4	3–4	5
Blue 221	Copper-formazan	3	3	5
Blue 28	Copper-monoazo	1–2	1	5
Blue 222	Azo	2–3	2–3	4–5
Black 5	H acid disazo	2	1	4–5



3.136

CI Reactive Black 5



3.137

CI Reactive Blue 19

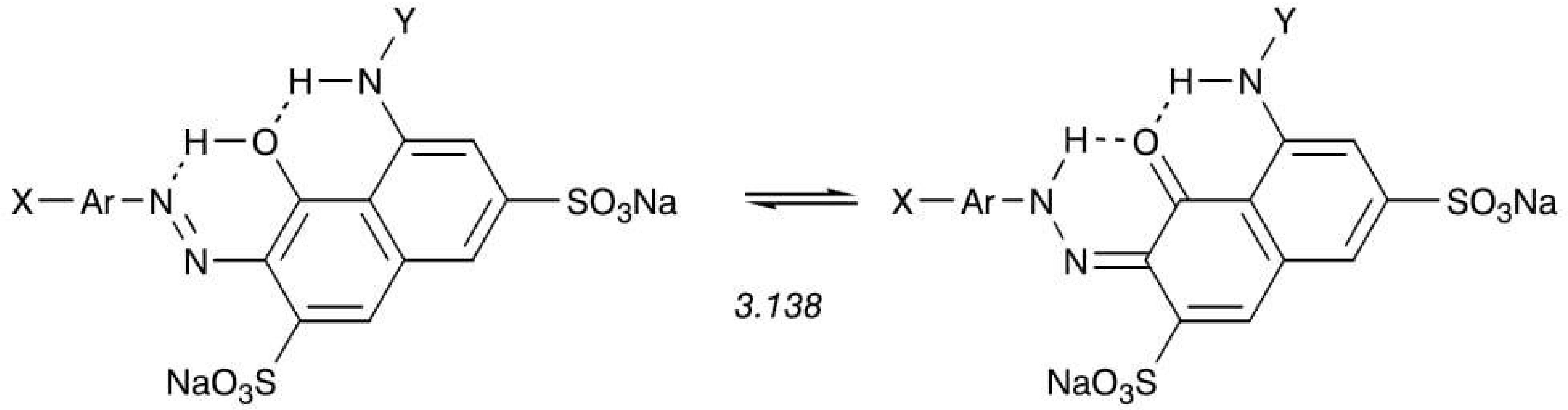
The tendency of Black 5 and other widely used azo reactive dyes of acceptable light fastness to give rise to customer complaints when exposed to light in the presence of perspiration was examined further. Dyeings of eight reactive dyes representing a variety of azo chromogens, mostly with a sulphatoethylsulphone reactive system but also including one dichlorotriazine dye and one with a bifunctional system, were subjected to ATTS tests and xenon arc exposure (Table 3.34). Surprisingly, the J acid dye was more resistant to perspiration/light fading than to a conventional light fastness test. The four dyes derived from H acid or K acid faded much more rapidly in the ATTS test, but the azopyrazolone, azonaphthalene and γ acid monoazo chromogens appeared to be unaffected by the presence of perspiration during exposure.

Table 3.34 Perspiration and light fastness of various azo reactive dyes [150]

Reactive system	Azo chromogen	Perspiration (acid)/light ATTS test	Light Xenon arc
Sulphatoethylsulphone (SES)	Azopyrazolone	4–5	5
Bifunctional (SES/MCT)	Azonaphthalene	5	5
SES	γ acid monoazo	4	4
Dichlorotriazine (DCT)	J acid monoazo	4–5	3–4
SES	H acid monoazo	2	4–5
SES	K acid monoazo	1	4–5
SES	H acid Cu-monoazo	1	4–5
SES	H acid disazo	1	4–5

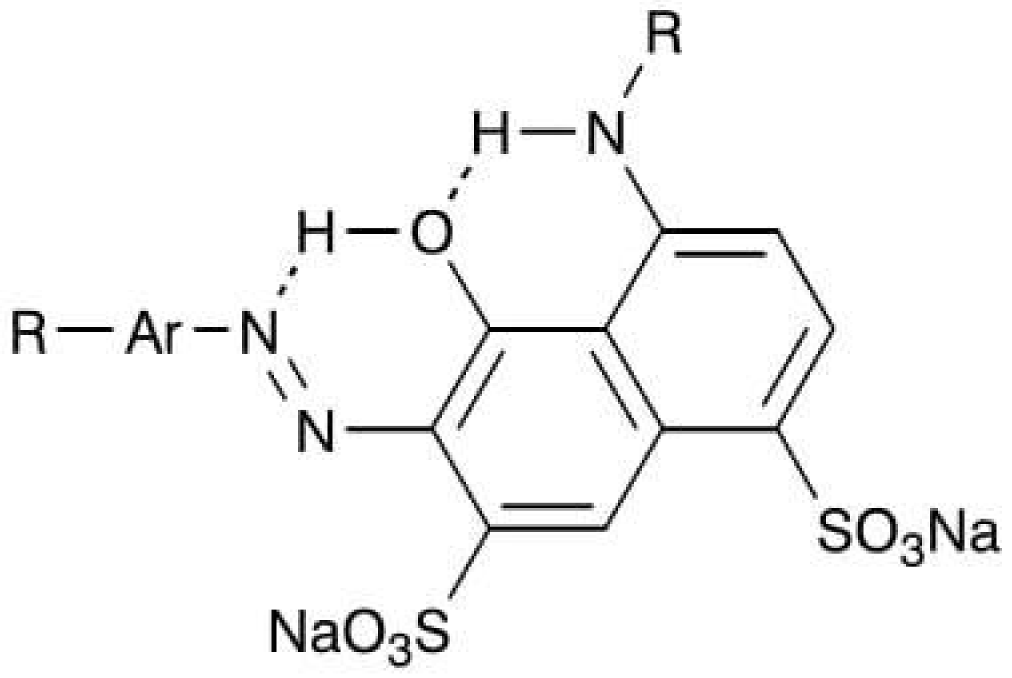
These marked differences in response between different types of azo chromogen have been interpreted [150] in terms of tautomerism of their aminonaphthol structures (Scheme 3.15). When the imino nitrogen is *peri* to the hydroxy group, as in H acid (3.138) and K acid (3.139) dyes, the reduction-sensitive hydroxyazo form is stabilised by hydrogen bonding with the imino grouping. In J acid (3.140) and γ acid (3.141) derivatives, however, hydrogen bond stabilisation of either tautomer by the imino group cannot take place. Independent studies of the fading behaviour of tautomeric azo dyes have shown that the hydrazone form is more resistant to photoreduction than the azo form, but has a lower stability to photo-oxidation by singlet oxygen [151]. In the monoazo red reactive dyes derived from H acid, the location and nature of the reactive system has a significant influence on fastness to the perspiration/light test (Table 3.35). When the reactive group is attached to the diazo component this leads to lower fastness ratings than when it is linked via an imino group to the coupling component (3.138).

The fading behaviour of azoic dyeings on cotton is determined mainly by the chemical characteristics of the diazo and coupling components. Although they show generally high fastness when exposed in full depths under dry conditions, this stability declines sharply with increasing humidity or decreasing applied depth. Electron-withdrawing substituents in the phenylazo grouping, especially trifluoromethyl or nitro, enhance light fastness but electron-donating groups such as *o*-methyl or *o*-methoxy usually lower the ratings. Substituents in the anilide nucleus of Naphtol AS combinations, however, influence light fastness in the opposite way. For example, in a series of coupling components used with *o*-nitroaniline as diazo component (3.142), the highest light fastness was found for R = *p*-methoxy and the lowest for R = *m*-nitro [152].



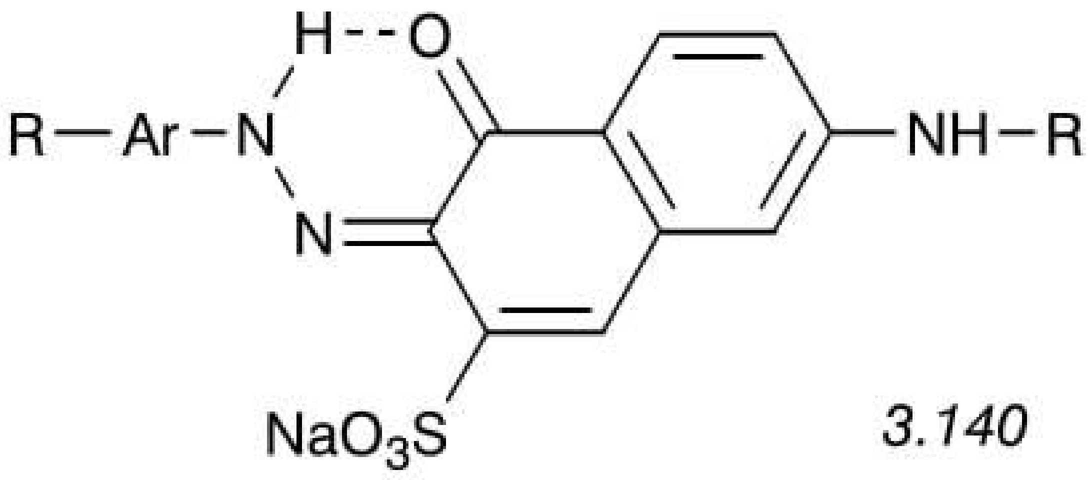
3.138

Scheme 3.15 H acid dyes



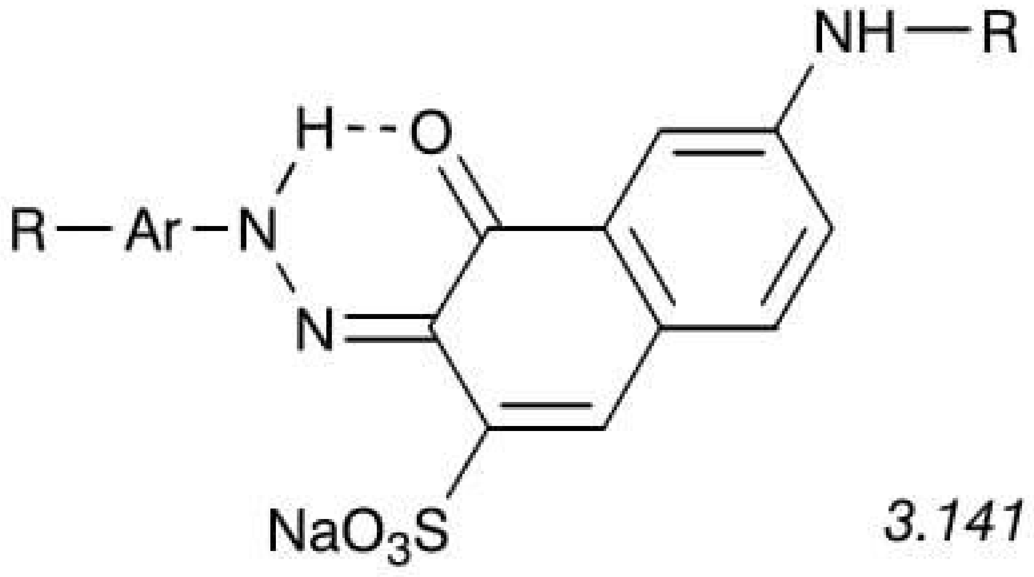
3.139

K acid dyes



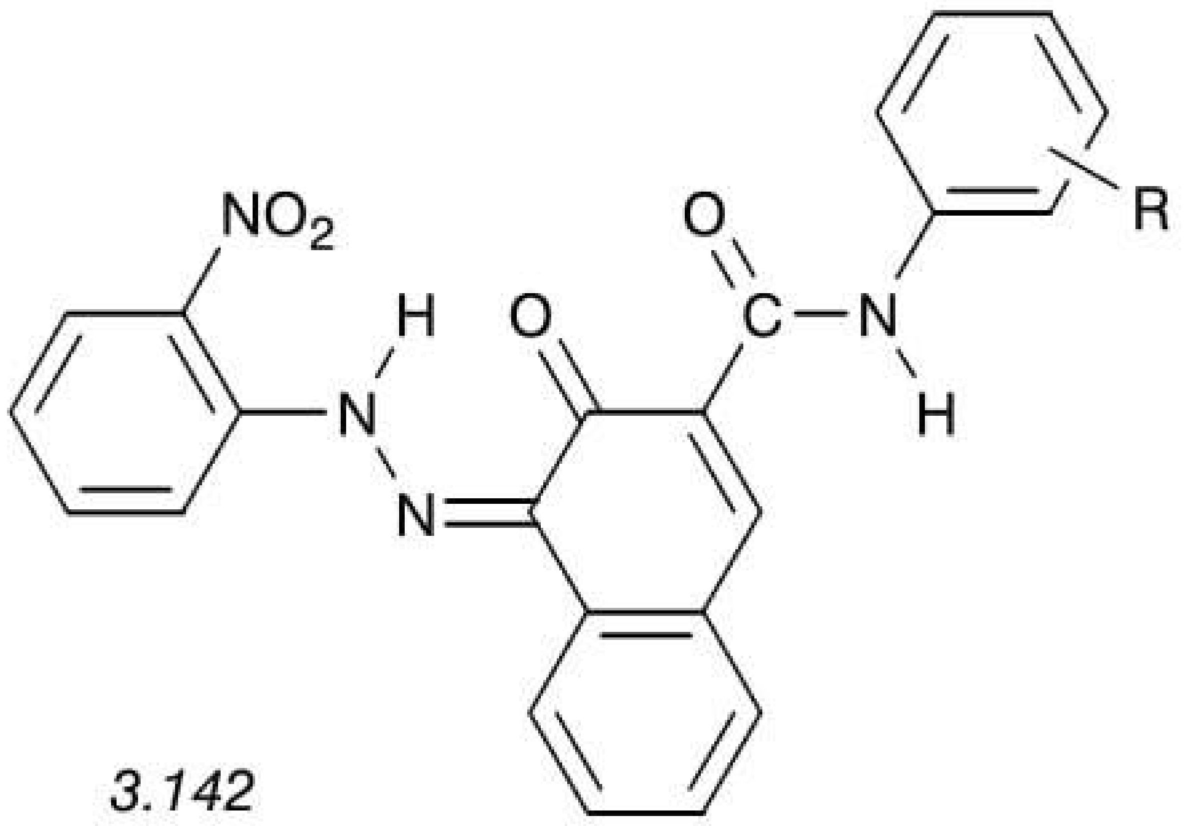
3.140

J acid dyes



3.141

γ acid dyes

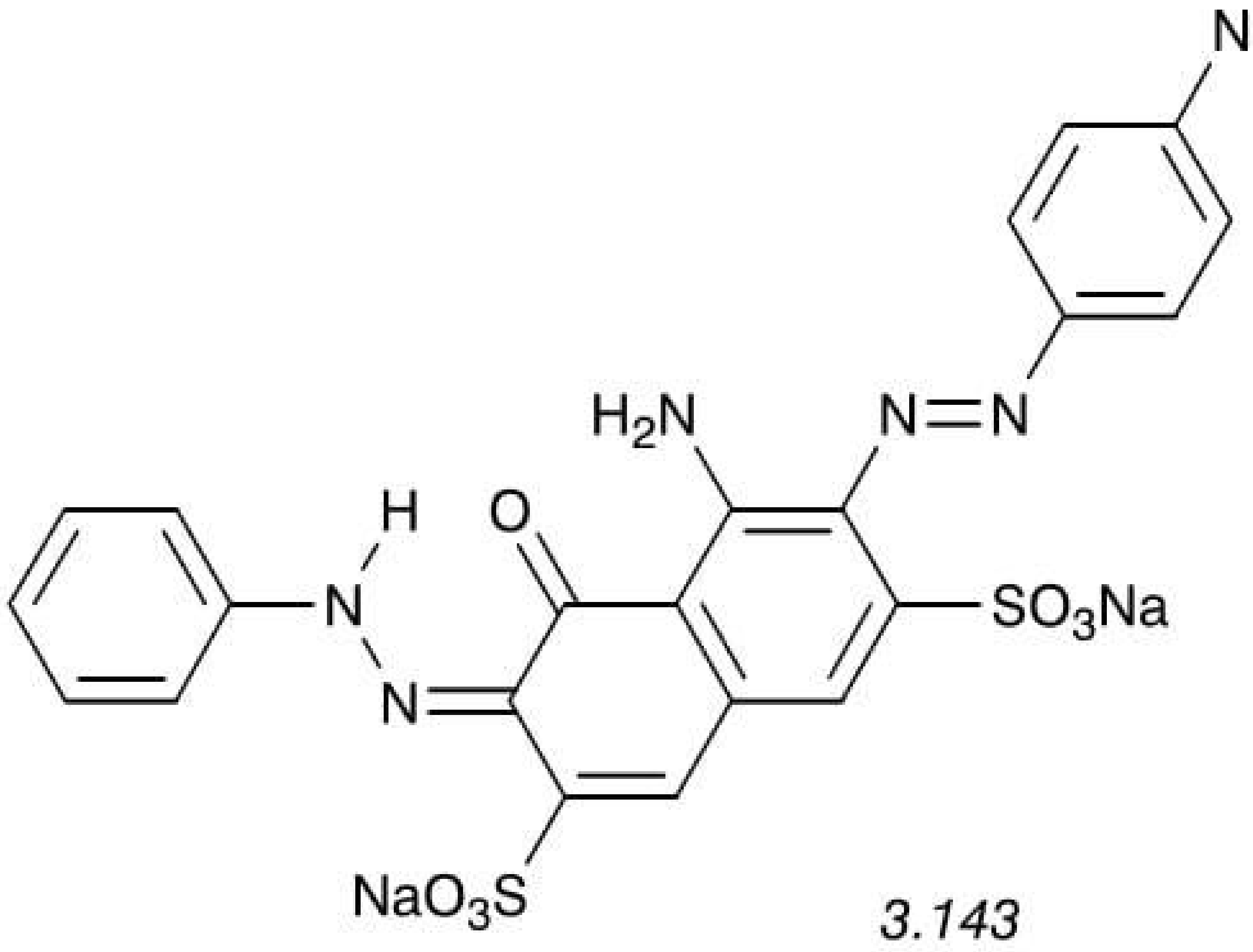


3.142

Table 3.35 Location of reactive system in H acid monoazo red reactive dyes [150]

		Perspiration/light ATTS test	
Reactive system	Location (3.138)	Acid	Alkali
Dichlorotriazine	Y	2	1–2
Monochlorotriazine (MCT)	Y	3	2–3
Dichloroquinoxaline	Y	2–3	2
Bifunctional (SES/MCT)	Y	3	2–3
Sulphatoethylsulphone	X	2	1–2
Sulphatoethylsulphone	X	1–2	1
Bifunctional (SES/MCT)	X	1–2	1

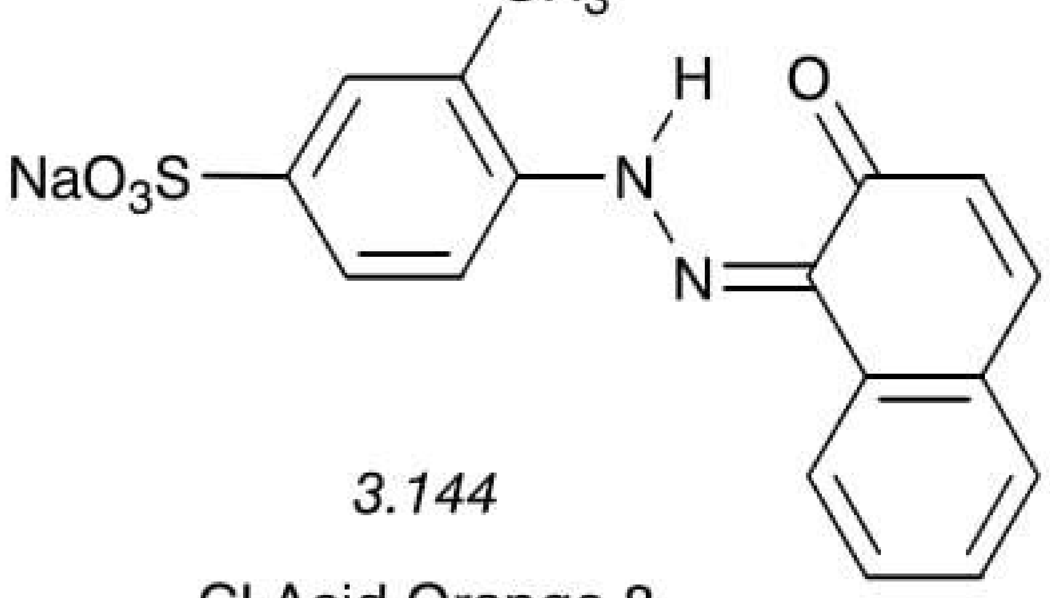
The fading of azo acid dyes for amide fibres has attracted a great deal of interest. Photochemical oxidation of the commercially important H acid disazo CI Acid Black 1 (3.143) in aqueous solution is accelerated by hydrogen peroxide but retarded by mannitol addition. The reaction rate is increased by incorporating a triplet-sensitising dye, suggesting that the azo groups, particularly the *o*-hydroxyazo in its hydrazone form, undergo attack by hydroxyl free radicals and triplet-sensitised degradation [153]. Measurements of the fading of a series of monoazo dyes of the phenylazo R acid type on wool demonstrated that this was a reductive process influenced particularly by the nature of *ortho* substitution in the diazo component;. Anionic groups (sulpho, carboxyl) conferred higher fastness to light but strongly electron-withdrawing nonionised substituents (chloro, nitro) had adverse effects [154]. A similar study of *p*-substituted phenylazo γ acid dyes revealed that electron-donating groups, such as ethoxy, amino or anilino, markedly lowered the light fastness.



3.143

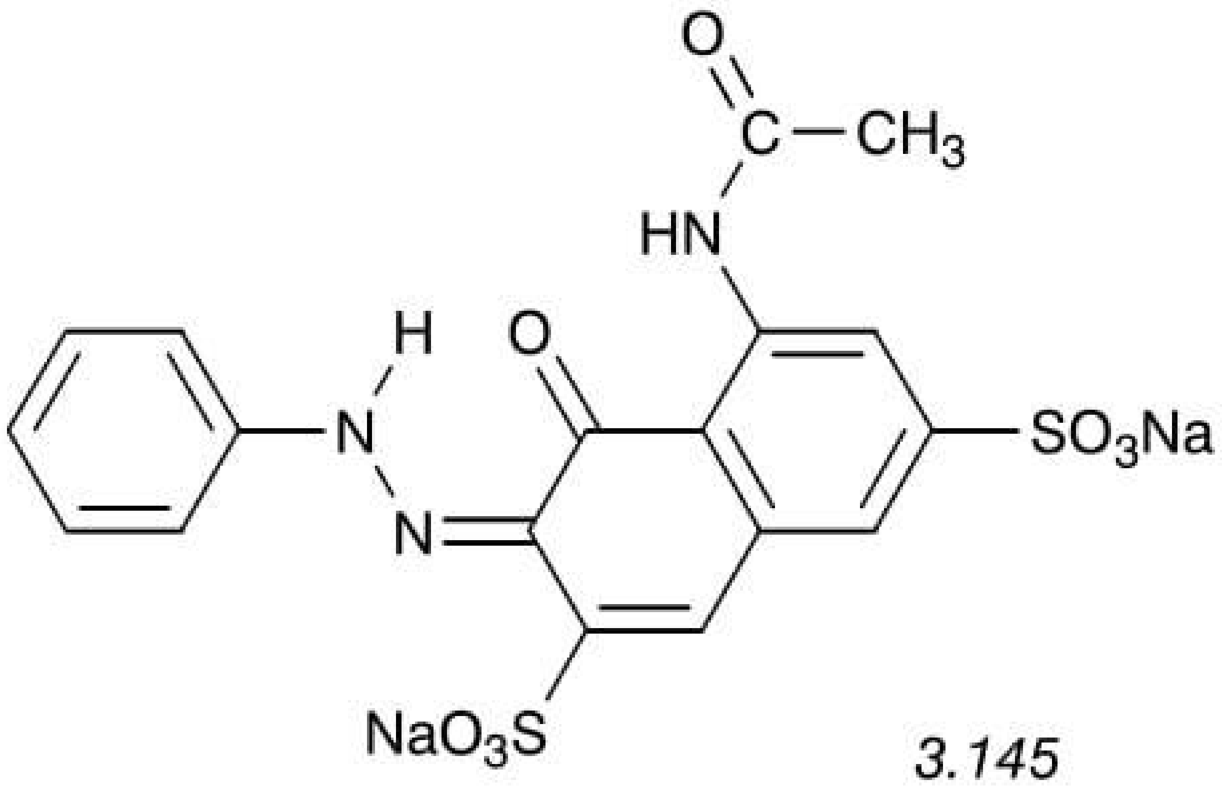
CI Acid Black 1

The kinetics of fading of the monoazo dyes CI Acid Orange 8 (3.144) and Red 1 (3.145) on exposure to sunlight in aqueous solutions at pH values in the range 2 to 4.5 and on silk fabric were investigated recently [155]. In the presence of silk these dyes were more photoreactive, exerting a protective action against photodegradation of the silk fibroin. As part of a broad chemometric strategy to design novel acid dyes for silk [156], eight phenylazo J acid dyes with *o*,*p*-substitution (3.146) were synthesised and their light fastness ratings compared on this fibre (Table 3.36). The results indicated that electron-withdrawing substituents (nitro, benzoyl), or an additional phenyl group in the *p*-position, enhanced light fastness slightly, whereas benzoate ester groups or an *o*-phenyl substituent lowered the fastness significantly. Disubstitution by propoxy did not modify the rating from that shown by the parent dye. All these dyes retained the 6-amino group in the coupling component, which tends to impair light fastness.



3.144

CI Acid Orange 8

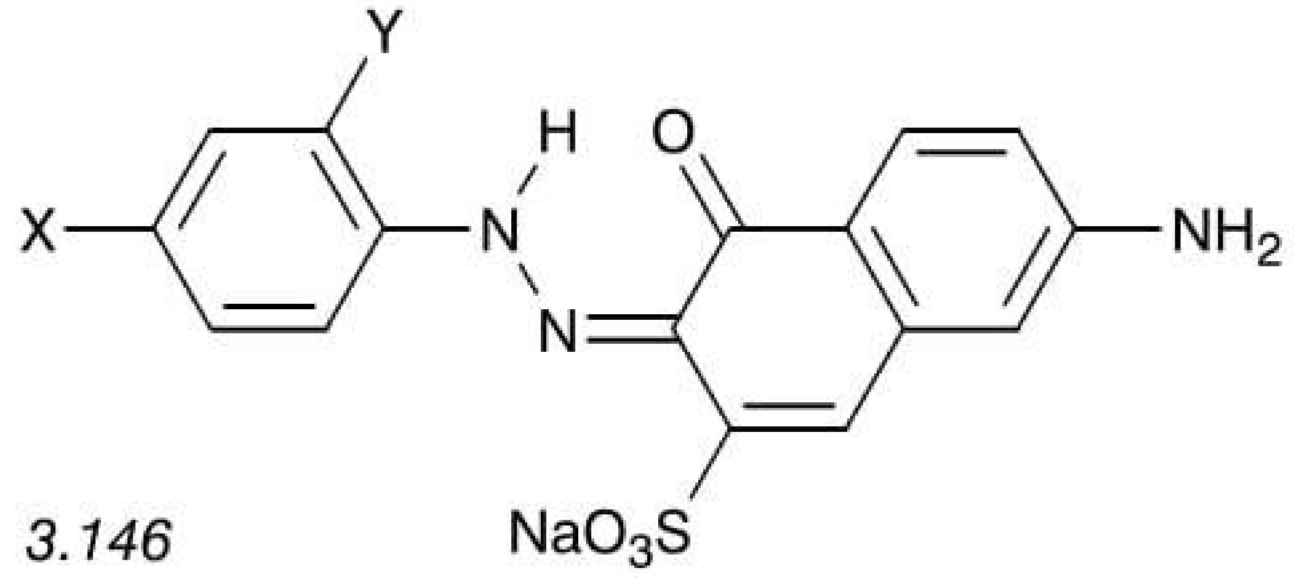


3.145

CI Acid Red 1

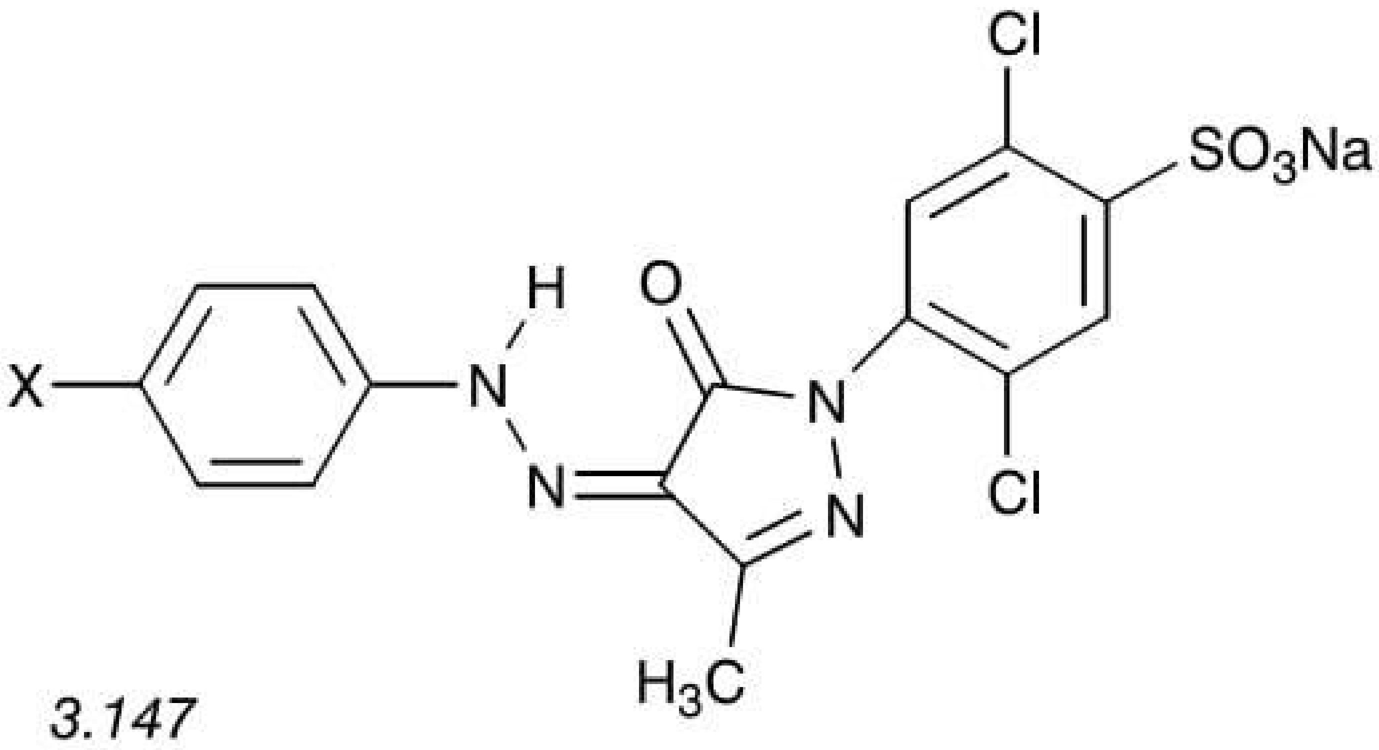
Table 3.36 Light fastness of substituted phenylazo J acid dyes on silk [156]

Substituents in structure 3.146	Light fastness
X = Y = nitro	4
X = H, Y = benzoyl	4
X = phenyl, Y = nitro	4
X = benzoyl, Y = H	4
X = Y = H	3–4
X = Y = propoxy	3–4
X = nitro, Y = phenyl	2–3
X = Y = benzoate	2



3.146

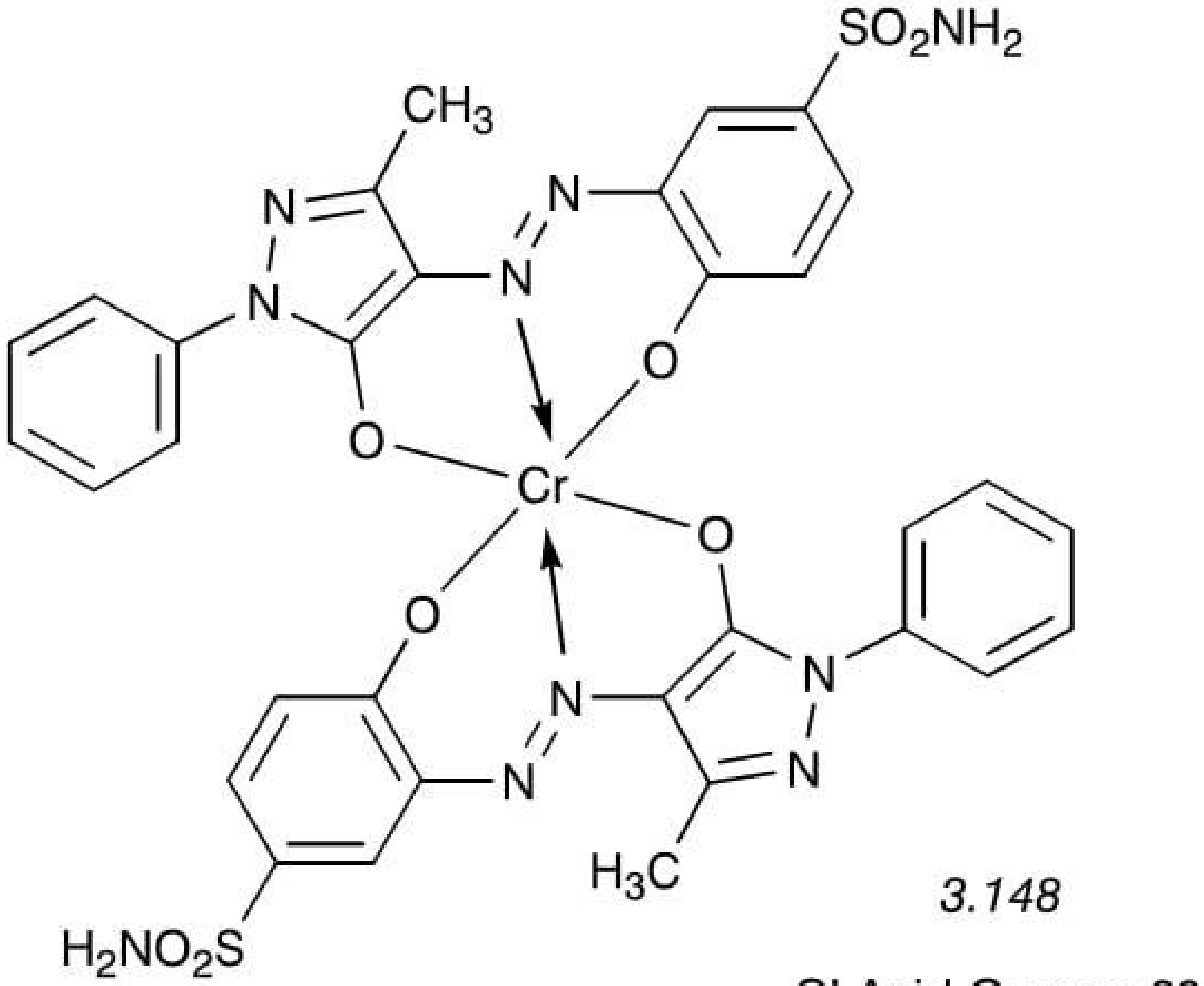
Aggregates of dye molecules normally fade more slowly than do single molecules distributed uniformly through the substrate. These aspects were examined in the dyebath and on nylon for three monoazo dyes, CI Acid Orange 10, Red 18 and Red 88 (for structures see Table 3.28). Aggregation was found to influence the fastness to light, washing and rubbing [157]. When alkyl groups are introduced into the structures of milling acid dyes to confer higher neutral-dyeing affinity and better wet fastness on wool, relatively short chains (C_4–C_6) can have a favourable influence on light fastness by promoting aggregation in the fibre [136]. If the chain length is increased (C_{12}–C_{16}), however, the fastness to light decreases markedly, owing to the higher surface activity of such dyes tending to destabilise aggregates in favour of monomolecular distribution [158]. For example, the light fastness on wool of the phenylazopyrazolone levelling acid dye (3.147; X = H) is 6 but that of the long-chain alkylated CI Acid Yellow 72 (3.147; X = n-dodecyl) is only 4–5.



3.147

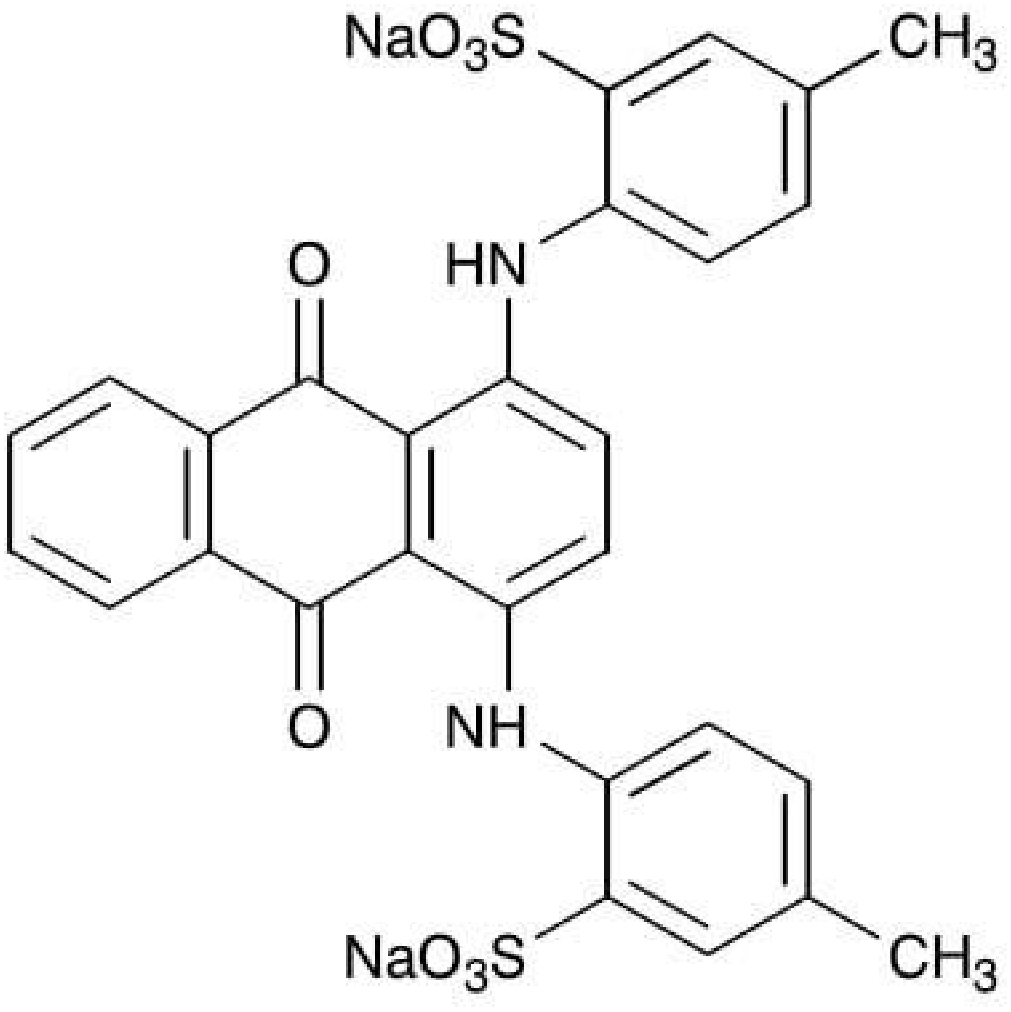
The influence of various dyeing and heat setting parameters on the light fastness of three acid dyes on nylon 66 has been examined recently. The capability of the dyes to quench the photoactive luminescent species in the polyamide matrix was found to be related closely to light fastness rating. Since acid dyes are linked to terminal amino groups through electrostatic bonds, they are able to protect their own chromogens and the polymer chain from photodecomposition through excitation energy transfer via the ionic bonds [159].

The nature of the substrate has little effect on the light fastness of anthraquinone acid dyes on amide fibres. Most substituents hardly affect the slow rate of fading of these structures, but photodealkylation may occur when alkylaminoanthraquinones are exposed to light. The fastness can be improved, however, by incorporating arylamino in place of alkylamino groups [160,161]. The photodegradation in dimethylformamide solution and in nylon 6.6 of the 1:2 chromium-complex CI Acid Orange 60 (3.148) and the important anthraquinone CI Acid Green 25 (3.149) used on nylon automotive carpets was studied. Each of the dyes was found to fade by a reductive mechanism in both media. Dimethylformamide was found to be a suitable model for nylon in characterising photofading [162]. Consequently, the photodecomposition of several 1:2 metal-complex azo dyes was investigated in DMF solutions exposed to daylight or ultraviolet radiation at 300 or 350 nm. The coordinated metal atom and the wavelength of photolysis influenced the degradation reaction significantly. The presence of a ketone sensitiser accelerated dye decomposition, confirming that hydrogen abstraction is responsible for initiation of the fading reaction. Dyes containing cobalt(II) atoms were found to be effective quenchers of singlet oxygen [163].



3.148

CI Acid Orange 60



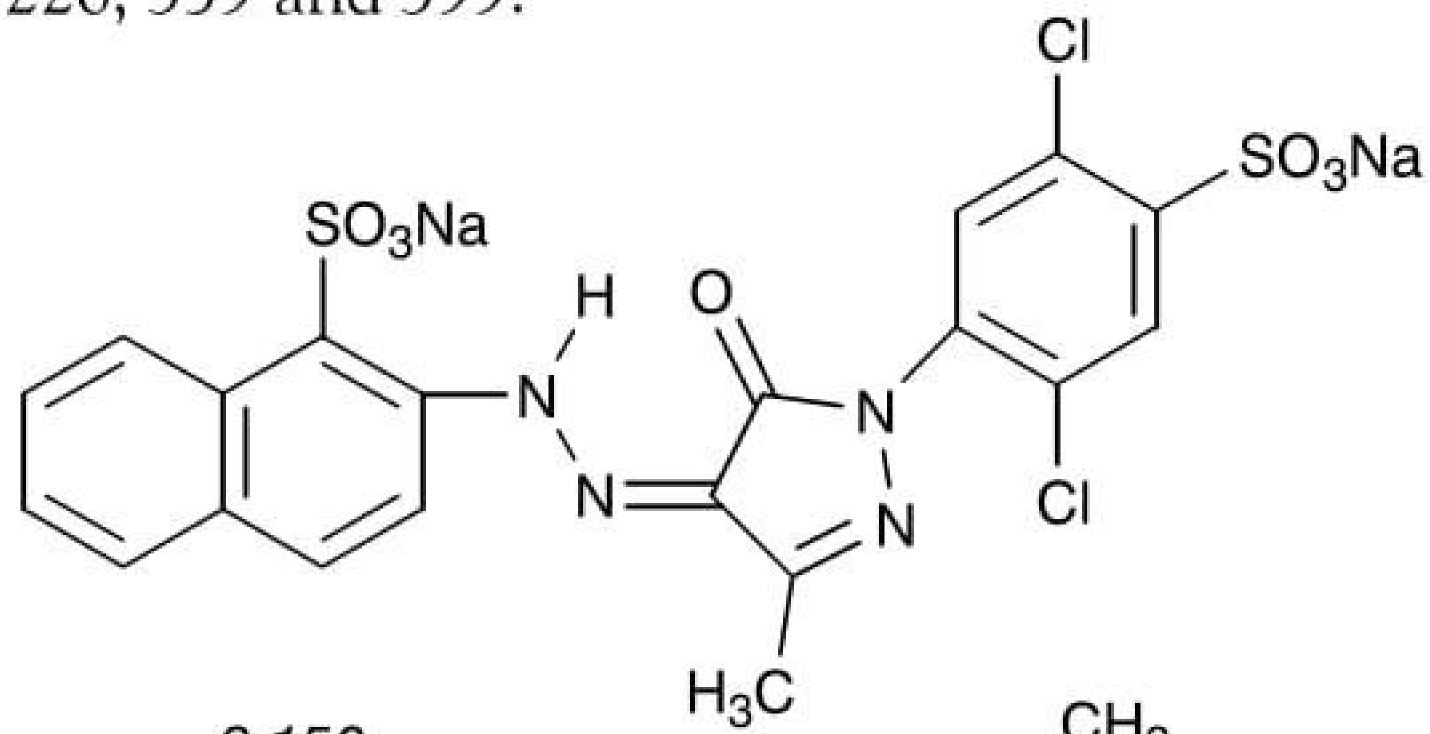
3.149

CI Acid Green 25

The photochemistry of four triphenylmethane acid dyes was studied in poly(vinyl alcohol), methylcellulose and gelatin films. These model systems were chosen with a view to elucidating the complex free-radical reactions taking place in the heterogeneous dyed wool/water/air system on exposure to UV radiation. The dye fading mechanism seems to involve an excited triplet state of the dye molecule [164]. The rate of fading is governed by:

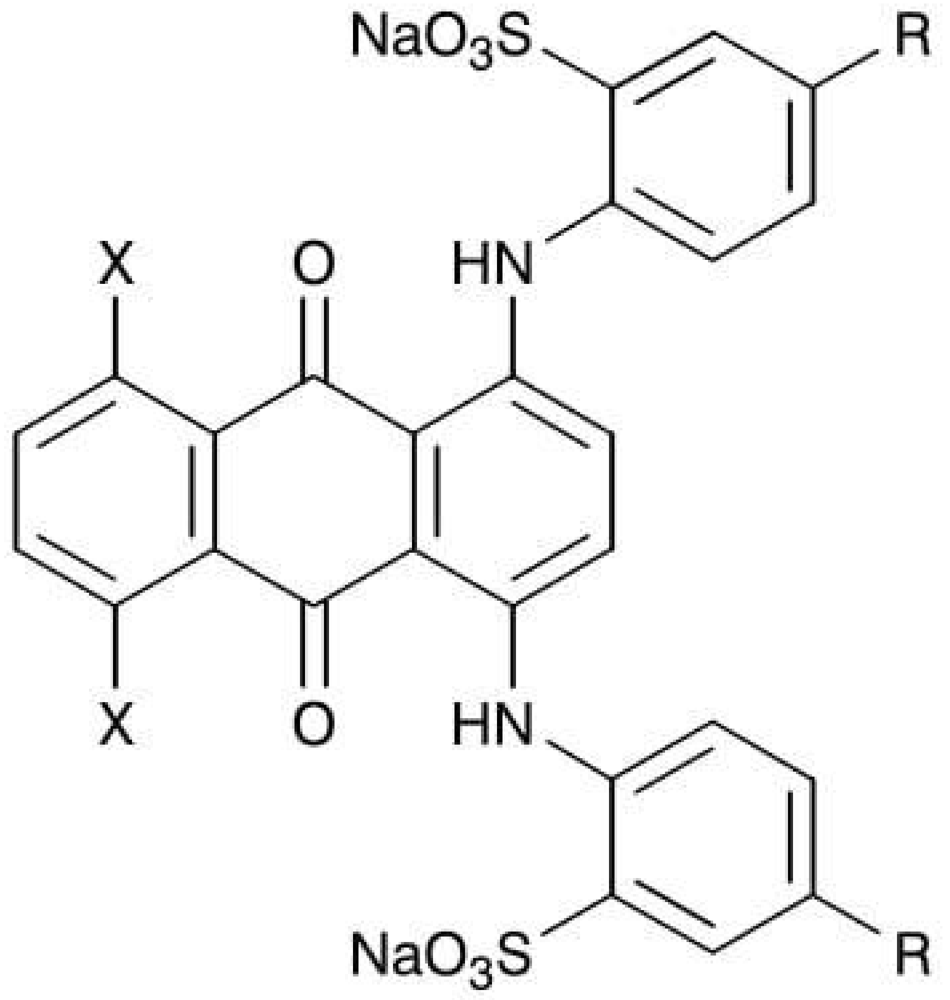
(1) the positions of the sulpho groups in the dye molecule
(2) the ability of the substrate or residual solvent to donate electrons or hydrogen atoms to the dye molecule
(3) the degree of aggregation of the dye in the substrate
(4) the internal physical and chemical structure of the substrate.

Catalytic fading of certain mixtures of acid dyes on nylon, wool and their blends is a particularly significant problem of dye selection for carpets [165]. Xenotest ratings as low as 3–4 (much bluer) were found for green shades on nylon containing an azopyrazolone component such as CI Acid Yellow 19 (3.150), which fades much more rapidly in the presence of the widely used disulphonated 1,4-bis(arylamino)anthraquinones (3.151) such as CI Acid Blue 140, Green 25 (X = H, R = Me), Green 27 (X = H, R = n-Bu) or Green 28 (X = OH, R = n-Bu). Furthermore, commercially important unmetallised azopyrazolones such as Yellow 19, 49 or 79 are catalytically faded by typical 1:2 chromium-complex azopyrazolone dyes from the yellow to violet sectors of the colour gamut, including CI Acid Yellow 59 (3.152; X = H), Brown 384 (3.152; X = SO$_3$Na) and substituted 2-hydroxyphenylazopyrazolone Reds 225, 226, 359 and 399.



3.150

CI Acid Yellow 19



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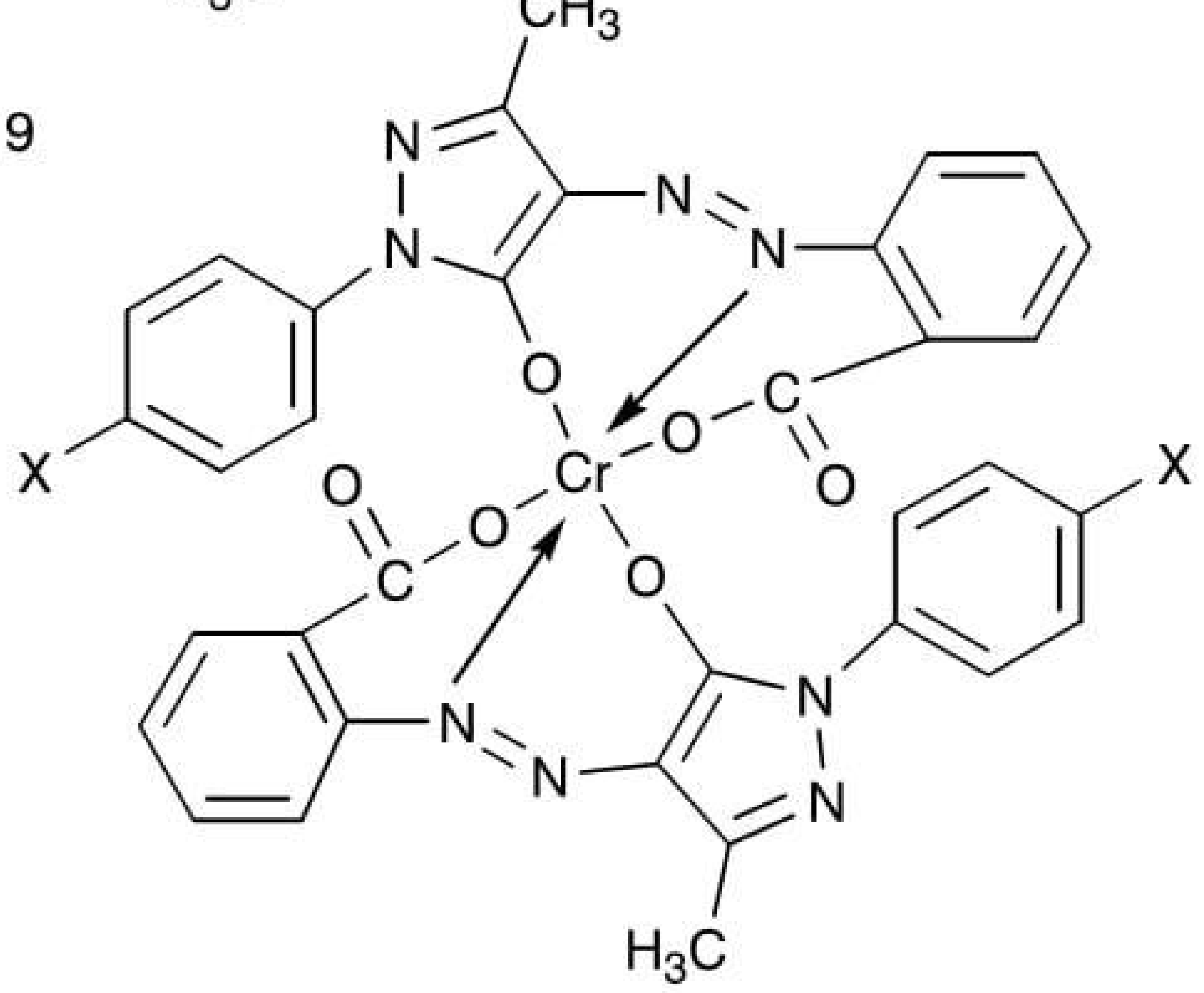
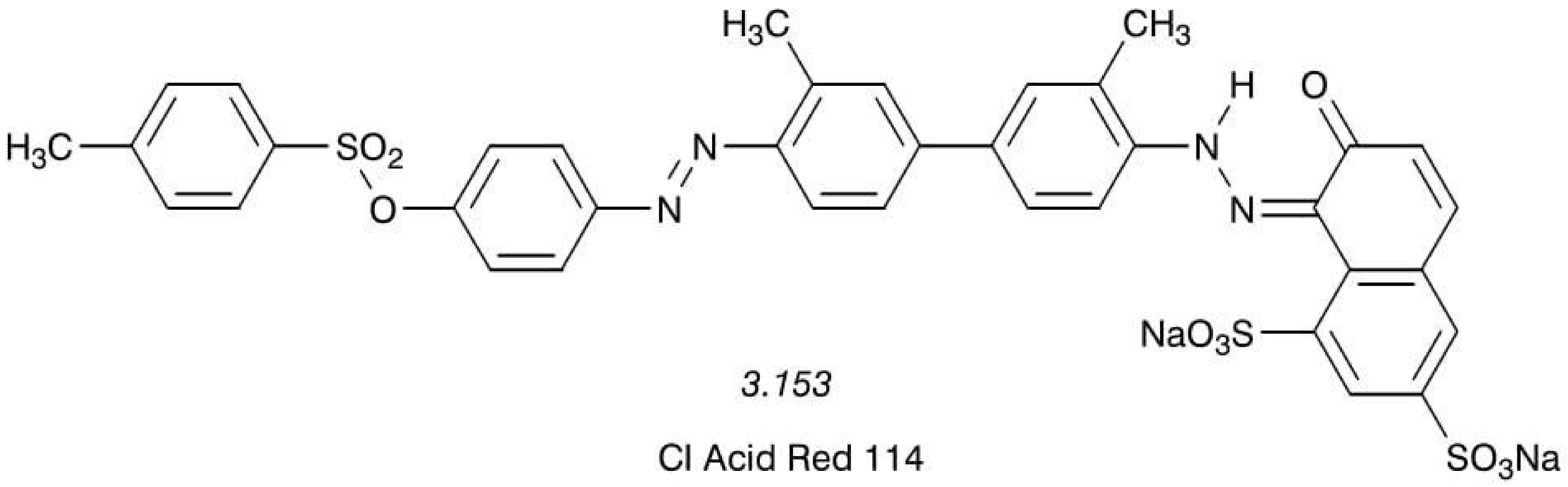


3.152

Apart from the catalytic effects between these fairly well-defined subclasses of acid dyes on nylon, that do not occur on wool [165], certain 1:2 metal-complex dyes such as CI Acid Yellow 59 (3.152; X = H) are able to catalyse the fading of various unmetallised milling acid dyes in mixture recipes on either wool or nylon [166]. For example, orange or scarlet shades formulated with Yellow 59 and Red 114 (3.153) can give light fastness as low as 2 (much yellower). Unacceptable off-tone fading can also arise in green mixtures of Yellow 59 with disulphonated 1,4-bis(arylamino)anthraquinones (3.151) that also fade much yellower. Photosensitised degradation of dyed nylon fibres is another practical problem that is characteristic of Yellow 59 and similar 1:2 chromium-complex azopyrazolone dyes.

For the same disperse dyes on various hydrophobic fibres the highest light fastness is



3.153

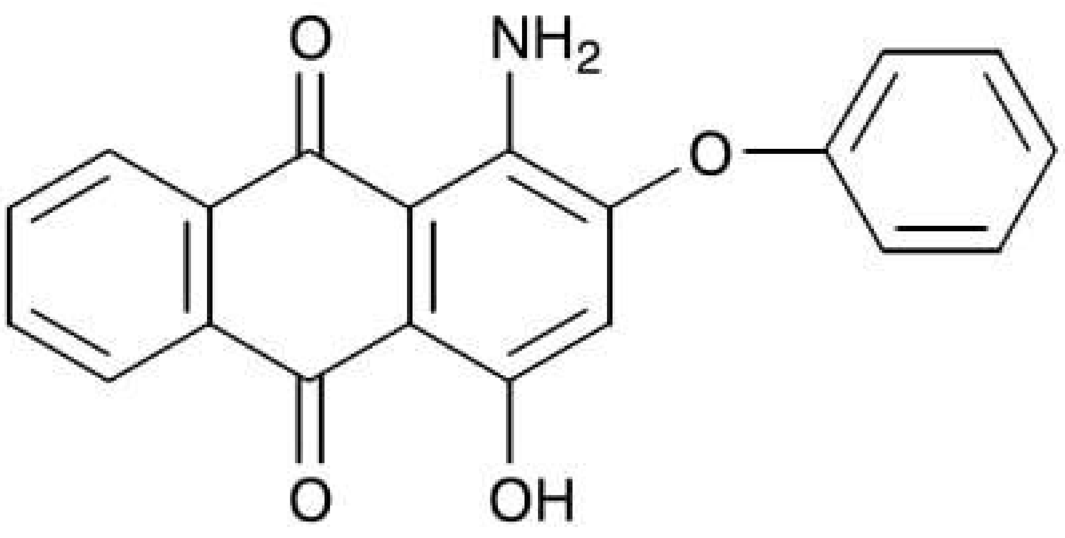
CI Acid Red 114

found on polyester, normally followed by cellulose acetate and triacetate, with nylon giving the lowest ratings. Anthraquinone disperse dyes often contain one or two primary or secondary amino groups in the 1,4-positions. Tetra-amino derivatives have lower fastness than mono- or diamino analogues. Light fastness on cellulose acetate or polyester may be enhanced by:

(1) a hydroxy group *para* to an amino group
(2) acetylation of a primary amino group
(3) replacement of an alkylamino by an arylamino group.

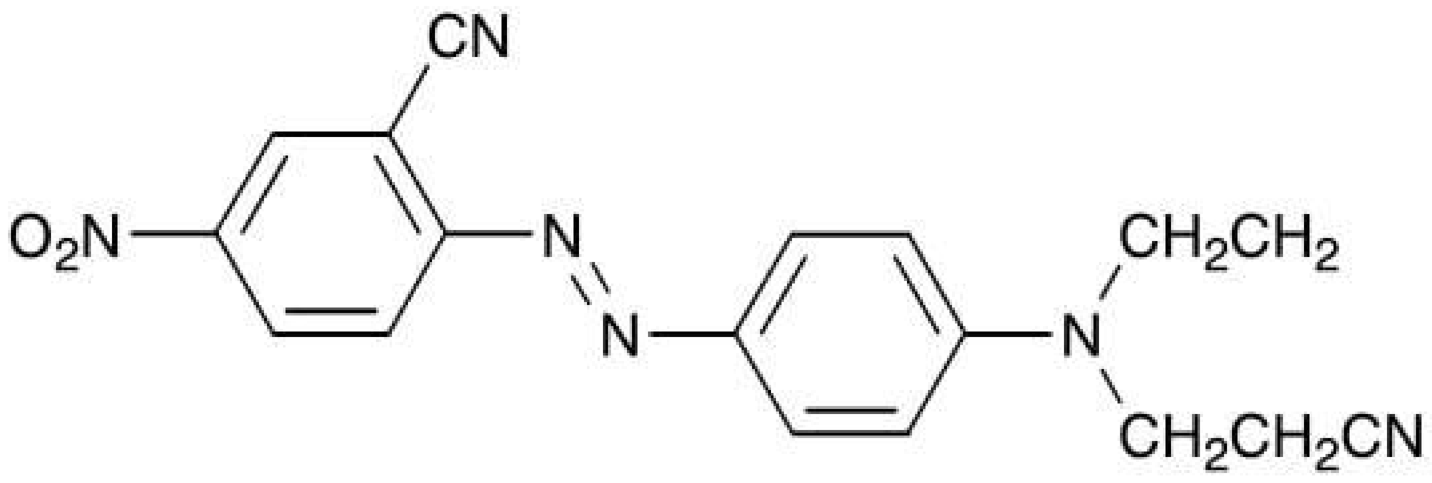
Electron-donating groups (amino, methylamino, hydroxy, methoxy) in the 2-position, on the other hand, are extremely undesirable because, unlike similar substituents in the 1,4-positions, they are unable to form intramolecular hydrogen bonds with the keto groups of anthraquinone and hence are highly susceptible to photo-oxidation [167].

The photochemical decomposition of typical azo and anthraquinone disperse dyes was found to correlate closely with the wavelength of UV radiation at which the fibre substrate showed maximum photodegradation (230 nm on cellulose acetate, 259 nm on triacetate and 316 nm on polyester). When exposed to UV radiation in ethyl acetate solution, the fading of CI Disperse Red 60 (3.154) occurred most rapidly in the 316 nm region [168]. Application of a UV absorber showing peak absorption in this region conferred some protection to dyeings of CI Disperse Red 73 (3.155) on polyester against dye fading and fibre photodegradation [169]. The primary mechanism of fading of the latter azo dye was a reductive reaction, whereas decomposition of the anthraquinone derivative Red 60 was essentially an oxidative process [168].



3.154

CI Disperse Red 60



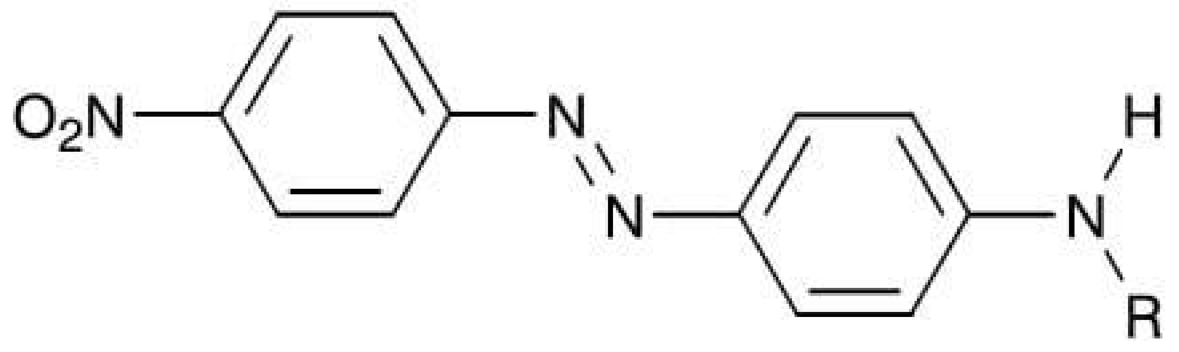
3.155

CI Disperse Red 73

The fading rates of substituted 4-phenylazo-1-naphthylamine dyes on cellulose acetate were consistent with a photo-oxidative mechanism [170], but studies of the fading of phenylazo-2-naphthol dyes on polypropylene were indicative of photoreduction [171,172]. In simple azobenzene derivatives on polyester, an electron-withdrawing 4-nitro or especially 3-nitro group enhances light fastness (Table 3.37). An electron-donating 3′-methoxy substituent in the opposite ring boosts these effects further, but the 2-nitro-3′-methoxy combination yields the same fastness as azobenzene itself. The 2′-methoxy-5′-methyl substitution pattern also reinforces the favourable influence of the 3- or 4-nitro group but markedly lowers the rating of 2-nitroazobenzene. All three nitroazobenzenes are adversely affected by a 2′-hydroxy-5′-methyl arrangement [173].

Table 3.37 Light fastness of substituted azobenzenes on polyester [173]

Azobenzene substituents	Light fastness
3-Nitro-3′-methoxy	7–8
3-Nitro-2′-methoxy-5′-methyl	7–8
4-Nitro-2′-methoxy-5′-methyl	7–8
3-Nitro	7
4-Nitro-3′-methoxy	7
4-Nitro	6–7
3-Nitro-2′-hydroxy-5′-methyl	6–7
2-Nitro	6
None	6
2-Nitro-3′-methoxy	6
4-Nitro-2′-hydroxy-5′-methyl	5
2-Nitro-2′-methoxy-5′-methyl	4–5
2-Nitro-2′-hydroxy-5′-methyl	3



3.156

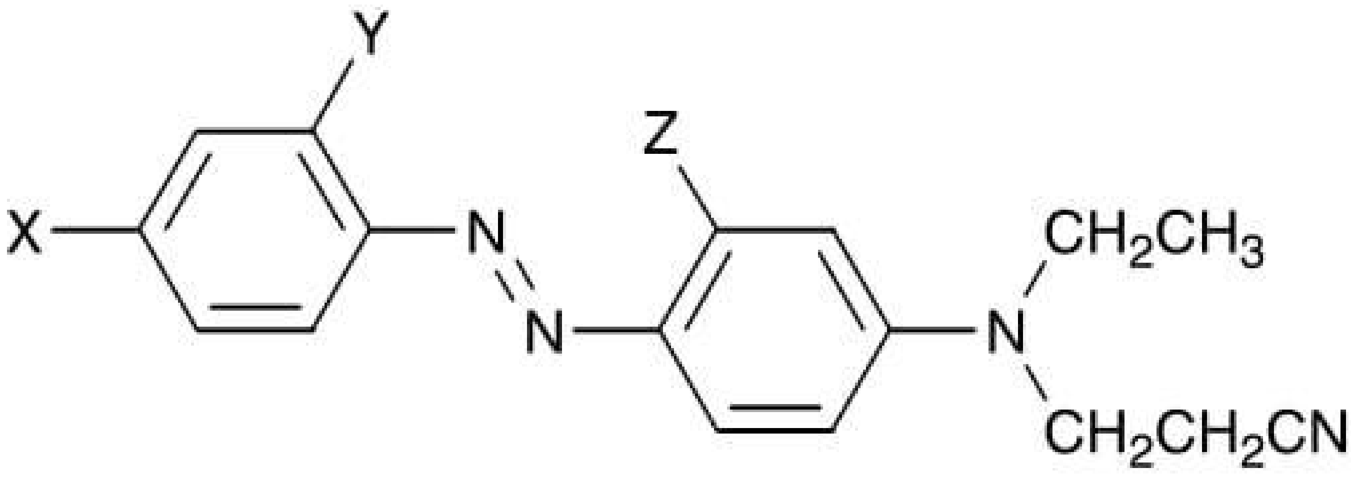
Photofading studies of the simple azobenzene derivatives CI Disperse Orange 1 (3.156; R = Ph) and Orange 3 (3.156; R = H) were carried out in solution and in the solid phase under a variety of conditions. Attempts were made to interpret light fastness ratings on nylon and polyester substrates in terms of behaviour of the dyes in solution in the presence of model compounds representing functional groups in the polymers. Various mechanisms of fading were postulated and potential photostabilisers evaluated [174].

Many important orange, red, brown and blue disperse dyes belong to the substituted *p*-phenylazoaniline subclass (Table 3.38). On nylon, light fastness in the *p*-nitrophenylazo series (3.157; X = NO_2) is marginally improved by electron donation (methyl, methoxy) but markedly lowered by electron withdrawal (chloro and especially cyano or nitro) in the *ortho* position [175]. On polyester, electron-withdrawing groups oriented *ortho* (chloro, cyano) or *para* (nitro, acetyl, methylsulphonyl or diethylaminosulphonyl) to the azo linkage improve the fastness but electron-donating substituents (methyl, methoxy) lower the ratings. The 2,4-dinitrophenylazo arrangement is also highly unfavourable. In the 2-chloro-4-nitrophenylazo series (3.158), the presence of *N*-cyanoethyl or *N*-acetoxyethyl groups in the coupling component confers much higher light fastness than the *N,N*-diethyl analogue but an *N*-2-hydroxyethyl group is slightly unfavourable in this respect.

Only a limited range of nitro, azo and anthraquinone disperse dyes exhibit adequate fastness to dry heat, light and weathering for application on polyester automotive fabrics. The structure of CI Disperse Yellow 86 was modified to incorporate UV absorbers of the benzophenone, benzotriazole or oxalanilide types into the dye molecule. The derived dyes showed better fastness properties than the parent unsubstituted dye. Positioning of the photostabilising moiety within the dye molecule had little influence on the light fastness obtained, however. Built-in benzophenone residues were more effective than the other two types [177]. Nevertheless, several further monoazo and nitrodiphenylamine disperse dye

Table 3.38 Light fastness of substituted aminoazobenzene dyes on nylon [175] and polyester [89,176]

CI Disperse	Structure	Light fastness	
		Nylon	Polyester
Orange 45	3.158; X = Y = CN		7
Red 54	3.158; X = CN, Y = $OCOCH_3$		7
Red 169	3.158; X = CN, Y = OCH_2CH_2CN		6–7
Red 186	3.158; X = Y = $OCOCH_3$		6–7
Red 73	3.157; X = NO_2, Y = CN, Z = H	1–2	6–7
Red 50	3.158; X = H, Y = CN	3–4	6
	3.158; X = H, Y = $OCOCH_3$		6
Orange 25	3.157; X = NO_2, Y = Z = H	4	5
	3.157; X = NO_2, Y = H, Z = CH_3		5
	3.157; X = NO_2, Y = CH_3, Z = H	4–5	4–5
Red 56	3.158; X = OH, Y = CN		4
	3.157; X = $COCH_3$, Y = H, Z = CH_3		4
	3.157; X = SO_2CH_3, Y = H, Z = CH_3		4
	3.158; X = Y = H		3–4
	3.157; X = NO_2, Y = OCH_3, Z = H	4	3–4
Red 13	3.158; X = H, Y = OH		3
	3.157; X = SO_2NEt_2, Y = H, Z = CH_3		3
	3.157; X = Y = NO_2, Z = H	1	2
	3.157; X = Y = H, Z = CH_3		2
	3.157; X = OCH_3, Y = H, Z = CH_3		2



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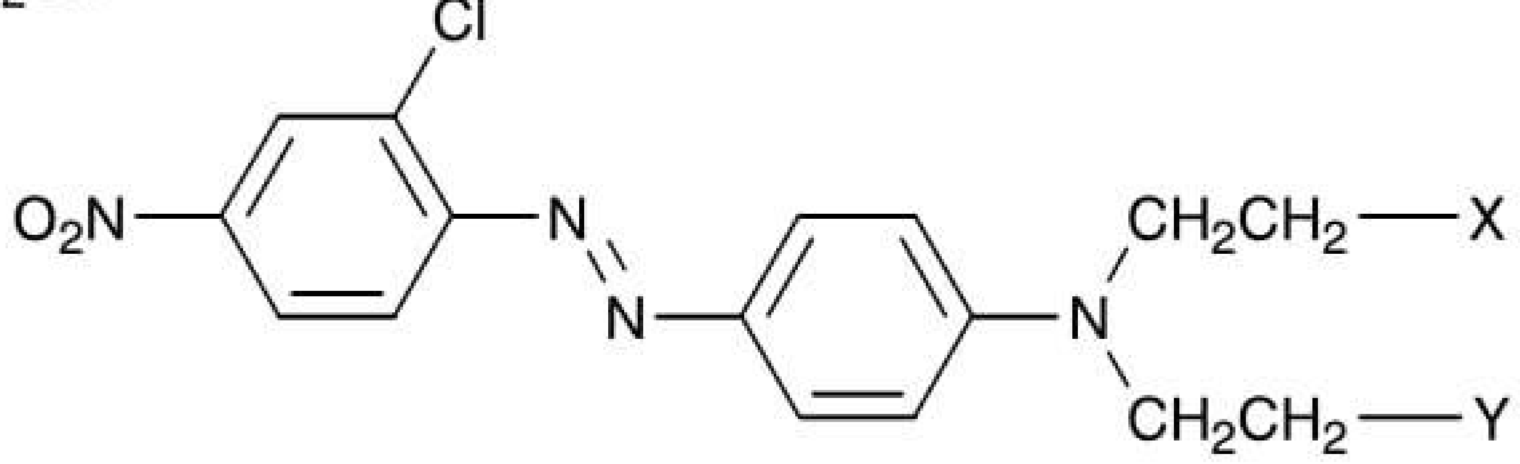

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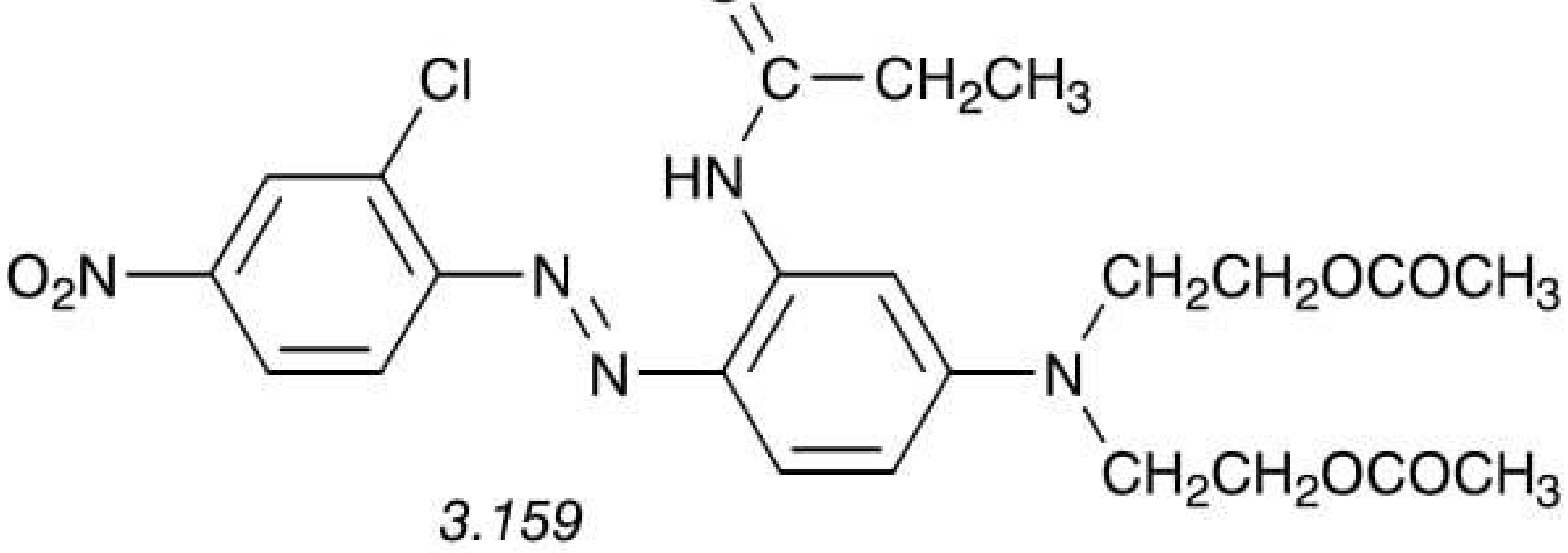
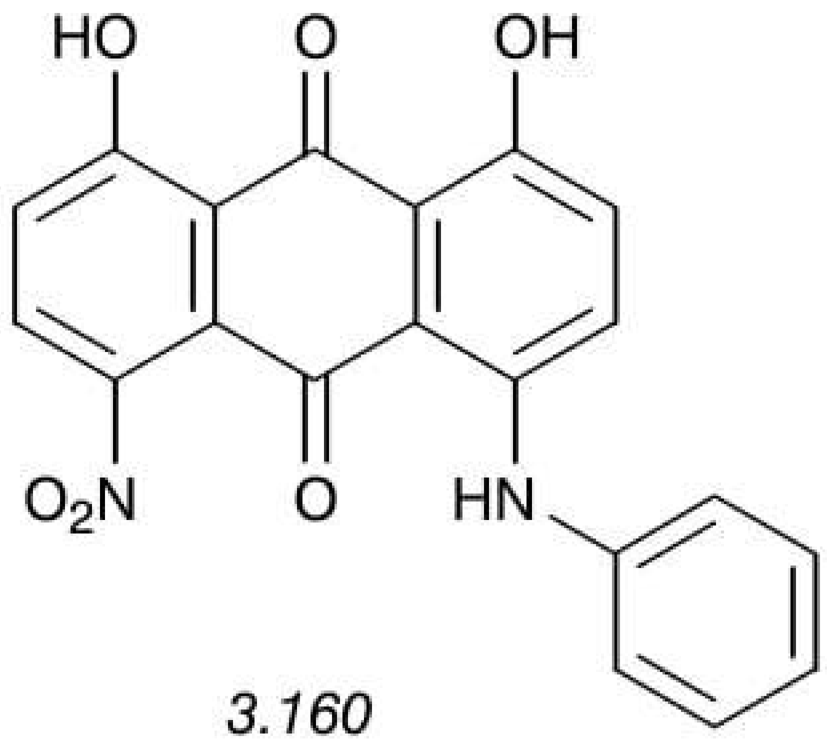


3.159

CI Disperse Red 167

structures containing an oxalanilide photostabilising grouping were synthesised and evaluated as potential dyes for automotive trims. The light fastness of CI Disperse Red 167 (3.159) was enhanced by inclusion of an electron-donating *o*-ethyl group in the diazo component [178].

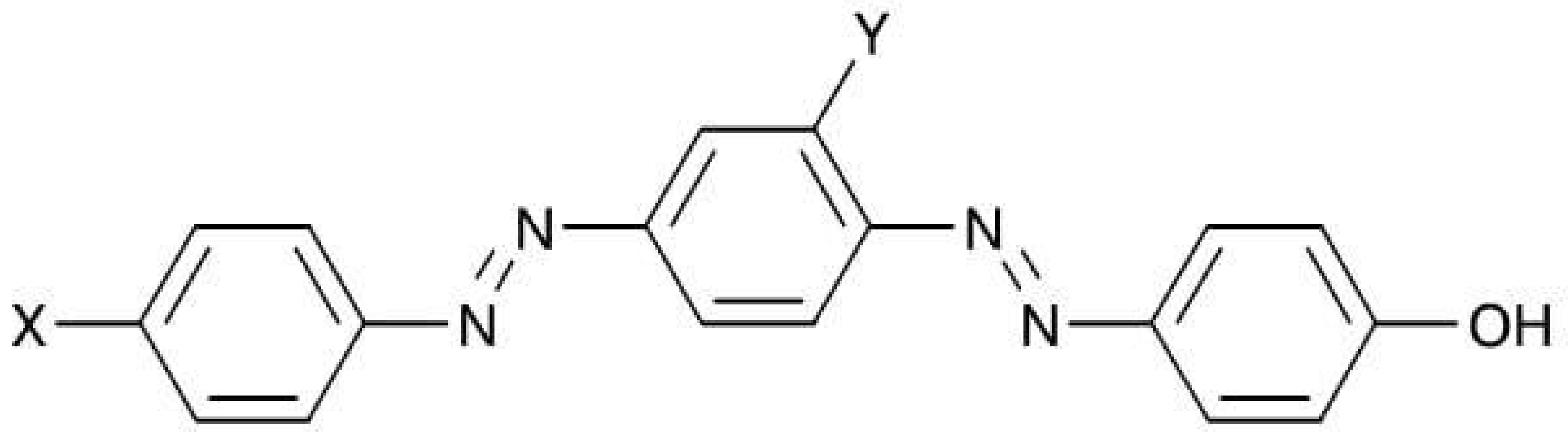
A similar approach has been adopted in modifying the anthraquinone system represented by CI Disperse Blue 77 (3.160), the aniline residue being replaced by a more elaborate arylamine with UV absorbing characteristics, The modifying intermediates selected included hydroxybenzophenone and chlorobenzotriazole derivatives, as well as a hindered photostabiliser. In general, the improvement in light fastness from this approach is inferior to that given by carefully formulated physical mixtures of the corresponding dye and stabilising agent. The modified dye structures tend to exhaust more slowly and show poor levelling but do offer higher fastness to sublimation [179].



3.160

CI Disperse Blue 77

Two commercial disazo disperse dyes of relatively simple structure were selected for a recent study of photolytic mechanisms [180]. Both dyes were found to undergo photoisomerism in dimethyl phthalate solution and in films cast from a mixture of dye and cellulose acetate. Light-induced isomerisation did not occur in polyester film dyed with the two products, however. The prolonged irradiation of CI Disperse Yellow 23 (3.161; X = Y = H) either in solution or in the polymer matrix yielded azobenzene and various monosubstituted azobenzenes. Under similar conditions the important derivative Orange 29 (3.161; X = NO_2, Y = OCH_3) was degraded to a mixture of *p*-nitroaniline and partially reduced disubstituted azobenzenes.



3.161

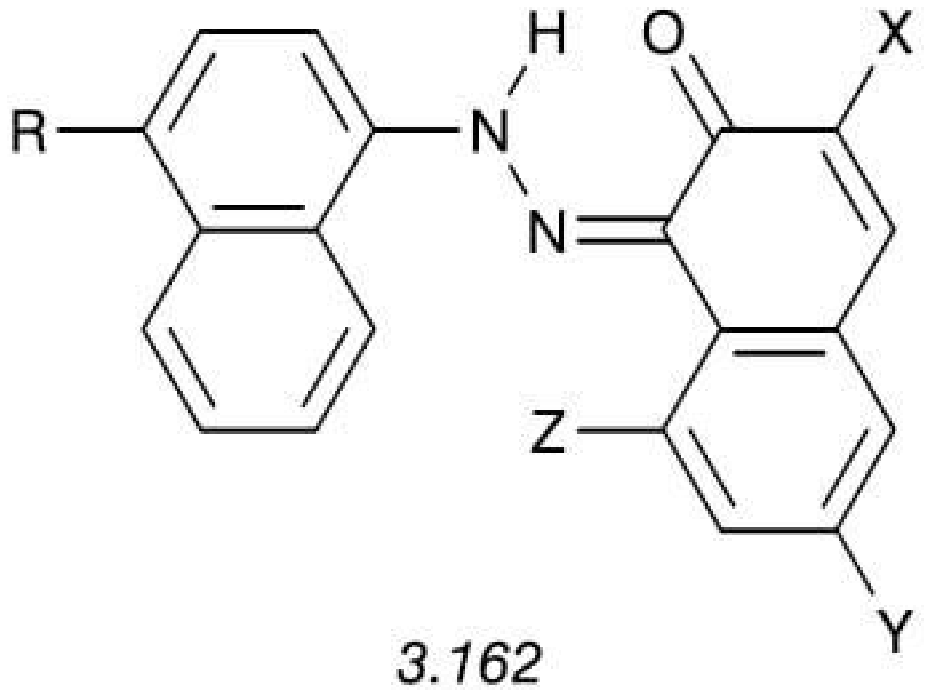
3.3.5 Dye structure and wet fastness

The fastness of a dye to wet treatments, such as washing or perspiration, is a function of kinetic (diffusion) and thermodynamic (affinity) effects. Certain trends can be discerned, but conclusions derived from simple structural changes in closely related structures have only limited applicability. Relationships between wet fastness ratings and molecular structure of direct dyes on cellulosic fibres are somewhat tenuous because of the major obscuring influence of hydrogen bonding and other forces of association between dye anions leading to aggregation within the substrate (sections 3.1.2 and 3.3.4). In general, the wet fastness of disperse dyes on hydrophobic fibres tends to increase with the molecular size of the dye and with the increasingly hydrophobic character of the substrate (acetate < nylon < triacetate < polyester).

Acid dyes are normally applied to wool at acidic pH values but are washed under neutral or mildly alkaline conditions. Forces of affinity between dye and substrate tend to retard desorption. The higher the degree of sulphonation in a series of naphthylazo-2-naphthol dyes (Table 3.39), the higher is the rate of desorption into sodium borate solution at 40 °C. With a series of monosulphonated acid dyes the desorption rate under these conditions was inversely related to the affinity of the dye for wool at pH 3 and 60 °C (Table 3.40).

Table 3.39 Basicity and desorption rate of monoazo acid dyes on wool [181]

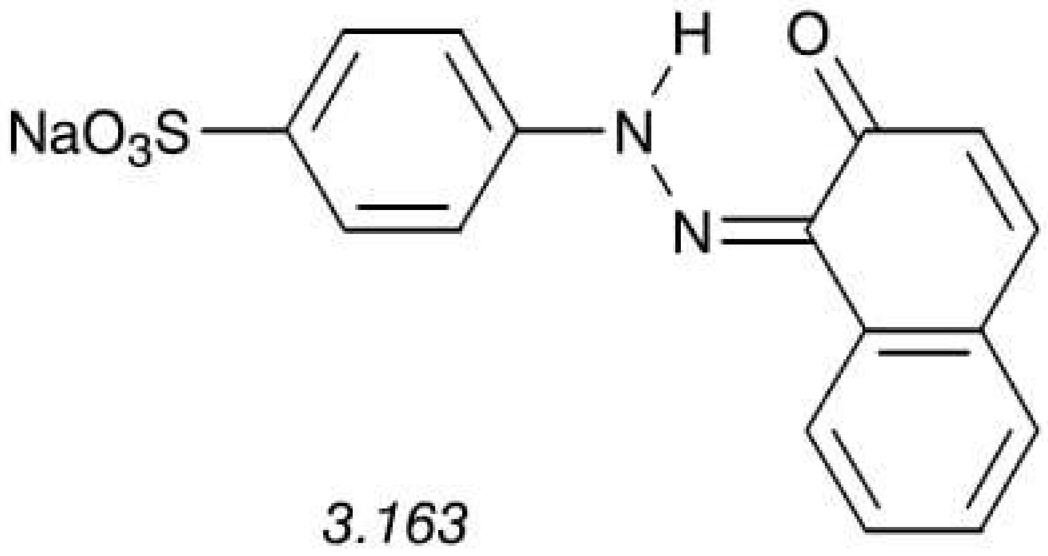
Substituents in 3.162	Basicity	Desorption rate (%/min)
R = X = Y = Z = SO_3Na	4	16.0
R = Y = Z = SO_3Na, X = H	3	12.1
R = X = H, Y = Z = SO_3Na	2	5.2
R = SO_3Na, X = Y = Z = H	1	1.6



3.162

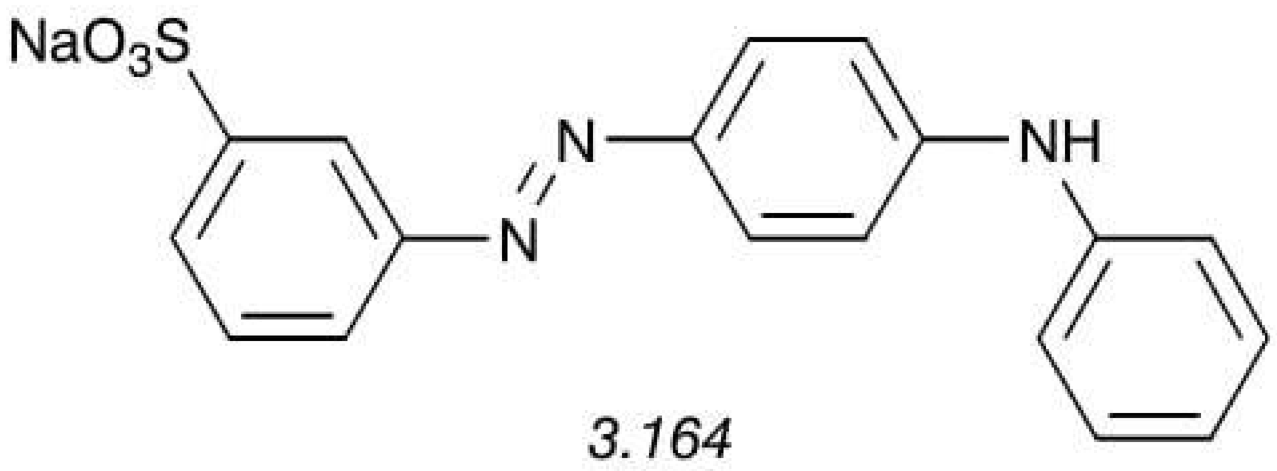
Table 3.40 Affinity and desorption rate of monosulphonated acid dyes on wool [181]

CI Acid	Structure	Affinity (kJ/mol)	Desorption rate (%/min) 40°C	Desorption rate (%/min) 60°C
Orange 7	3.163	–18.4	6.4	18.5
Yellow 36	3.164	–21.7	5.4	16.6
Violet 43	3.165	–27.3	3.0	9.1
Blue 25	3.166	–29.7	2.0	6.0



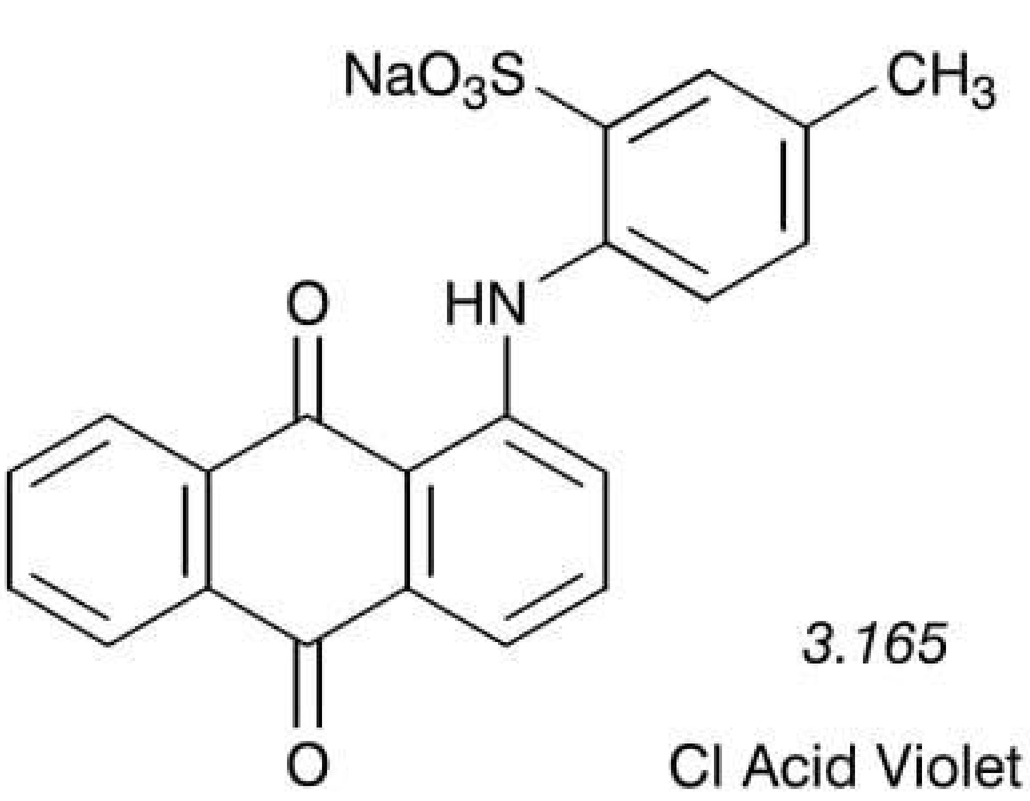
3.163

CI Acid Orange 7



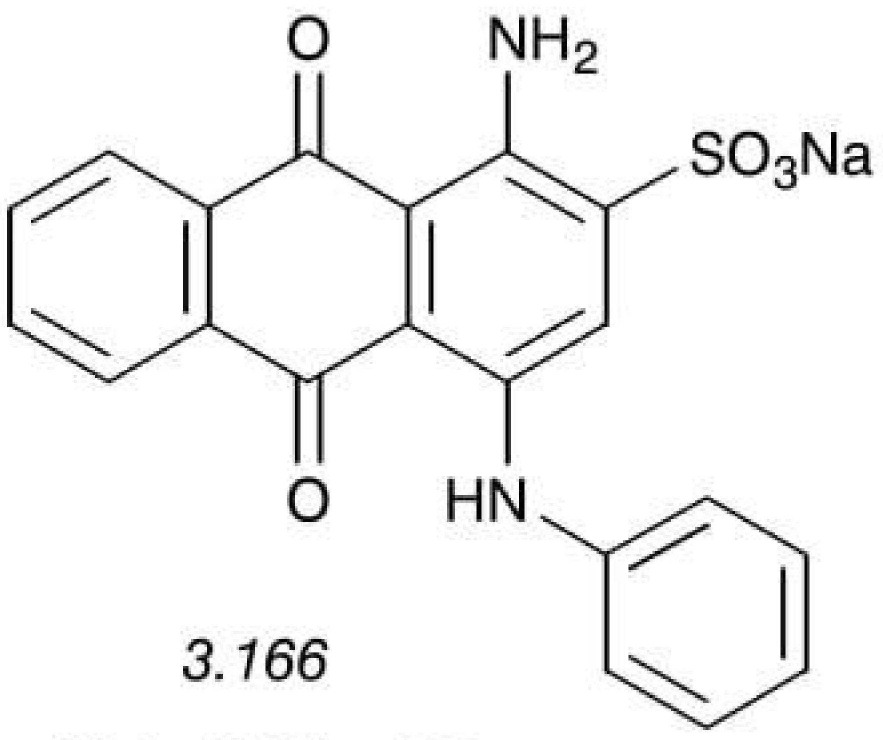
3.164

CI Acid Yellow 36



3.165

CI Acid Violet 43



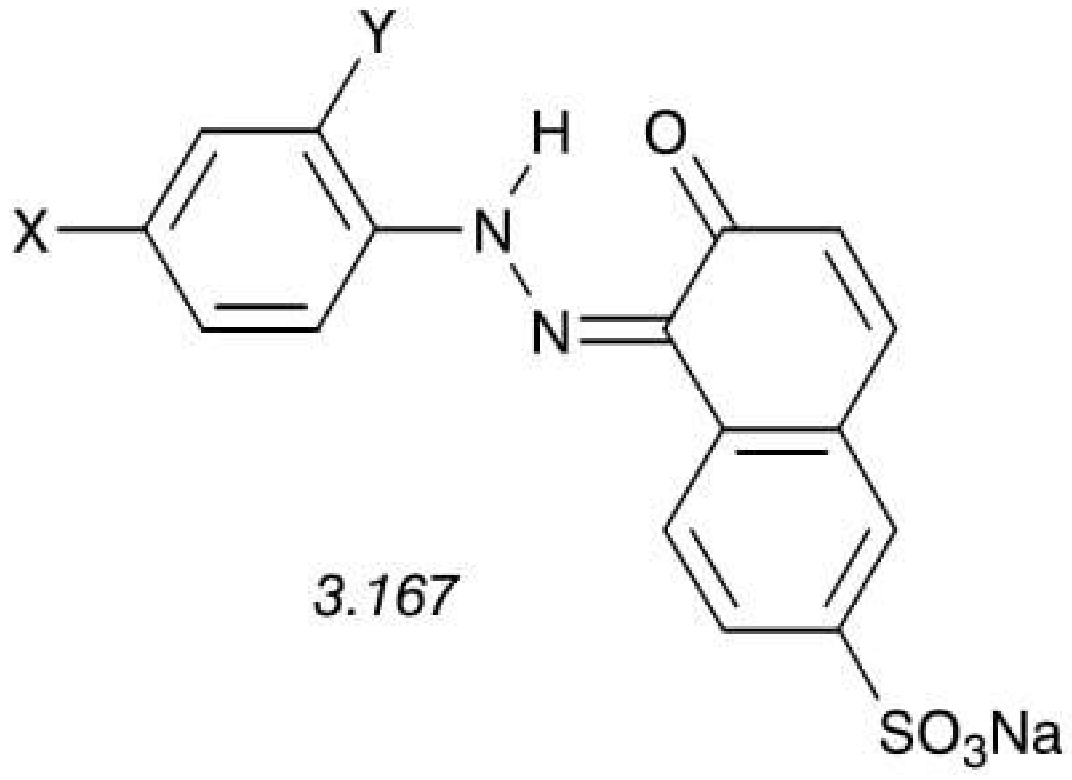
3.166

CI Acid Blue 25

The increase in affinity for wool imparted to acid dye structures by the inclusion of long-chain alkyl groups has a noteworthy effect on wet fastness. Thus the incorporation of such a group into the levelling acid dye CI Acid Red 1 (3.129; R = H) to form the 'super-milling' acid dye Red 138 (3.129; R = n-dodecyl) raises the fastness to washing at 50 °C (effect on pattern) from 2–3 to 4–5. Similar effects for a series of alkylated phenylazo-2-naphthol-6-sulphonate dyes are recorded in Table 3.41.

Table 3.41 Structure and wash fastness of monoazo dyes on wool [182]

Substituents in 3.167	Wash fastness (effect on pattern)
X = $(CH_2)_{11}CH_3$, Y = H	4
X = $(CH_2)_3CH_3$, Y = H	3
X = CH_2CH_3, Y = H	2
X = H, Y = CH_2CH_3	2
X = CH_3, Y = H	1–2
X = Y = H	1

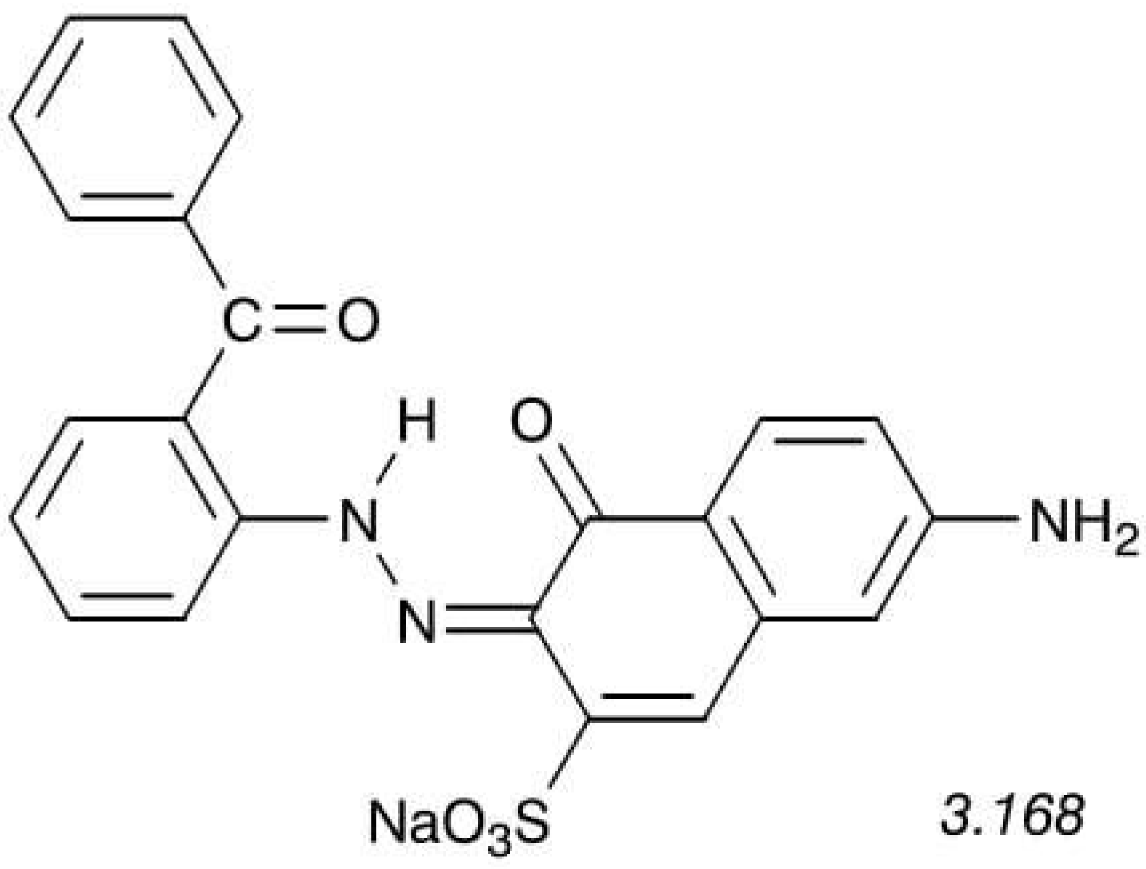


3.167

The series of eight phenylazo J acid dyes with *o*,*p*-substitution in the diazo component (3.146) synthesised for evaluation on silk was subjected to various wet fastness tests (Table 3.42). The results indicated that fastness to these agencies was lowered slightly by *o*,*p*-benzoate ester disubstitution or by a benzoyl group in the *p*-position. Increases in fastness ratings with dipropoxy, dinitro, *o*-nitro-*p*-phenyl or *p*-nitro-*o*-phenyl substitution were also slight, but an *o*-benzoyl grouping was surprisingly effective in this respect. Possibly the keto moiety stabilises this dye in its hydrazone form (3.168) by hydrogen bonding, implying that the tautomeric hydroxyazo form of these dyes has lower affinity for silk than the corresponding ketohydrazone.

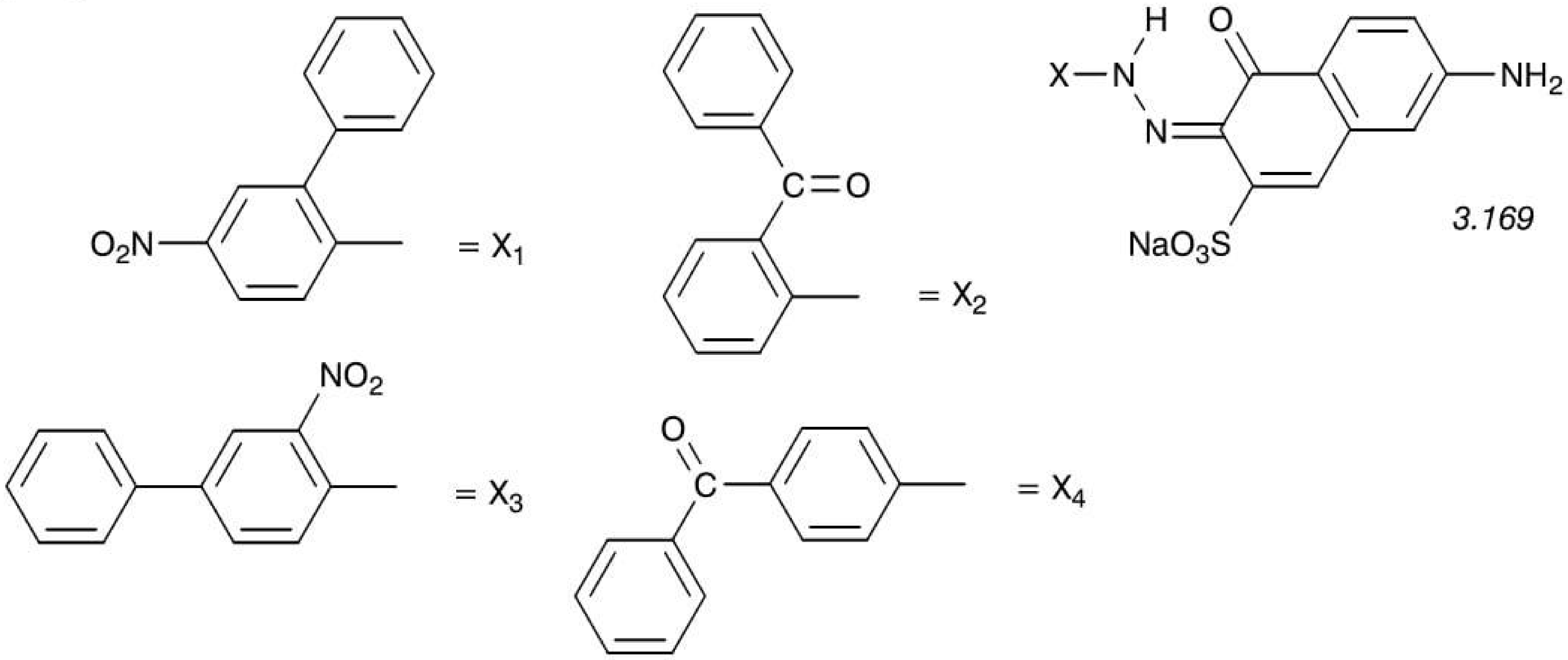
Table 3.42 Wet fastness of substituted phenylazo J acid dyes on silk [156]

	Washing			Perspiration	
Substituents in structure 3.146	40°C	50°C	60°C	Acid	Alkaline
X = benzoyl, Y = H	5	4	3	5	5
X = Y = propoxy	4	2–3	1	5	5
X = Y = nitro	3–4	3	1	5	5
X = nitro, Y = phenyl	4	2	1	4–5	5
X = phenyl, Y = nitro	4	2	1	4–5	5
X = Y = H	3	2	1	5	5
X = H, Y = benzoyl	3–4	3	1	4	4
X = Y = benzoate	2–3	1–2	1	4	5



3.168

In a further exploration of the relationship between dye structure and wet fastness on silk, four novel monoazo J acid derivatives (3.169; $X = X_1$ to X_4), including 3.168 ($X = X_2$) made from 2-aminobenzophenone, were synthesised. Silk was dyed at pH 4 and 85 °C and the dyeings tested for fastness to washing, perspiration and dry cleaning. The highest allround fastness was shown by the 4-aminobenzophenone derivative ($X = X_4$), a structure that resembles the anti-parallel pleated sheet arrangement of polypeptide chains in silk [183].

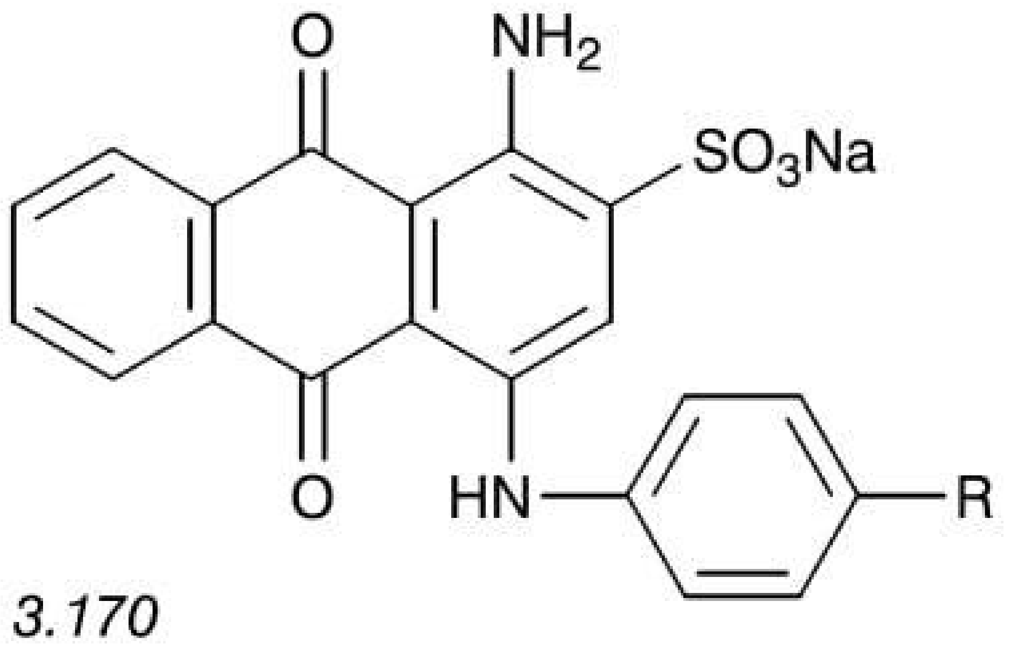


3.169

Affinity values were determined for an interesting series of five anthraquinone acid dyes [184]. The first four were monosulphonated derivatives that differed only in the length of the n-alkyl R substituent (3.170). The fifth dye (3.171) was composed of two monosulphonated molecules linked at the R position by means of a methylene group. The affinity for nylon increased progressively with relative molecular mass as the length of the n-alkyl chain was extended (Table 3.43). The average increment per methylene group up to n-butyl was -2.55 kJ/mol. The affinity of the disulphonated dye could be calculated to a good approximation from the sum of twice that of the non-alkylated control dye plus the increment for the linking methylene group, as in Equation 3.1.

$$2(-23.8) + (-2.55) = -50.15 \text{ kJ/mol} \tag{3.1}$$

The wet fastness of these dyeings increased consistently with the M_r of the dye.



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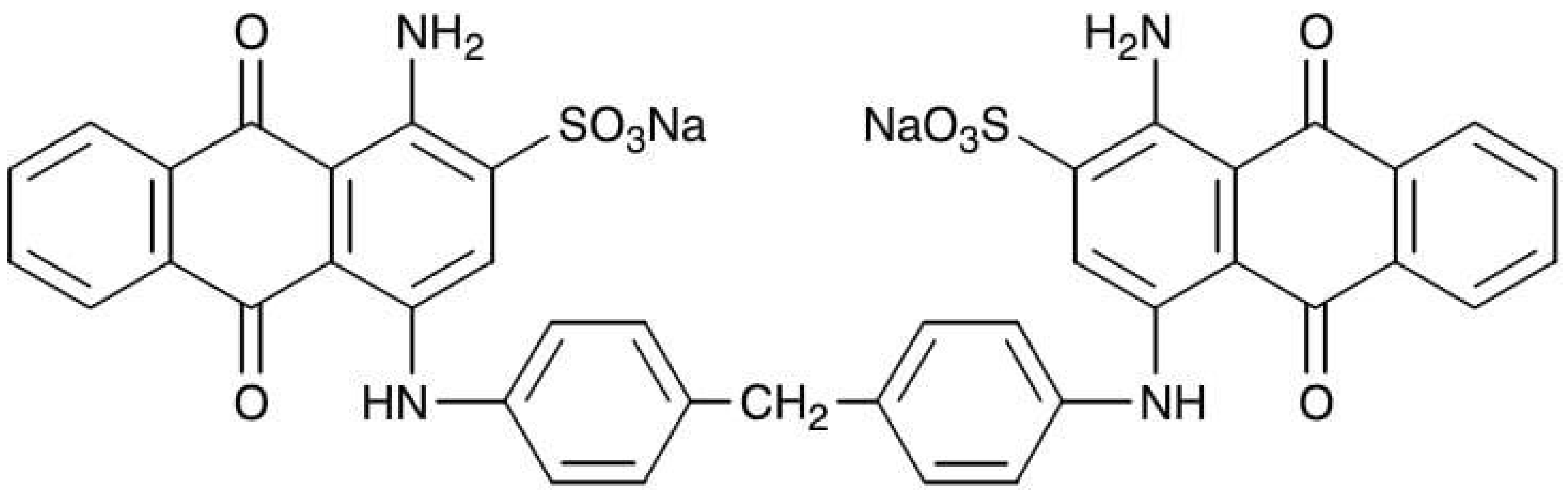


3.171

Table 3.43 Affinity and relative molecular mass of anthraquinone acid dyes on nylon [184]

Structure	M_r	Affinity (kJ/mol)
3.170; R = H	394	–23.8
3.170; R = methyl	408	–26.6
3.170; R = n-butyl	450	–34.0
3.170; R = n-dodecyl	562	–45.6
3.171	800	–52.8

3.3.6 Dye structure and heat fastness

This fastness requirement is of practical significance only for disperse dyes on hydrophobic fibres. Dyes of low fastness are sublimed from the surface of the heated fibre at a rate dependent on the temperature of treatment. The diffusion coefficient of the dye in the dry polymer controls the rate at which loss of dye from the surface by volatilisation is replenished from the interior of the fibre. Dye decomposition during the heat fastness test can be highly significant in determining the overall rating attainable with a given dye structure [185].

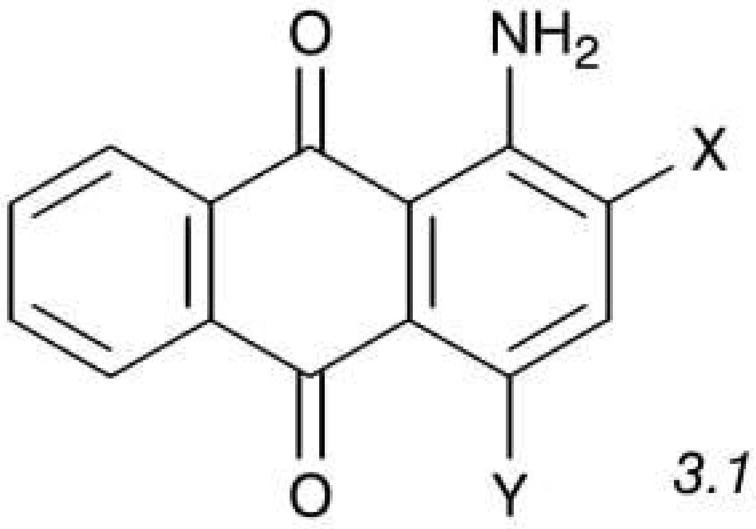
Inverse relationships between the vapour pressure of disperse dyes and their molecular size and polarity have been established [186]. In Table 3.44 the vapour pressure values at 200 °C for three typical disperse dyes of low relative molecular mass are given. A decrease of only 5% in M_r between CI Disperse Red 11 (3.172; X = OCH_3, Y = NH_2) and Violet 4 (3.172; X = H, Y = $NHCH_3$) produces a tenfold increase in vapour pressure, although a further decrease of 4% to give Orange 3 (3.173) has only a doubling effect. A more striking example appears in Table 3.45. The 12% decrease in M_r from Blue 14 (3.174; X = $NHCH_3$) to Red 9 (3.174; X = H) has profound effects, raising the diffusion coefficient in polyester about sixfold and the vapour pressure almost 700-fold. Both factors have an adverse

Table 3.44 Vapour pressure and relative molecular mass of disperse dyes [187]

CI Disperse	Structure	M_r	Vapour pressure at 200°C × 10^3 (kPa)
Orange 3	3.173	242	18.4
Violet 4	3.172; X = H, Y = $NHCH_3$	252	9.67
Red 11	3.172; X = OCH_3, Y = NH_2	268	1.03

Table 3.45 Vapour pressure, diffusion coefficient and structure of disperse dyes [188]

CI Disperse	Structure	M_r	Vapour pressure at 160°C × 10^5 (cm Hg)	Diffusion coefficient × 10^{13} (m^2/s)
Red 9	3.174; X = H	237	692	6.87
Yellow 3	3.175	269	13.5	2.39
Blue 14	3.174; X = $NHCH_3$	266	1.01	(1.2)



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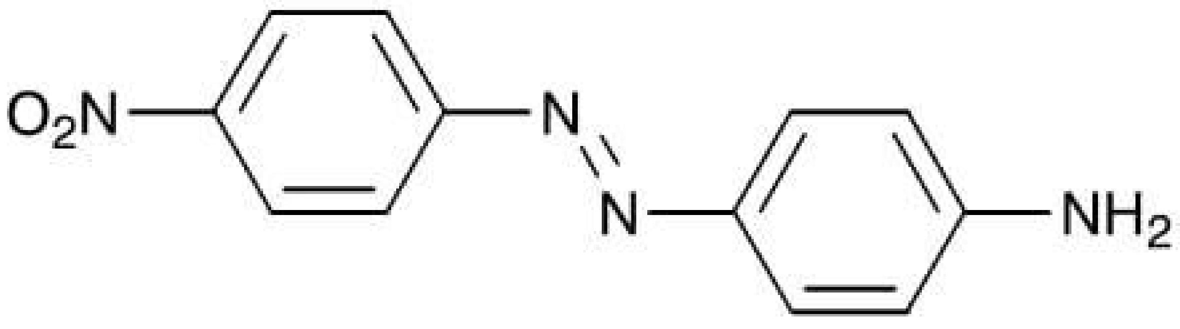
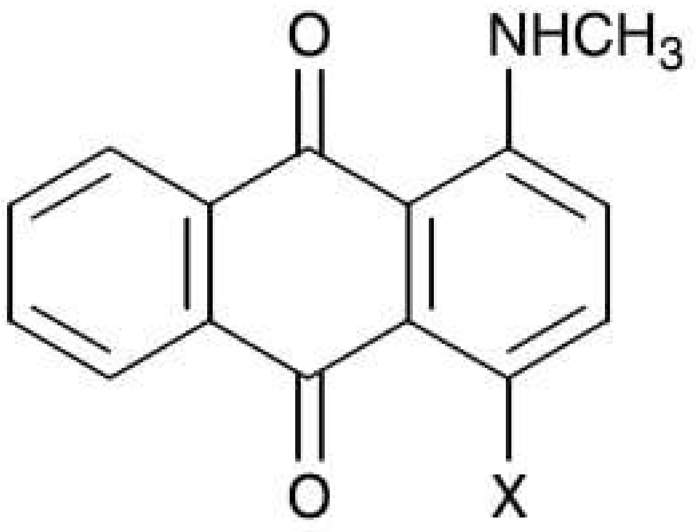


3.173

CI Disperse Orange 3



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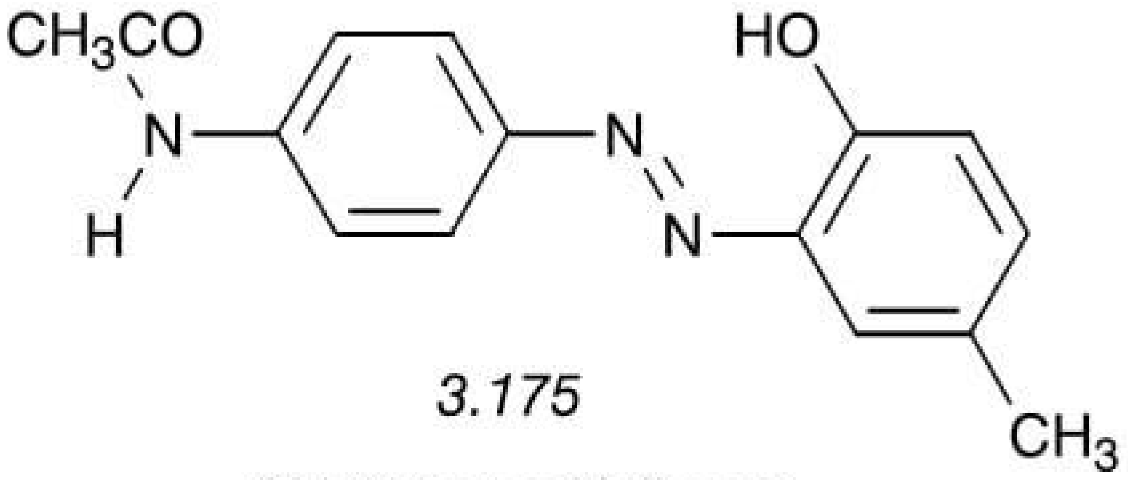


3.175

CI Disperse Yellow 3

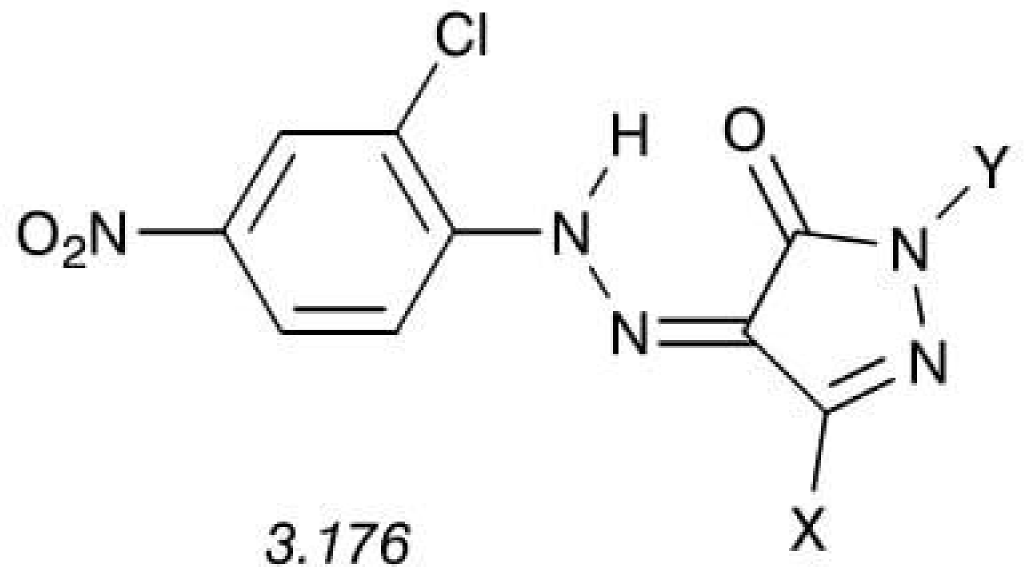
influence on heat fastness. The monoazo Yellow 3 (3.175) is almost identical with Blue 14 in M_r but diffuses twice as rapidly and vaporises much more readily, possibly because it has only two aryl nuclei and a linear conformation.

The requirements of disperse dyes for the transfer printing of polyester fabrics are almost exactly opposite to those of the dyer. Adequate sublimation during the transfer step can normally be achieved only with dyes of low M_r (<350) that are substantially free from highly polar substituents [189]. For steric reasons, however, there are some exceptions to this general rule. Thus 2,4,6-trisubstituted phenylazo groups, which often feature in useful brown and navy blue members of the aminoazobenzene class, can interfere with the coplanarity of such structures. This may hinder dye-dye and dye-fibre bonding to such an extent that such dyes of M_r exceeding 400 can sometimes be used for transfer printing.

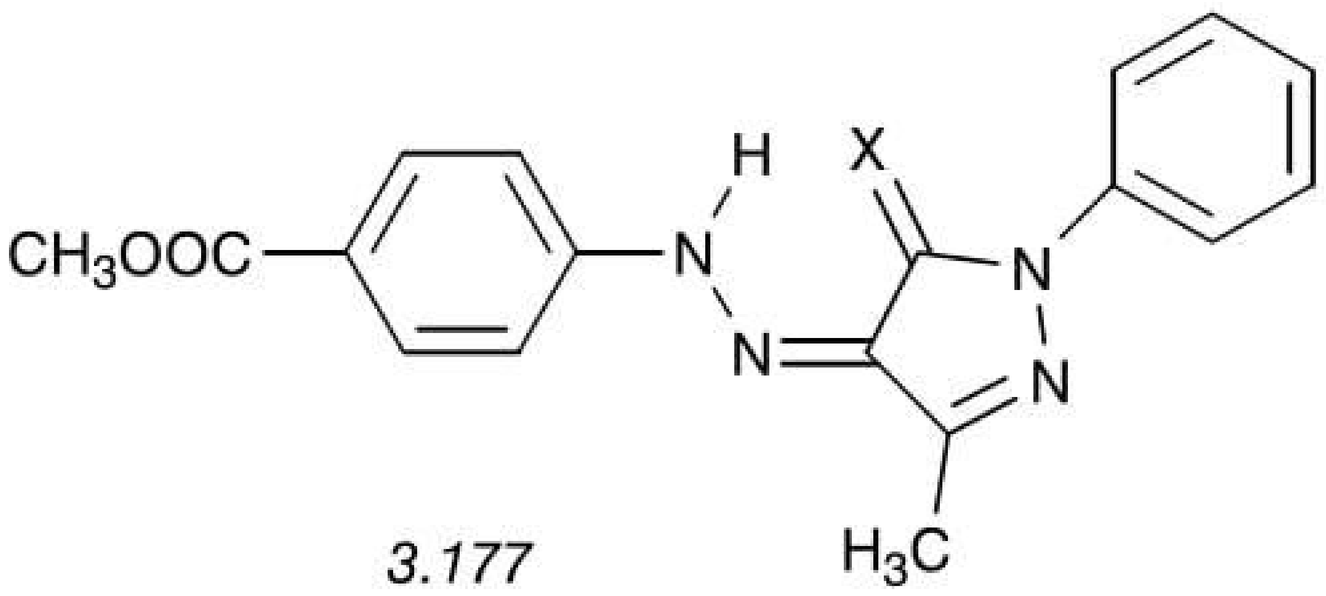
The relationships between dye structure and heat fastness for two series of phenylazopyrazolone dyes (Table 3.46) demonstrate the significance of changes in molecular

Table 3.46 Structure and heat fastness of phenylazopyrazolone disperse dyes on polyester [175]

Structure	Heat fastness
3.176; X = CH_3, Y = 	5
3.176; X = $COOCH_2CH_3$, Y = Ph	3–4
3.177; X = NH	3–4
3.176; X = CH_3, Y = Ph	2–3
3.177; X = O	2–3
3.176; X = CH_3, Y = H	1–2



3.176



3.177

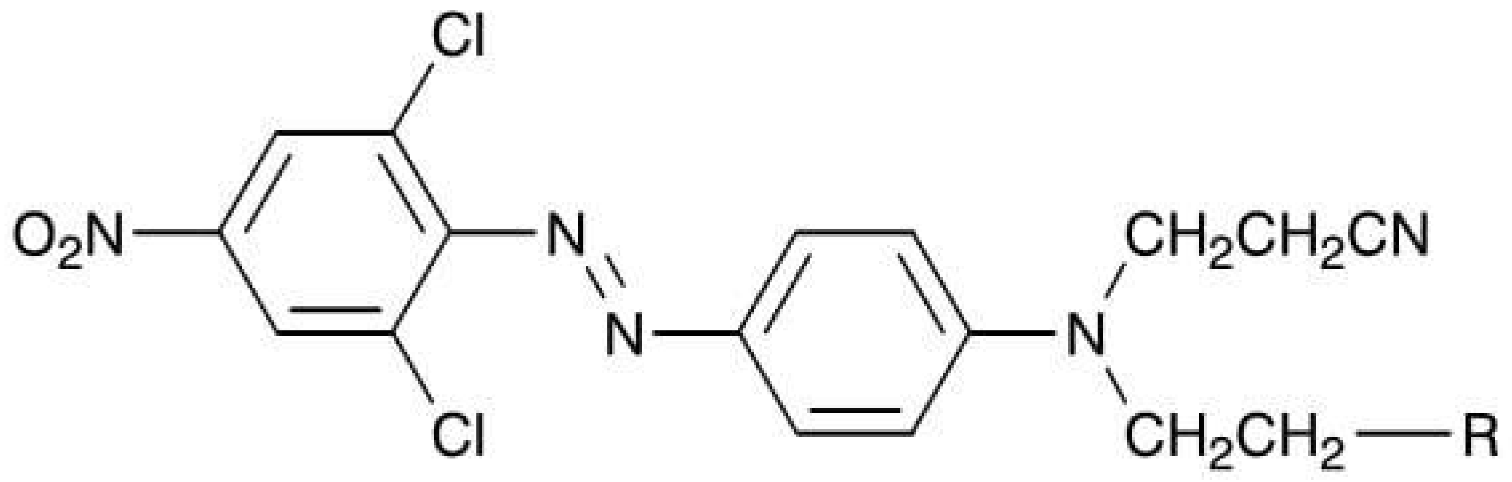
size and polar substituents for this property [175]. In the 2-chloro-4-nitrophenylazo (3.176) series, the tetramethylenesulphone ring enhances heat fastness far more than does a conventional *N*-phenyl group, even though both changes in molecular size are relatively modest. A 3-carbethoxy substituent in the pyrazolone ring raises heat fastness about one point higher than that of the 3-methyl analogue, a difference roughly equivalent to the insertion of an *N*-phenyl ring into the 3-methylpyrazolone parent dye. In the 4-carbomethoxyphenylazo (3.177) structure, an improvement of this magnitude can be achieved merely by using the pyrazol-5-imine instead of the pyrazol-5-one as the coupling component.

Variations in the dialkylamino terminal substitution pattern of typical alkylaminoazobenzene derivatives have a greater effect on heat fastness than have substituents in the aryl nuclei of the diazo and coupling components [138]. The fastness can be significantly improved by incorporating polar groups (acetoxy, acetylamino, cyano) capable of hydrogen bonding or dipole–dipole interaction with polymer segments. The effect on heat fastness of replacing an acetate ester by a benzoate ester group in the coupling component is clearly illustrated by comparing two commercially important yellow brown disperse dyes of the 2,6-dichloro-4-nitrophenylazo series (Table 3.47).

Dyes of high M_r with numerous substituents or bulky groups almost invariably show higher fastness to sublimation than simpler aminoazobenzene or aminoanthraquinone analogues [182]. An interesting and comprehensive survey of 2,4,6-trisubstituted phenylazo dyes comparing the relative influence of all four possible halogeno substituents explored many such mutual steric and electron-withdrawing effects in the diazo components (Table 3.48). In all three series of structures represented (3.179–3.181), heat fastness of the trisubstituted derivatives increased consistently in the order: 2,6-dihalogeno-4-nitro < 2,4-dinitro-6-halogeno < 2-cyano-4-nitro-6-halogeno. As expected, heat fastness increased markedly with the size of the halogen atom and in the halogenated phenylazo-*N*-

Table 3.47 Structure and heat fastness of esterified *N*-hydroxyethyl disperse dyes on polyester [89]

CI Disperse	Substituent R in structure 3.178	Heat fastness (30s at 210°C)
Orange 62	O.CO.Ph	4–5
Orange 30	O.CO.Me	3–4



3.178

cyanoethyl-*N*-hydroxyethylanilines (3.179) heat fastness increased in the order: 4-halogeno < 2-halogeno < 2-halogeno-4-nitro. Heat fastness in Tables 3.48, 3.50 and 3.51 is defined as the dry heat treatment temperature at which a 2.5% o.w.f. dyeing on polyester gives a satisfactory rating [190].

Proton-donor groups (amino, hydroxy) in the 2-position of 1,4-disubstituted anthraquinone dyes enhance the fastness to heat because they are readily able to form intermolecular hydrogen bonds with the substrate or other dye molecules. Similar groups in the 1,4-positions normally form intramolecular hydrogen bonds with the keto groups of anthraquinone. The main drawback of electron-donating groups in the β-positions of anthraquinone dyes, however, is their usually adverse effect on light fastness (section 3.3.4).

Table 3.48 Structure and heat fastness of halogenated phenylazo disperse dyes on polyester [190]

	Sublimation for 2.5% depth (°C)			
Structure	Iodo	Bromo	Chloro	Fluoro
3.179; X = nitro, Y = halogeno, Z = cyano	210	210	210	
3.181; X = nitro, Y = halogeno, Z = cyano	200	190	180	
3.180; X = nitro, Y = halogeno, Z = cyano	200	180	180	
3.181; X = Z = nitro, Y = halogeno	200	180	170	170
3.179; X = Z = nitro, Y = halogeno	190	180	180	170
3.180; X = Z = nitro, Y = halogeno	190	180	170	170
3.180; X = nitro, Y = Z = halogeno	190	180	170	
3.181; X = nitro, Y = Z = halogeno	190	180	170	
3.179; X = nitro, Y = Z = halogeno	190	170	170	
3.179; X = nitro, Y = halogeno, Z = H	180	170	170	160
3.179; X = Z = H, Y = halogeno	170	160	160	150
3.179; X = halogeno, Y = Z = H	170	150	160	140

Table 3.49 Structure and heat fastness of substituted aminohydroxyanthraquinone disperse dyes on polyester [175]

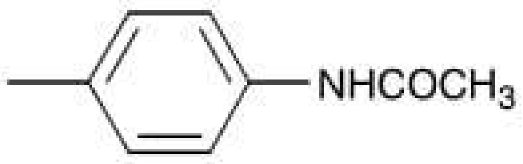
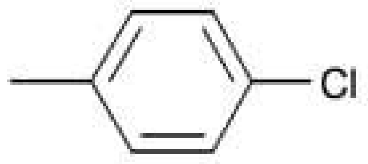
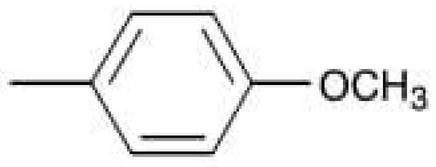
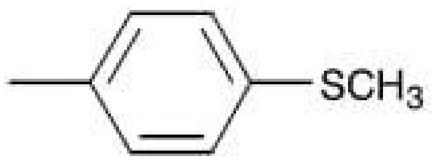
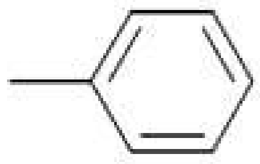
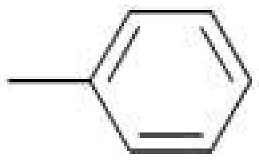
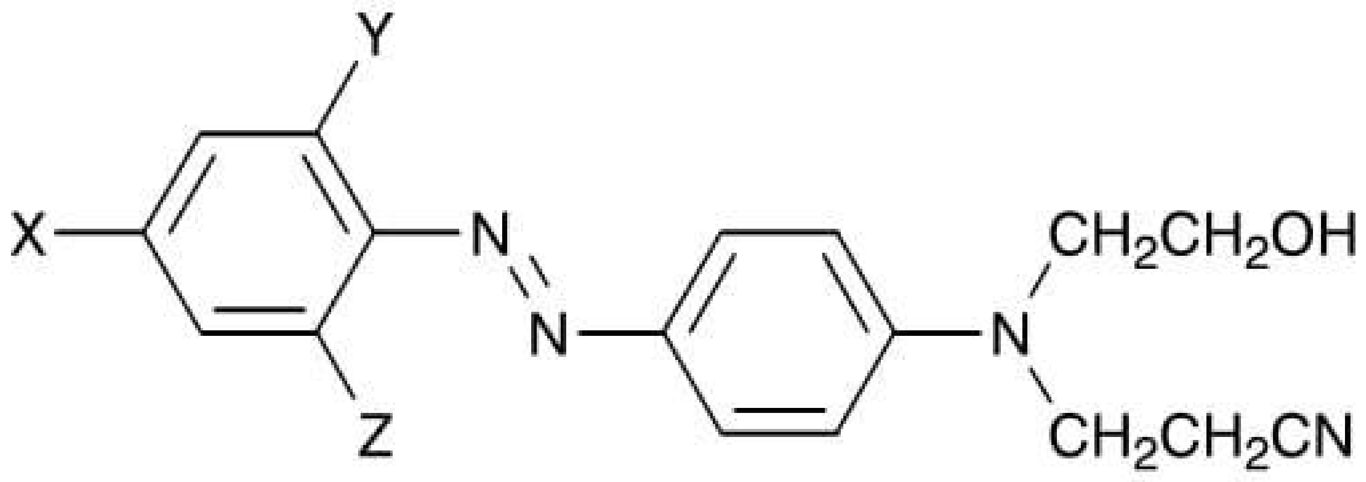
Structure	Heat fastness
3.182; X = 	4–5
3.183; R = 	4–5
3.182; X = 	3–4
3.183; R = 	3–4
3.183; R = $-CH_2CH_2CH_2CH_2CH_2CH_2OH$	3–4
3.182; X = 	2–3
3.182; X = $-CH_2CH_2COOCH_2CH_3$	2–3
3.183; R = 	2–3
3.183; R = 	2–3
3.182; X = 	1–2
3.182; X = H	1–2
3.183; R = CH_3	1–2

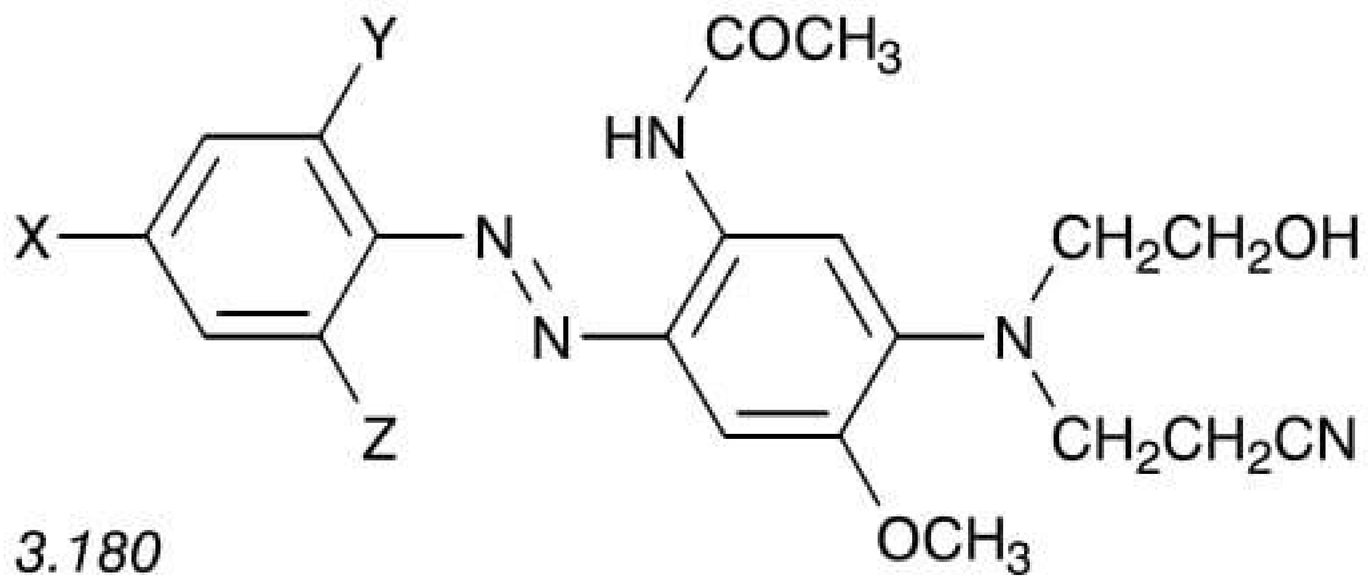
Table 3.50 Structure and heat fastness of N-substituted aminodihydroxyanthraquinone disperse dyes on polyester [190]

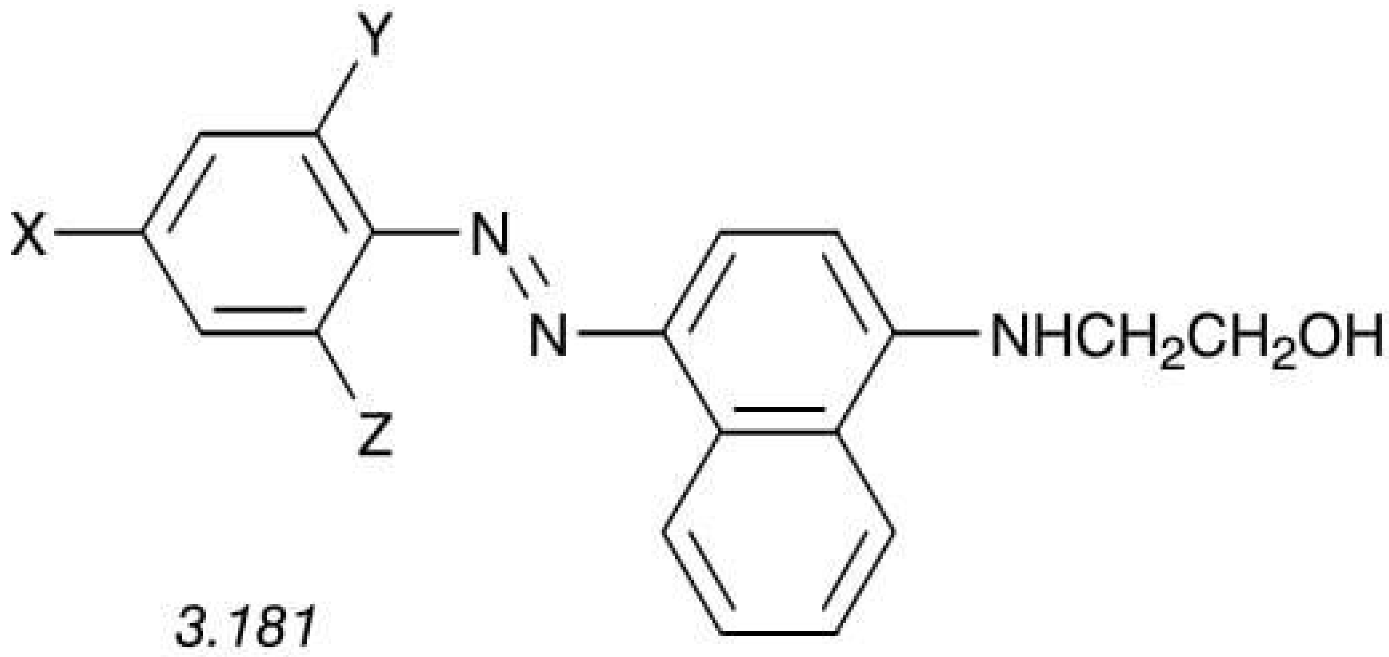
Substituent R in structure 3.184	Sublimation for 2.5% depth (°C)
Benzothiazol-2-yl	180
4-n-Dodecylphenyl	180
3-Fluoromethylphenyl	180
Morpholin-4-ylpropyl	160
Pyrid-3-ylmethyl	160
Phenyl	160
2,3-Dihydroxypropyl	160
2-Hydroxypropyl	160
Morpholin-4-ylethyl	150
Benzyl	150
Cyclohexyl	150
Methoxypropyl	150
Hydroxypropyl	150
Hydroxyethyl	150
Pyran-2-ylmethyl	140
Methoxyethyl	140
Ethyl	140
Methyl	140
Hydrogen	140

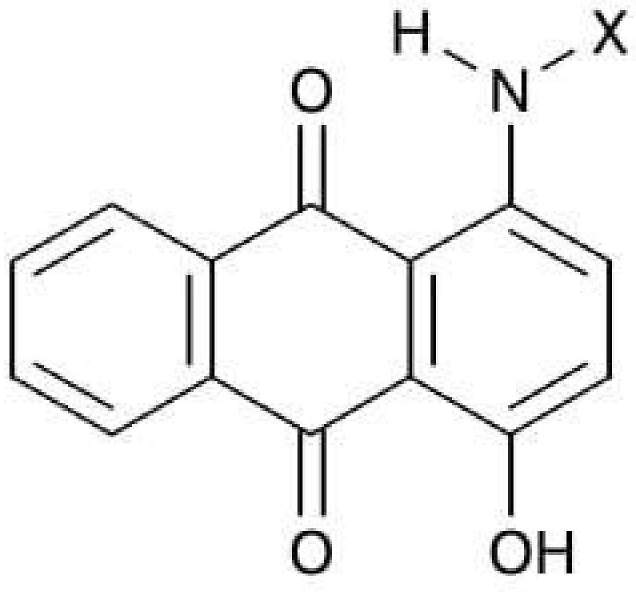
Table 3.51 Structure and heat fastness of *p*-substituted anilinoanthraquinone disperse dyes on polyester [192]

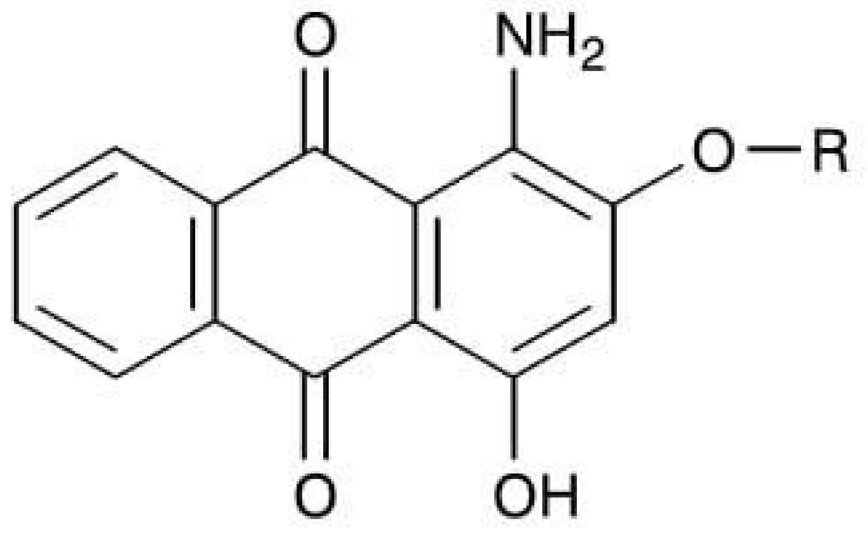
	Sublimation for 2.5% depth (°C)			
	Anthrarufin derivatives		Chrysazin derivatives	
	3.187	3.188	3.189	3.190
Substituent R in 3.187–3.190	1-amino-5-anilino	1-anilino-5-nitro	1-amino-8-anilino	1-anilino-8-nitro
Benzoylamino	200	200	210	210
Acetylamino	200	200	200	210
Aminosulphonyl	200	200	200	200
Benzoyl	190	200	200	210
Carbethoxy	210	190	210	190
Acetyl	180	190	200	190
Hydroxyethyl	170	180	160	180
Methoxy	170	160	160	180
Ethoxy	160	170	160	170
Methyl	160	170	160	170
Hydrogen	160	160	160	170

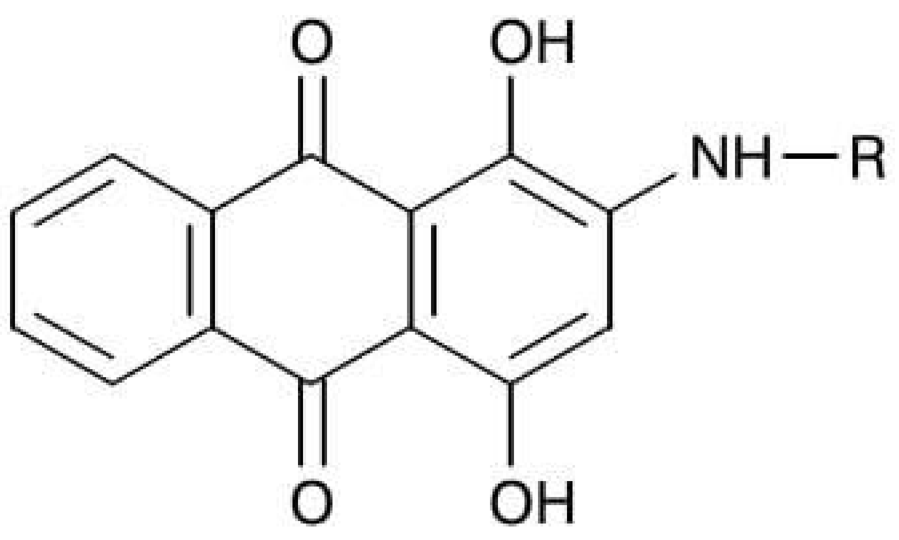

3.179

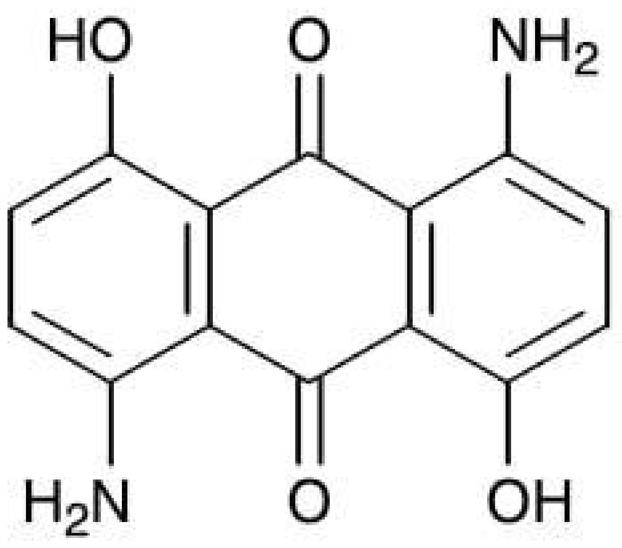

3.180


3.181

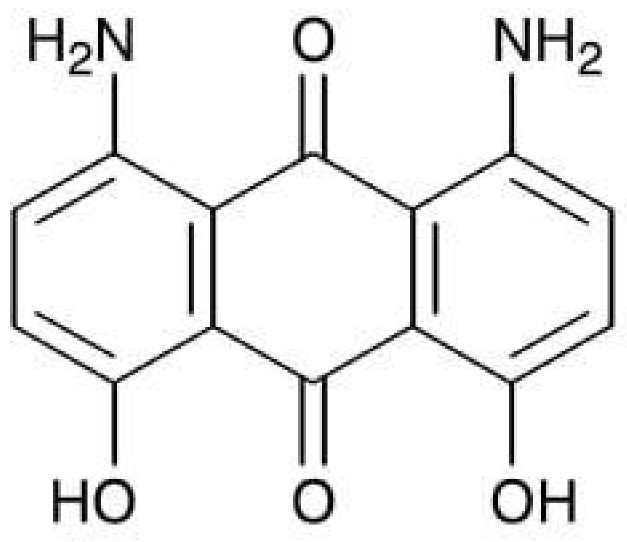

3.182


3.183

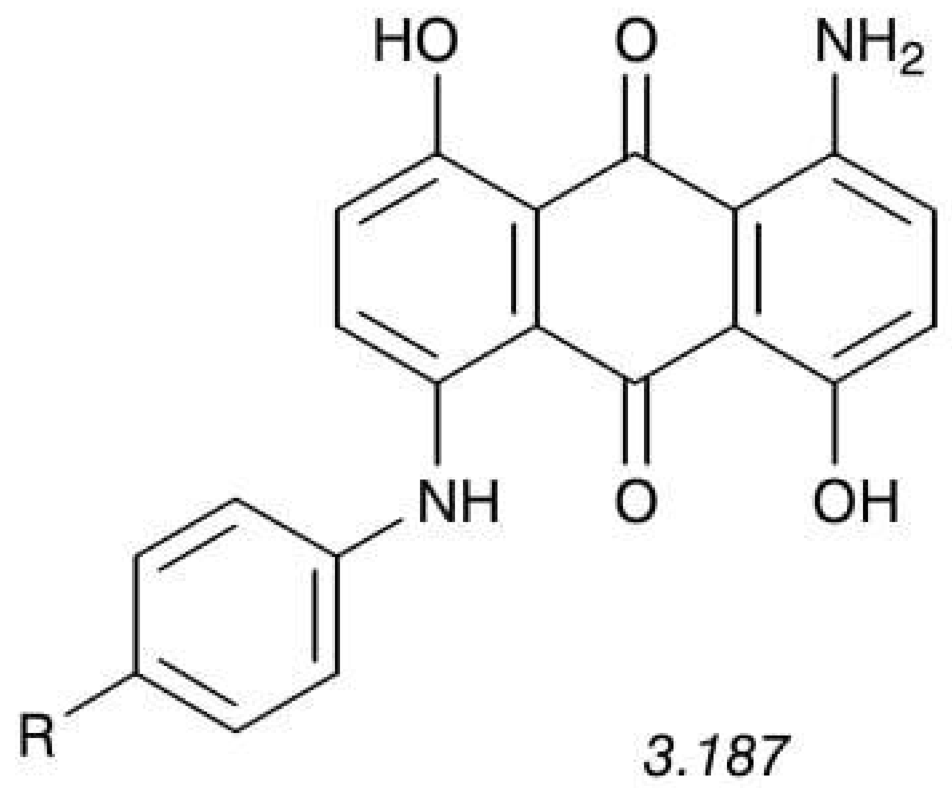

3.184



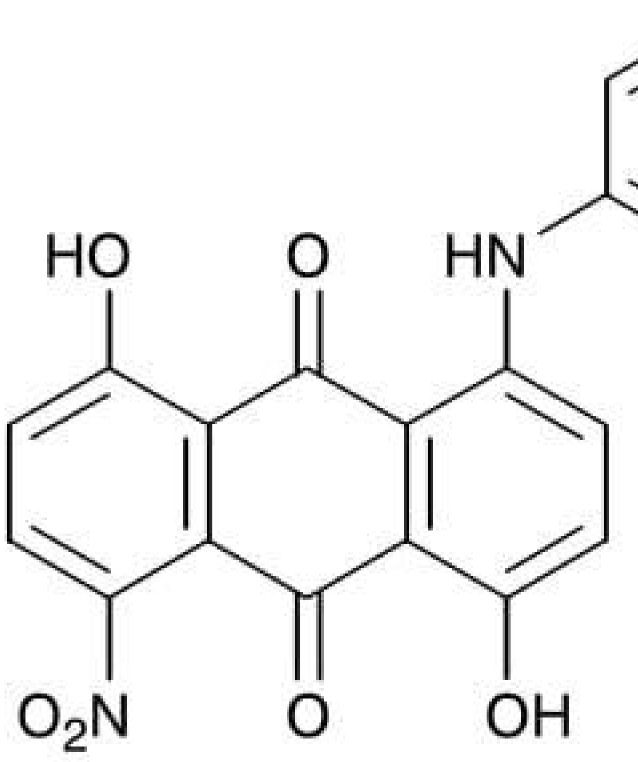
3.185



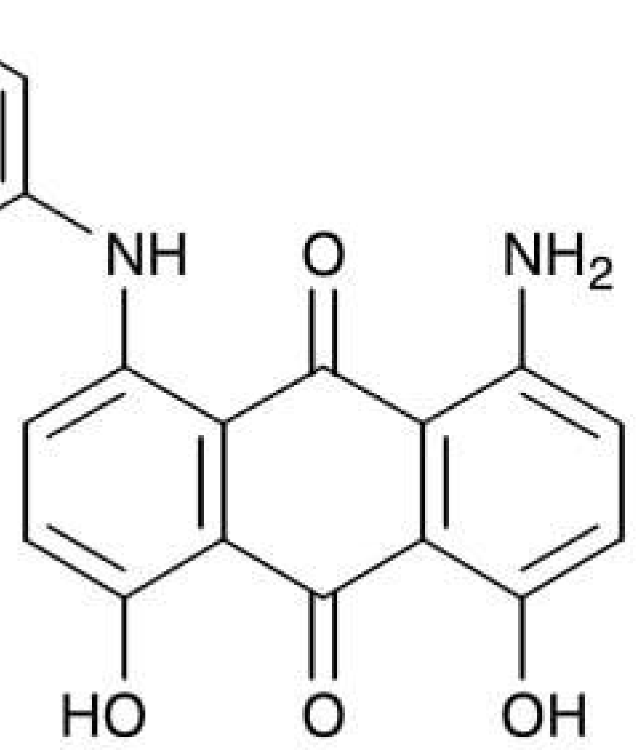
3.186



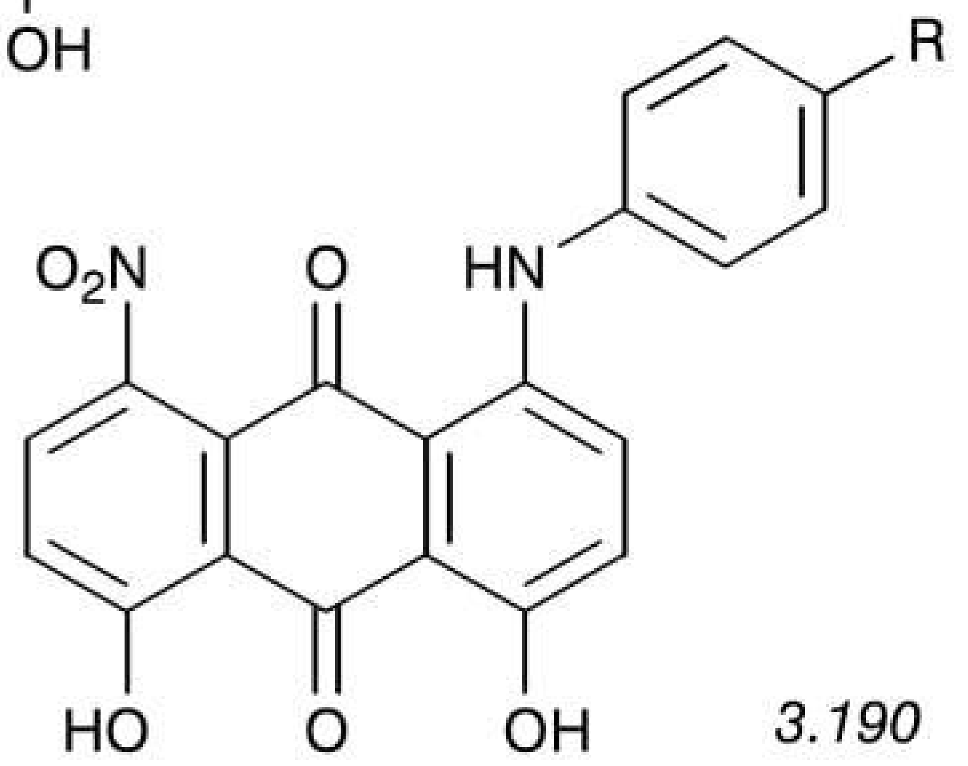
3.187



3.188



3.189



3.190

Trends indicating the capability of various polar and nonpolar substituents to enhance the low heat fastness of 1-amino-4-hydroxyanthraquinone (3.182; X = H) and its 2-hydroxy derivative (3.183; R = H) are revealed in Table 3.49. In the series of secondary amino derivatives (3.182) a phenyl group offers little or no improvement. An ethyl propionate residue or a *p*-methoxyphenyl group produces a modest increase in fastness but more polar moieties such as tetramethylenesulphone or *p*-acetanilide groupings are necessary to achieve high ratings. Methylation of the 2-hydroxy group in structure 3.183 improves the light fastness but not the fastness to sublimation. A phenyl or *p*-methylthiophenyl group raises heat fastness somewhat, but more marked improvements follow with 6-hydroxy-n-hexyl, *p*-chlorophenyl and the complex alkoxyalkylsulphamoylphenyl grouping shown in Table 3.49.

In a related series of 1,2,4-trisubstituted anthraquinone compounds, the effectiveness of various polar and nonpolar substituents to improve on the low heat fastness of 2-amino-1,4-dihydroxyanthraquinone (3.184; R = H) was examined (Table 3.50). Short-chain alkyl groups (methyl, ethyl) and even the pyranylmethyl ether are relatively ineffective but hydroxyalkyl, cyclohexyl, benzyl and morpholinylethyl groups show moderate increases. Further improvement is given by phenyl, pyridylmethyl and morpholinylpropyl. Outstandingly effective, however, are the benzothiazolyl, dodecylphenyl and fluoromethylphenyl groupings.

The influence of the number and orientation of bromo substituents on heat fastness in two systematic series of multibrominated derivatives of 1,5-diaminoanthrarufin (3.185) and

1,8-diaminochrysazin (3.186) was investigated in detail [191]. More recently, *p*-substitution of the aryl ring in four series of aminoanilino and anilinonitro analogues has been studied (Table 3.51). Only moderate improvements in heat fastness were afforded by methyl, methoxy or ethoxy substituents. Groupings incorporating more polar moieties, including hydroxyethyl, acetyl, carbethoxy and benzoyl, were much more effective, but the highest ratings were shown by the amido groupings, namely aminosulphonyl, acetylamino and benzoylamino.

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