CHAPTER 4

Chemistry of azo colorants

Geoffrey Hallas

4.1 INTRODUCTION

Shortly after Perkin had produced the first commercially successful dyestuff, a discovery was made which led to what is now the dominant chemical class of dyestuffs, the azo dyes. This development stemmed from the work of Peter Griess, who in 1858 passed 'nitrous fumes' (which correspond to the formula N_2O_3) into a cold alcoholic solution of 2-amino-4,6-dinitrophenol (picramic acid) and isolated a cationic product, the properties of which showed it to be a member of a new class of compounds [1]. Griess extended his investigations to other primary aromatic amines and showed his reaction to be generally applicable. He named the products *diazo* compounds and the reaction came to be known as the *diazotisation* reaction. This reaction can be represented most simply by Scheme 4.1, in which HX stands for a strong monobasic acid and Ar is any aromatic or heteroaromatic nucleus.

$$Ar-NH_2 + HX + HNO_2 \longrightarrow Ar-\overset{+}{N}\equiv N \ X^- + 2H_2O$$
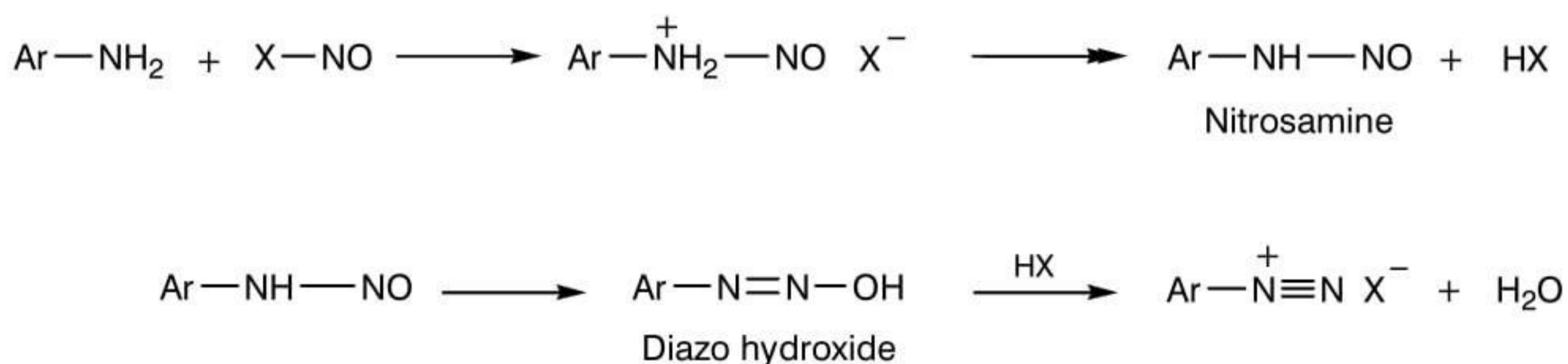
Scheme 4.1

Griess subsequently recognised that the orange compound formed by the reaction of *diazobenzene* with phenol in neutral solution contained two benzene nuclei joined together via an azo (–N=N–) linkage [2] and again the reaction was found to be general and not confined to phenols. This second reaction became known as the *diazo coupling* reaction and the products as azo compounds. The wide applicability of this reaction opened the way to a vast multitude of compounds produced in generally high yields in simple plant and led to the azo dyes becoming the largest and most versatile class of dyes.

The high reactivity of diazonium salts enables them to enter into a great many reactions other than the azo coupling reaction, but these fall outside the scope of the present chapter. Various other methods can be used for the preparation of azo compounds, although these are of minor importance compared with the diazo coupling reaction and they will only be touched on briefly where appropriate.

## 4.2 MECHANISM OF DIAZOTISATION AND COUPLING

Studies of the mechanism of the diazotisation reaction date back to the end of the nineteenth century and have continued ever since, progressively incorporating the growing knowledge of theoretical chemistry [3,4]. The reaction, which involves nitrosation, has been studied under a wide range of acidities using a variety of amines and nitrosating agents.

Numerous effects arising from variations in conditions have been described. In essence, the accepted mechanism is represented by Scheme 4.2, in which X–NO represents one of the many varieties of nitrosating species such as nitrous acid (HO–NO), nitrosyl chloride (Cl–NO), dinitrogen trioxide (O_2N–NO), the nitrosyl cation (NO^+) or the nitrous acidium ion ($H_2NO_2^+$) that may be present in solutions containing nitrous acid. According to the conditions employed, either the formation of the nitrosating agent or its initial attack on the amine is the slowest reaction step and therefore determines the overall rate, the subsequent steps in the reaction sequence being rapid. The concentrations of the various possible nitrosating species can be influenced by other ions, such as chloride ions, or compounds, such as thiourea, present in the reaction mixture so that catalytic effects are observed.

$$Ar\text{—}NH_2 + X\text{—}NO \longrightarrow Ar\text{—}\overset{+}{N}H_2\text{—}NO\ X^- \longrightarrow Ar\text{—}NH\text{—}NO + HX$$

<center>Nitrosamine</center>

$$Ar\text{—}NH\text{—}NO \longrightarrow Ar\text{—}N\text{=}N\text{—}OH \xrightarrow{HX} Ar\text{—}\overset{+}{N}\text{≡}N\ X^- + H_2O$$

<center>Diazo hydroxide</center>

Scheme 4.2

The diazonium ion is a powerful electrophile that can readily attack compounds having a nucleophilic centre, with the expulsion of a proton, or other entity, from the site of attack [5]. This mode of behaviour leads to the formation of azo compounds by the azo coupling reaction, the compound with the nucleophilic site being termed the coupling component. Suitable coupling components include arylamines, phenols, naphthols and keto–enol compounds. The mechanism with an arylamine coupling component can be represented by Scheme 4.3. In the coupling component illustrated both the *o*- and *p*-positions are activated by the dialkylamino group. However, an approach of the diazonium ion to the *o*-position would cause the electron-donating group to be twisted out of plane and thus to lose its activating influence. For this reason, coupling occurs selectively at the *p*-position. The situation is somewhat different in non-aqueous media where the counter-ion of the diazonium salt can influence the *o-/p*-ratio. In dichloromethane, diazonium halides couple to 1-naphthol almost exclusively in the 4-position whereas the corresponding haloacetates couple mainly in the 2-position [6].
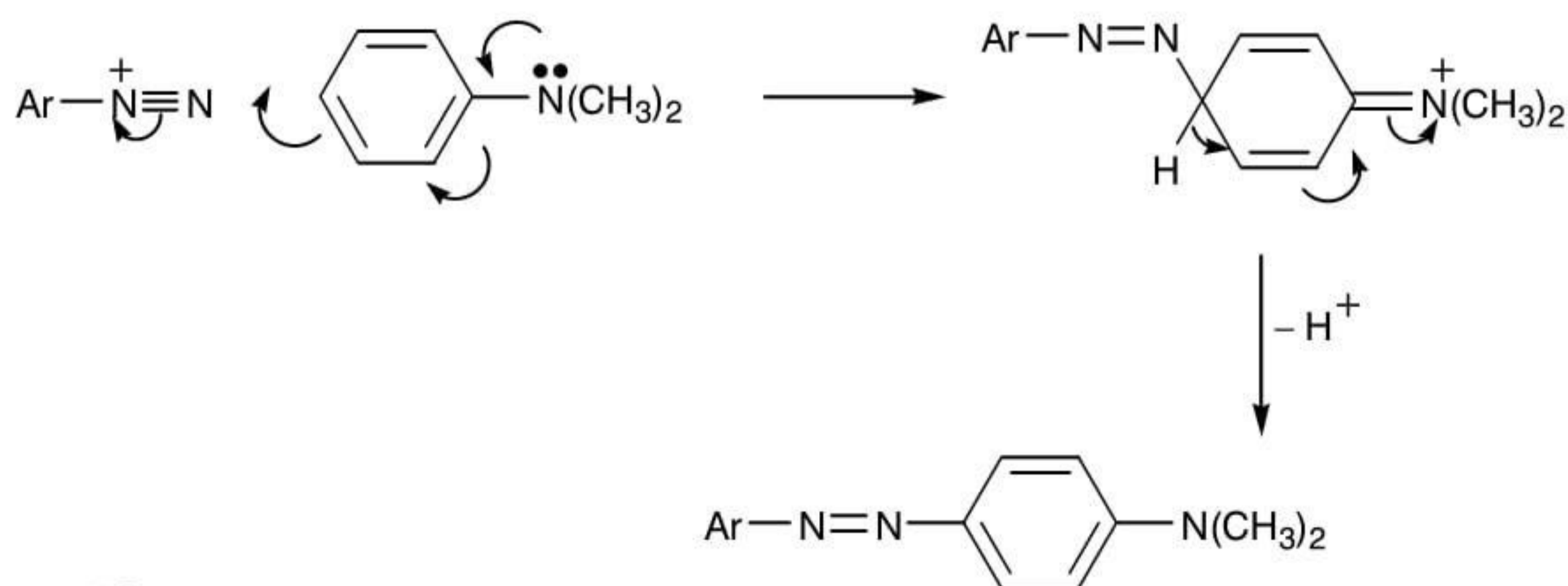

Scheme 4.3

With a phenol, naphthol or keto–enol coupling component the mechanism is given by Scheme 4.4, in which blocking of the *p*-position forces coupling at the *o*-position. In certain cases involving the use of feebly reactive diazonium salts, loss of the proton from the transition state (4.1) in Scheme 4.4 may be slow but may often be facilitated by the addition of a tertiary base, such as pyridine, to the coupling mixture [7,8].
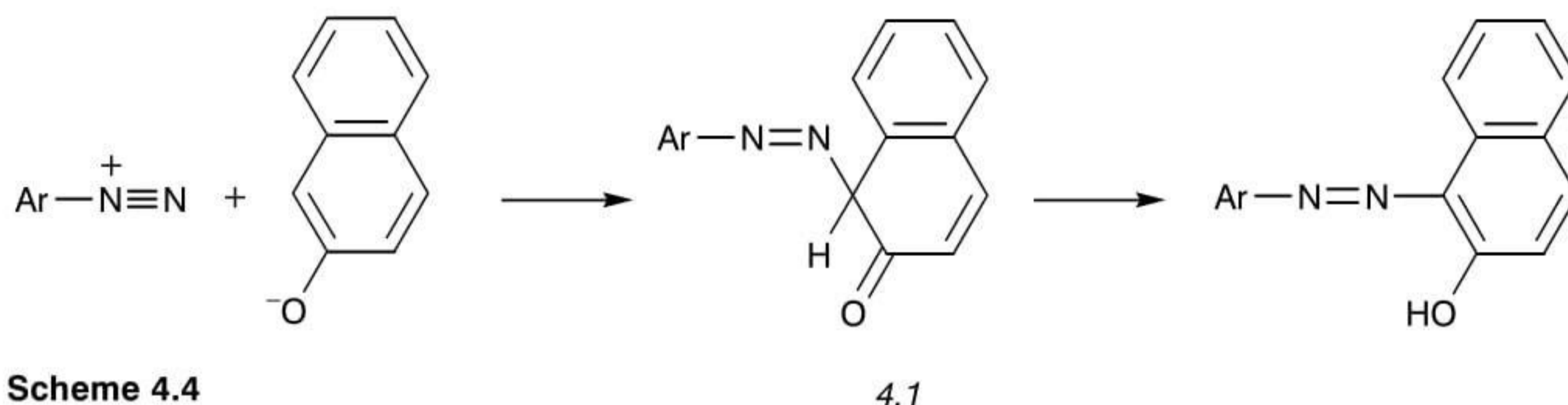
Scheme 4.4   *4.1*

In these two coupling schemes the arylamine participates in the reaction as the free base, whereas the naphthol coupling component reacts in its ionised form. Thus, whilst raising the pH increases the rate of coupling in both cases, much higher pH values are required to bring about satisfactory coupling with hydroxy compounds than with arylamines. This situation is taken advantage of in the case of certain aminonaphthol coupling components, particularly 8-amino-1-naphthol-3,6-disulphonic acid (4.2; H acid), where one azo group can be selectively directed into the molecule by the amino group at low pH, followed by a second azo group directed by the ionised hydroxy group at higher pH.

4.2

H acid
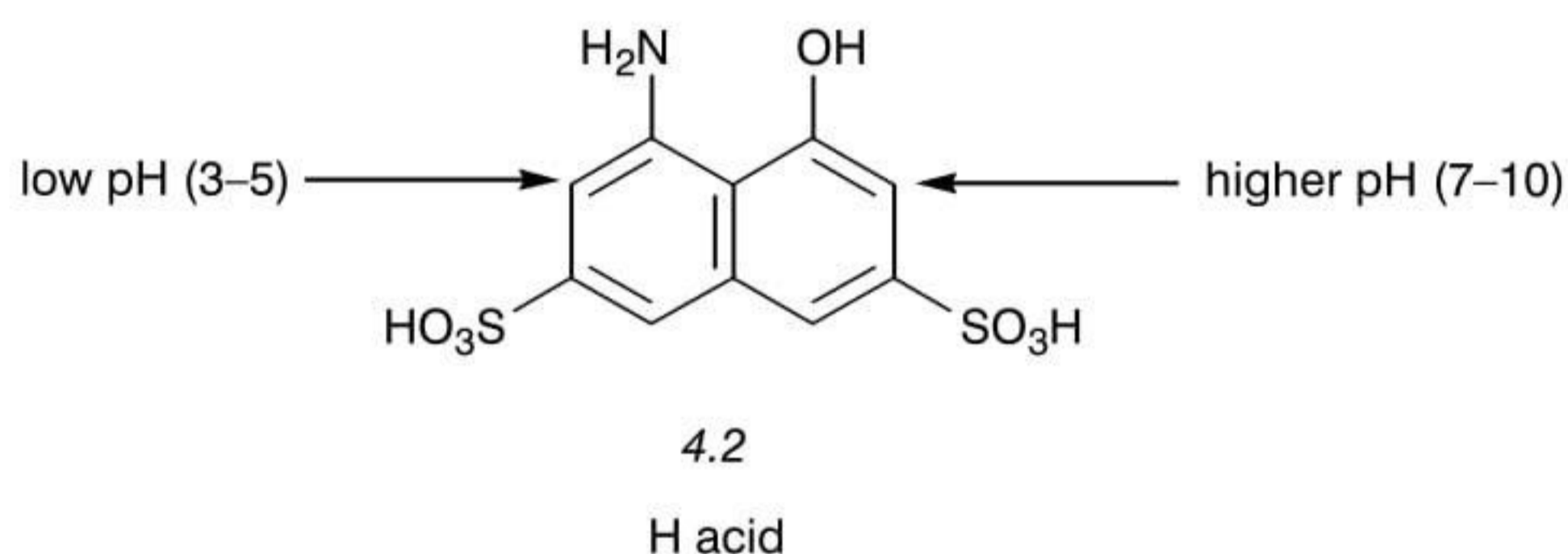
4.3 DIAZO COMPONENTS AND DIAZOTISATION METHODS

A vast array of arylamines can be converted into the corresponding diazonium salts; from these *diazo components* and the host of available coupling components an almost limitless range of azo dyes is accessible.

It has already been pointed out (section 1.7.4) that various arylamines are hazardous. In July 1994, the German government introduced, unilaterally, stringent regulations banning imports of various textile and clothing products which contain specific arylamine-based azo dyes. Only those colorants which on cleavage of one or more azo groups could form any one of the twenty listed arylamines were affected. These amines (Table 4.1) are classified as proven carcinogens. Two additional arylamines, 2-methoxyaniline and 4-aminoazobenzene, were added subsequently by the EU. The German ordinance restricts the use of only about 5% of azo dyes (about 150 products). Similar regulations have been introduced in the

Table 4.1 List of specified arylamines

Name on list	Alternative name
o-Aminoazotoluene	2-Amino-4,4′-dimethylazobenzene
4-Aminobiphenyl	
Benzidine	4,4′-Diaminobiphenyl
p-Chloroaniline	4-Chloroaniline
4-Chloro-o-toluidine	4-Chloro-2-methylaniline
3,3′-Dichlorobenzidine	
3,3′-Dimethoxybenzidine	o-Dianisidine
3,3′-Dimethylbenzidine	o-Tolidine
4-Methoxy-m-phenylenediamine	2,4-Diaminoanisole
6-Methoxy-m-toluidine	2-Methoxy-5-methylaniline
4,4′-Methylene-bis(2-chloroaniline)	4,4′-Diamino-3,3′-dichlorodiphenylmethane
4,4′-Methylenedianiline	4,4′-Diaminodiphenylmethane
4,4′-Methylene-o-toluidine	4,4′-Diamino-3,3′-dimethyldiphenylmethane
4-Methyl-m-phenylenediamine	2,4-Diaminotoluene
2-Naphthylamine	2,Aminonaphthalene
5-Nitro-o-toluidine	2,Methyl-5-nitroaniline
4,4′-Oxydianiline	4,4′-Diaminodiphenyl ether
4,4′-Thiodianiline	4,4′-Diaminodiphenyl thioether
o-Toluidine	2-Methylaniline
2,4,5-Trimethylaniline	

Netherlands and in France. By mid 1997, most azo pigments, due to their very low solubility, had been exempted [9]. The legislative requirements have been discussed [10]. A voluntary registration scheme for harmless dyestuffs is available and makes use of the Internet [11].

In 1996 an official German analytical method was published for the detection of banned amines in relation to cotton, viscose, wool and silk; a second method was introduced for leather. The official procedure uses sodium dithionite in a weakly acidic citrate-buffered medium; more aggressive methods are known to produce false positive results where the amine detected is an artefact of the test procedure, resulting from chemical reactions other than azo cleavage. Reactions not involving azo groups can sometimes lead to the formation of forbidden amines [12]. Methods of detection involving thin-layer chromatography, leading to the unequivocal identification of the specified amines, have been devised [13,14]. 2-Naphthylamine has been detected in dyes derived from 1-naphthylamine [15], due to contamination of the intermediate. Benzidine can be formed from 4-nitroaniline after diazotisation by dediazoniation, followed by radical coupling to give 4,4′-dinitrobiphenyl and finally reduction [15].

A variety of diazotisation techniques has been evolved to cope with the variation in physical properties across the range of amines.
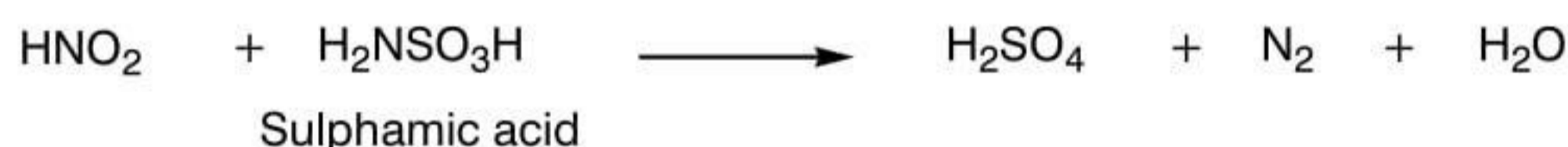
4.3.1 Direct method

The rudiments of the diazotisation technique consist of treating the amine with at least 2.25 equivalents of a mineral acid (usually hydrochloric acid) and one equivalent of sodium nitrite, in accordance with Scheme 4.5. The slight excess of acid specified is required to ensure that the reaction medium remains acid throughout the diazotisation. In the direct method sodium nitrite is added to a solution of the amine in dilute mineral acid. This
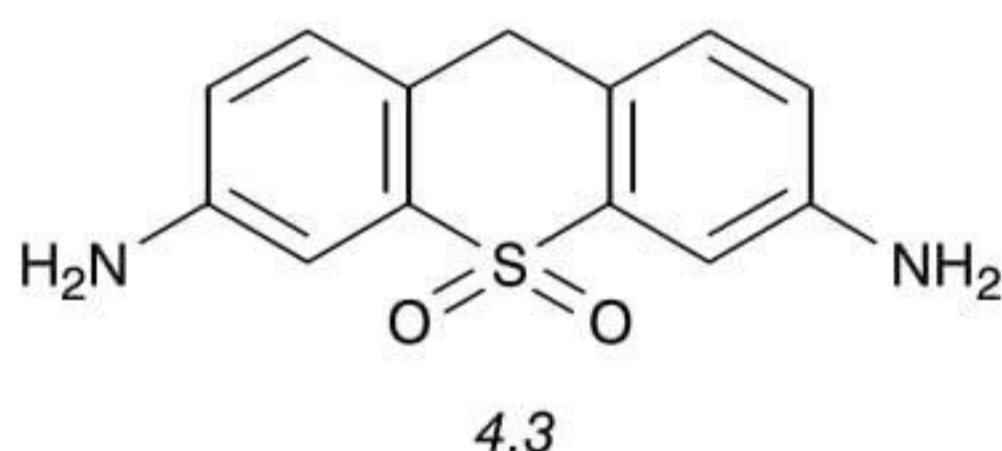
method is suitable for aniline and its simple derivatives with groups such as alkyl, alkoxy or chloro as substituents in the aromatic ring, simple naphthylamines and benzidine derivatives, many of which are known carcinogens. These compounds can be readily diazotised or tetrazotised by dissolving the amine in dilute hydrochloric acid, cooling the solution to 0–5 °C with ice and adding the requisite amount of sodium nitrite solution as rapidly as the nitrous acid formed from it is used in the reaction. Spotting the solution onto starch–iodide paper is carried out to test for an excess of nitrous acid. On occasions when it is difficult to determine the end point with starch–iodide paper, a dilute acid solution of 4,4′-diaminodiphenylmethane-2,2′-sulphone (4.3), which gives a bright blue colour with nitrous acid, can be used [16]. The reaction is complete when a slight excess of nitrous acid has persisted for about 15 minutes. The excess of nitrous acid is then conveniently and rapidly destroyed by the addition of a little sulphamic acid, in accordance with Scheme 4.6, producing innocuous products. The diazonium salt solution is then ready for immediate use in dye synthesis.

$$Ar-NH_2 \ + \ 2HX \ + \ NaNO_2 \ \longrightarrow \ Ar-\overset{+}{N}\equiv N \ \ X^- \ + \ NaX \ + \ 2H_2O$$

Scheme 4.5

$$HNO_2 \ + \ H_2NSO_3H \ \longrightarrow \ H_2SO_4 \ + \ N_2 \ + \ H_2O$$
Sulphamic acid

Scheme 4.6

4.3

For the diazotisation reaction to succeed, it is necessary that the amine should be completely converted into the hydrochloride before the addition of sodium nitrite, because any free amine can react with the diazonium salt to form a diazoamino compound (Scheme 4.7). This complication needs to be avoided in the case of amines, such as the dichloro-anilines, which do not dissolve easily in dilute hydrochloric acid [17]. With such compounds it is convenient first to dissolve them in a hot acid solution, which is then cooled to 0–5 °C. This procedure ensures the absence of free amine, and even if the hydrochloride precipitates on cooling it readily redissolves as the diazotisation proceeds. Similar precautions are required with the nitroanilines and here an increased amount of mineral acid is advantageous [18].

$$Ar-NH_2 \ + \ Ar-\overset{+}{N}\equiv N \ \ X^- \ \longrightarrow \ Ar-NH-N=N-Ar \ + \ HX$$

Scheme 4.7

Low temperatures are generally necessary for successful diazotisation, except in a few cases where the diazonium salt is exceptionally stable. Temperatures of 50–60 °C are used for the diazotisation of 3-aminodibenzofuran (4.4), for example [19].
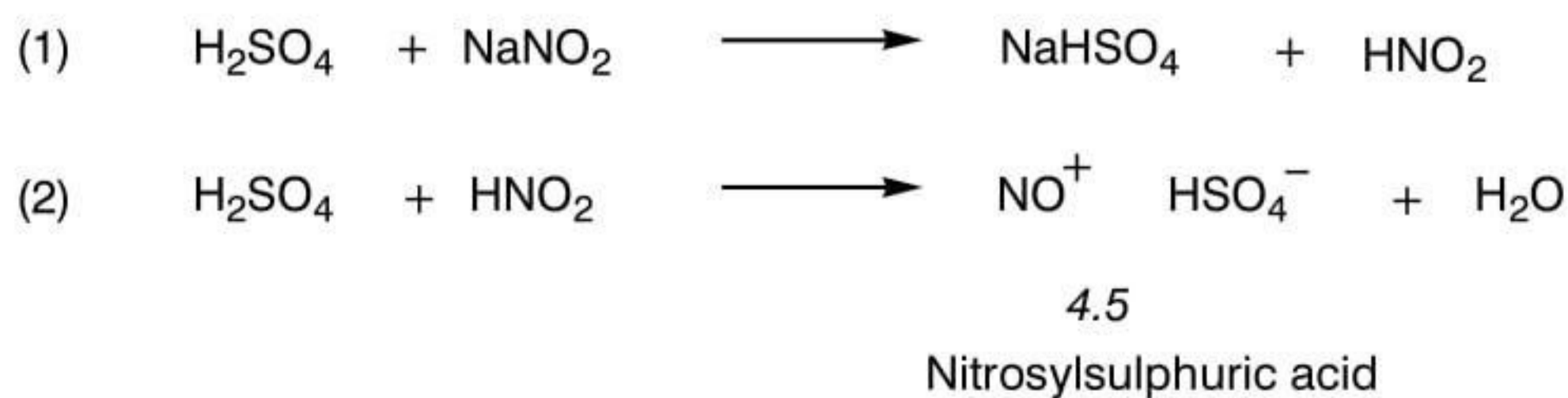

4.4

3-Aminodibenzofuran
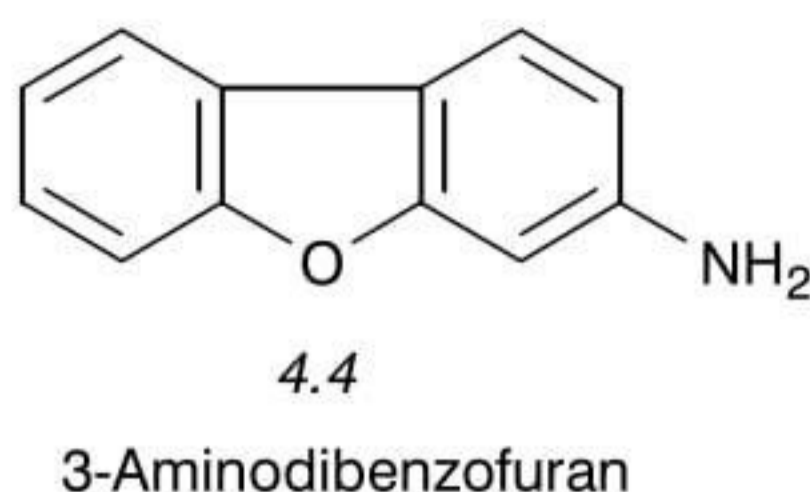
4.3.2 Inverse method

In this method the order of addition of the reactants is changed. The most general application is to the diazotisation of aniline- and naphthylamine-sulphonic acids, many of which are sparingly soluble in acidic media and form sparingly soluble diazonium salts. Typically, the arylaminesulphonic acid is dissolved as its sodium salt in dilute alkali and sodium nitrite is then added to the solution. The resulting solution is run slowly into a mixture of hydrochloric acid and ice, the diazonium salt being formed almost instantaneously.

In a variation of this procedure [19], a small amount of acid is added to a suspension of a sulphonated amine in sodium nitrite solution; the sulphonic acid group on the amine generates nitrous acid and diazotisation proceeds to completion.

4.3.3 Use of nitrosylsulphuric acid

Very feebly basic amines cannot usually be diazotised in dilute acid media and in these instances the reaction has to be carried out in a concentrated acid, normally sulphuric acid. The usual technique is first to dissolve dry sodium nitrite in the concentrated acid, when reaction occurs in two stages (Scheme 4.8), resulting in the formation of nitrosylsulphuric acid (4.5). The nitrosyl ion – nitrous acid equilibrium has been evaluated spectroscopically. In 96% sulphuric acid the ^{15}N-n.m.r. signal is characteristic of the free nitrosyl ion [4]. Reaction (2) of Scheme 4.8 is slow at room temperature and it is desirable to heat the mixture to 70 °C in order to attain equilibrium within a reasonable time. After cooling, the amine is added gradually and after a short time the reaction mixture is poured onto ice, giving an aqueous solution of the diazonium salt [20].

This technique is used to diazotise anilines carrying two or more electron-withdrawing substituents, such as 2,4-dinitro- and 2-cyano-4-nitro-aniline, as well as aminoanthra-quinones and heteroaromatic amines [4]. Some diazonium salts prepared by this technique, such as those from 6-halogeno-2,4-dinitroanilines, are unstable in water and have to be added directly to the coupling component solution.

(1) H_2SO_4 + $NaNO_2$ $\longrightarrow$ $NaHSO_4$ + HNO_2

(2) H_2SO_4 + HNO_2 $\longrightarrow$ NO^+ HSO_4^- + H_2O

4.5

Scheme 4.8   Nitrosylsulphuric acid

4.3.4 Other methods

Although not used in dye preparation, three other methods of diazotisation deserve passing mention, one being chiefly of historical interest and the other two are sometimes of use in preparative work. The oldest is the method originally used by Griess (section 4.1), who generated the first recognised diazonium salt by passing 'nitrous gases' into a cold ethanolic solution of the amine. This reagent is produced by reducing nitric acid with arsenic(III) oxide or starch; it behaves as if it consisted of dinitrogen trioxide. The method can be useful for the preparation of solid diazonium salts, but a better procedure is that due to Knoevenagel [21]. In this second method an alkyl nitrite is added to a solution of the amine and sulphuric acid in ethanol or other non-aqueous solvent. This procedure allows greater control of the reaction than is possible in the Griess method.

Finally, in a method originated by Witt [22], which is occasionally useful for the diazotisation of stable amines of high relative molecular mass that pose solubility problems, the amine is dissolved in nitric acid before the addition of sodium metabisulphite. Nitrous acid is produced in the medium according to Scheme 4.9, enabling diazotisation to proceed.

$$Na_2S_2O_5 \ + \ 2HNO_3 \ \longrightarrow \ Na_2S_2O_7 \ + \ 2HNO_2$$

Scheme 4.9

Diazonium salts vary greatly in electrophilicity and therefore in reactivity thereby affecting the ease with which they couple. The presence in the aromatic nucleus of electron-attracting groups, such as nitro and cyano groups, causes difficulties in the diazotisation step but helps the resulting diazonium salt to couple extremely readily. Electron-donating substituents such as methoxy and acetylamino groups, which facilitate diazotisation, diminish the coupling power. An extreme case is posed by the diazonium salts derived from o- and p-aminophenols and aminonaphthols, which are very feeble couplers, requiring highly alkaline conditions and often the use of a coupling assistant such as pyridine to bring about a satisfactory reaction. This very low level of reactivity is due to the hydroxy substituent interacting structurally with the diazonium group, leading to a mesomeric system in which the limiting forms are represented by Scheme 4.10 [23].
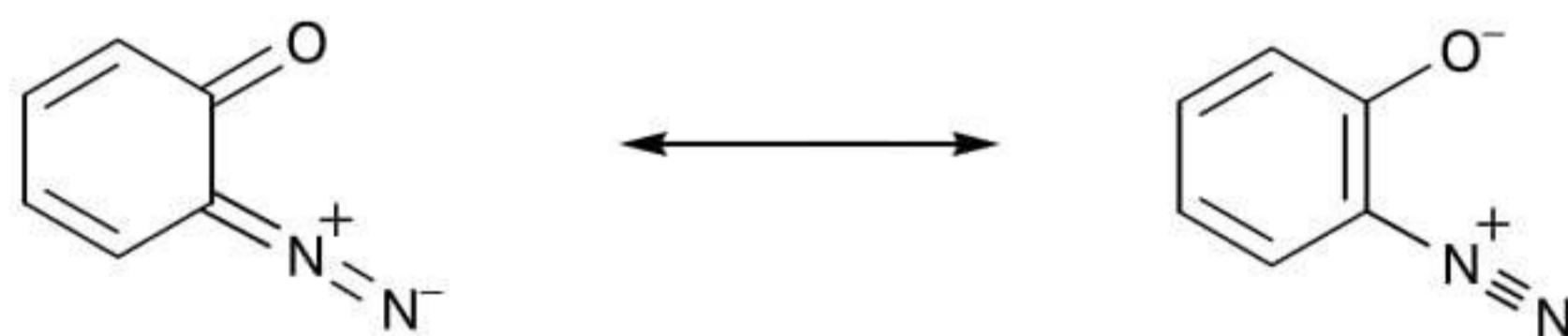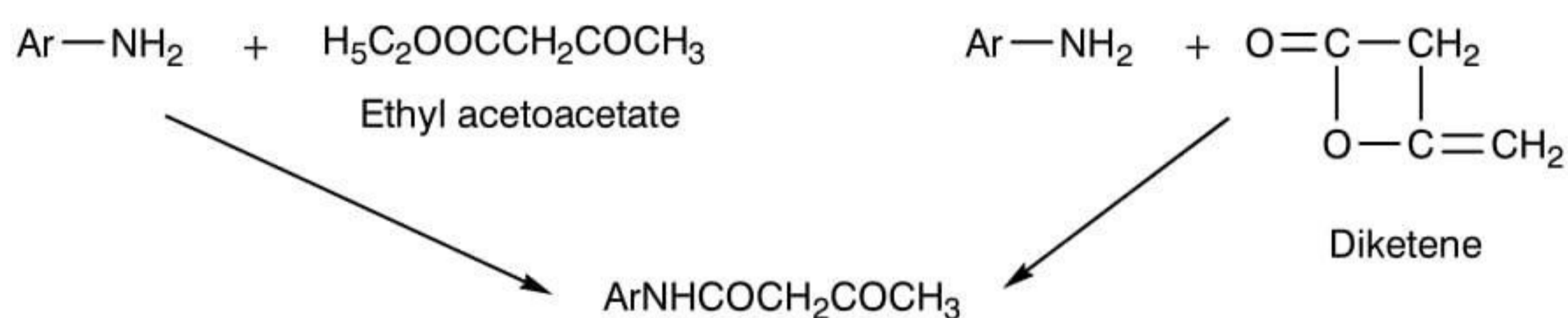

Scheme 4.10

4.4 PREPARATION AND USE OF COUPLING COMPONENTS

As well as being presented with an array of primary amines that can be used for the preparation of azo dyes, the dye chemist has available a multiplicity of coupling components. The coupling components useful in the synthesis of azo dyes cover a range of chemical types which can all be seen to contain a keto–enol system, a hydroxy or an amino group. Since the use of these compounds is largely restricted to the azo dye field, their preparation is in many cases not covered in the common organic chemistry books. In the discussion of these classes, therefore, a brief mention of methods of preparation is given where appropriate.

4.4.1 Acetoacetarylamides

Coupling components of this class have the general structure 4.6 (Scheme 4.11), in which Ar represents an aromatic, usually benzenoid, nucleus that may carry substituents. Initially such compounds were prepared by the reaction of an arylamine with ethyl 3-oxobutanoate (ethyl acetoacetate) but now are more conveniently made by treatment of an arylamine with diketene (Scheme 4.11). The electron-attracting effect of the two carbonyl groups flanking the methylene group in structure 4.6 gives the protons on this latter group an acidic character permitting solubility in alkaline solution, the negative charge produced by the ionisation being spread over the molecule as shown in Scheme 4.12. This resonance provides an electron-rich site on the carbon atom of the methylene group, at which coupling occurs. Coupling of simple diazotised arylamines with acetoacetarylamides produces greenish yellow pigments and dyes of particular value in the direct and azoic dye ranges, under which headings specific structures are mentioned. Related to the acetoacetarylamides is barbituric acid (4.7), which has found similar use as a coupling component in synthetic dyes.

Scheme 4.11   *4.6*

Scheme 4.12
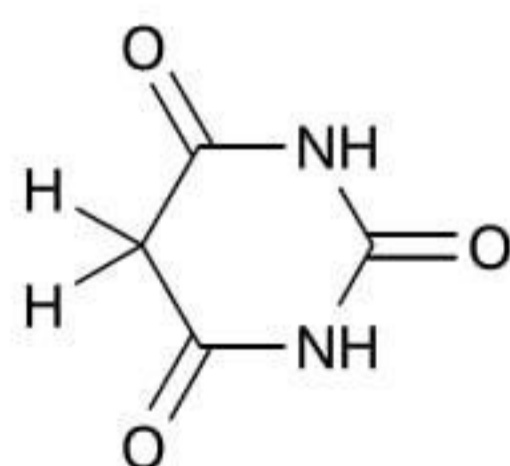
4.7

Barbituric acid

4.4.2 Pyridones

The pyridone coupling components (4.8), which came into use in the 1960s chiefly for the preparation of greenish yellow disperse and reactive dyes, are made by the condensation of an alkylamine with ethyl acetoacetate and ethyl cyanoacetate. Coupling occurs at the position indicated by the arrow in Scheme 4.13.

Ethyl acetoacetate   Ethyl cyanoacetate   4.8
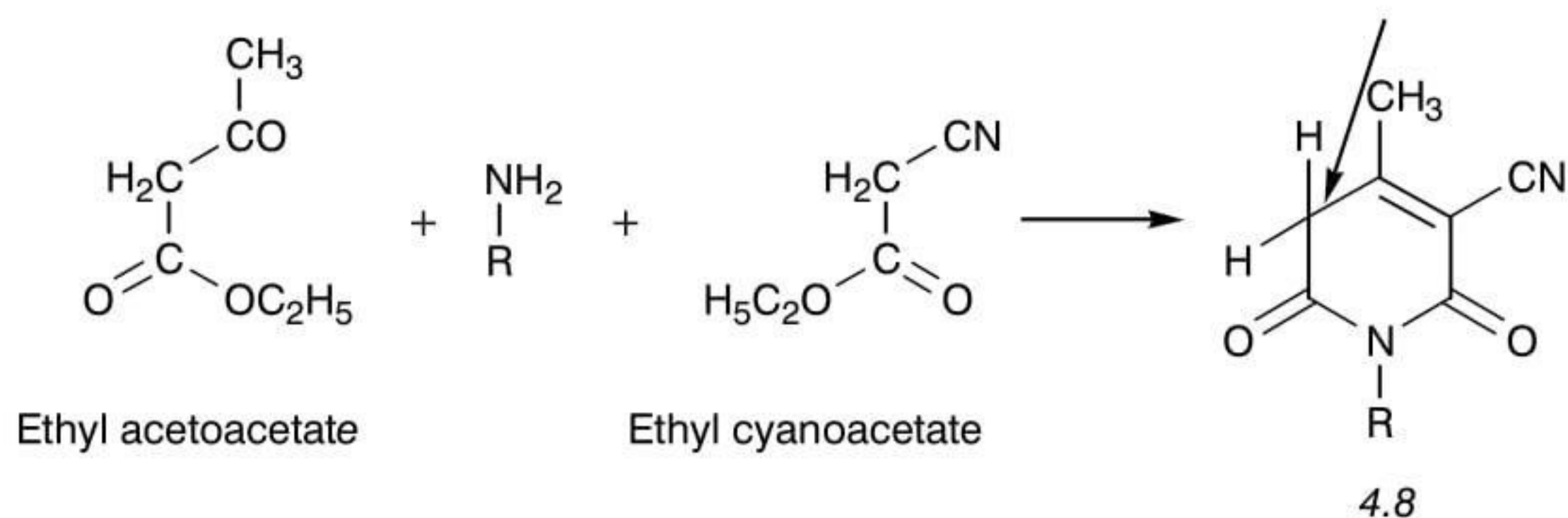
Scheme 4.13

4.4.3 Pyrazolones

The 1-arylpyrazol-5-ones (4.9), prepared by the two-step condensation of an arylhydrazine with ethyl acetoacetate, are the most commonly used coupling components for the synthesis of greenish yellow azo dyes. Coupling occurs at the 4-position of the pyrazolone ring which, as in the case of the acetoacetarylamides discussed above, is activated towards electrophilic attack by the two flanking unsaturated carbon atoms (Scheme 4.14).
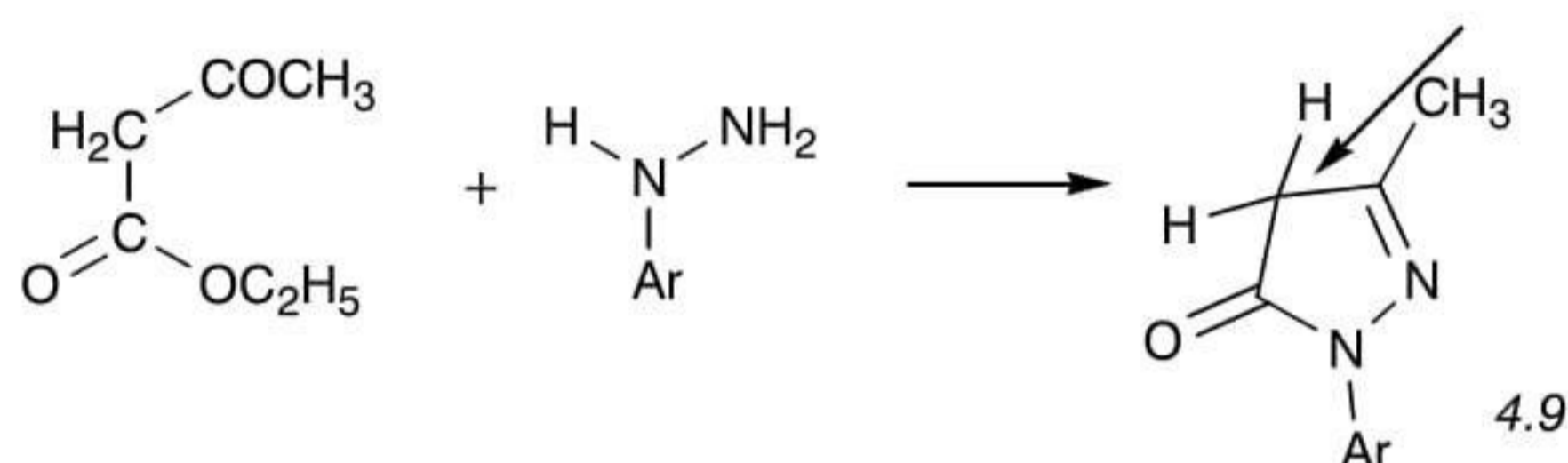
Scheme 4.14

4.4.4 Aminopyrazoles

Closely related to the pyrazolones, but less commonly used, are the 5-aminopyrazoles (4.10). Again, these compounds give greenish yellow dyes when coupled at the activated 4-position indicated by the arrow in Scheme 4.15. The aminopyrazoles are prepared by condensation of an arylhydrazine with 3-aminobut-2-enenitrile (diacetonitrile), which is itself produced by dimerisation of ethanenitrile (acetonitrile) over a nickel catalyst.
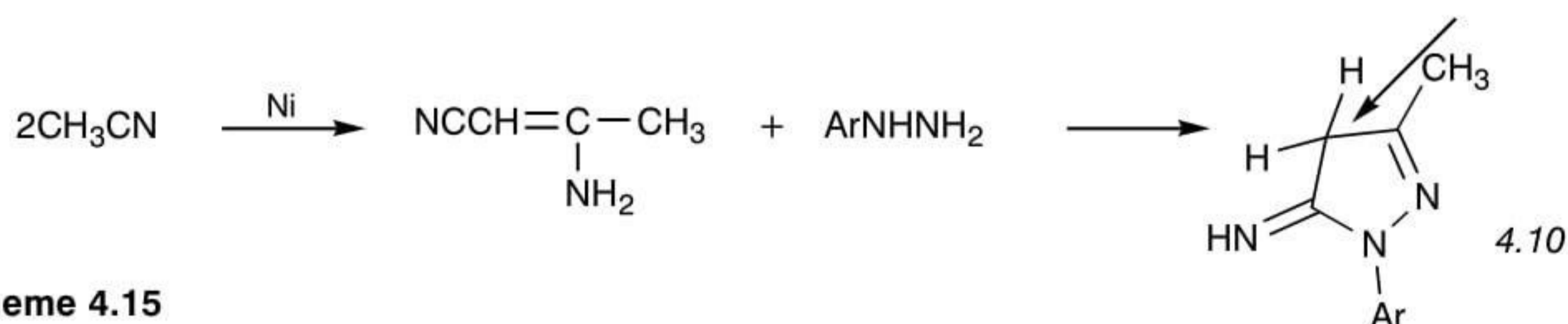
Scheme 4.15

4.4.5 Phenols

When phenol is treated with one equivalent of a diazonium salt at pH 7–8 coupling occurs mainly at the 4-position of the benzene ring, but small amounts of the 2-azo and 2,4-disazo compounds are also formed [24]. With an excess of diazonium salt under neutral conditions the 2,4-disazo derivative is formed [25] and under strongly alkaline conditions the 2,4,6-

trisazo derivative is produced. These factors can lead to impure products so that phenol itself is not often used as a coupling component. 4-Arylazophenols have the disadvantage of being pH-sensitive, ionisation of the hydroxy group under alkaline conditions resulting in a marked change of hue. With 2-arylazophenols, hydrogen bonding between the hydroxy group and the azo linkage (4.11) prevents such ionisation. Because of this effect the most commonly employed simple phenols are compounds such as 4-methylphenol (p-cresol) in which blocking of the 4-position ensures that coupling takes place at the 2-position. With simple diazonium salts p-substituted phenols yield yellow azo compounds.
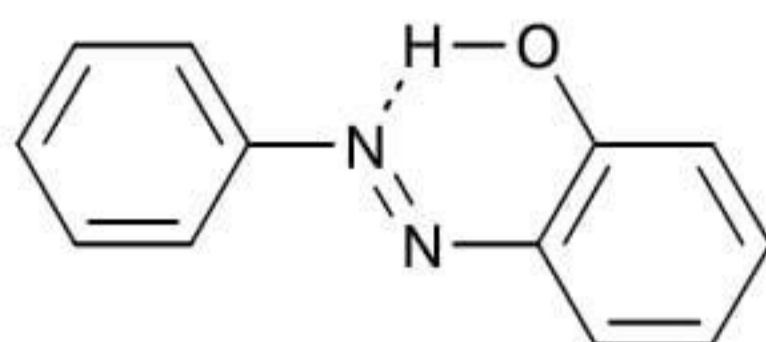
4.11

Benzene-1,3-diol (resorcinol), in which the two hydroxy groups reinforce one another, is of greater technical importance than phenol, not only because it couples much more strongly but also because the presence of two activating hydroxy groups allows more than one azo group to be introduced into the molecule. The preferred first coupling under neutral conditions takes place at the 4-position [24] and when a further equivalent of diazonium salt is added in the presence of sodium acetate or carbonate a second azo group is introduced into the 2-position. In the presence of sodium hydroxide the second group enters the 6-position. At a sufficiently high pH 2,4,6-trisazo compounds are produced [26–28]. The ability to introduce two different azo groups into resorcinol is exploited in the production of brown dyes mainly for use on leather.

The other two dihydric phenols, benzene-1,2-diol (catechol) and benzene-1,4-diol (hydroquinone) are of little interest in this context since they reduce diazonium salts on attempted coupling, being themselves oxidised to the corresponding quinones.

4.4.6 Aniline derivatives

Aniline itself couples inefficiently with normal diazonium salts [29], the reaction product of a diazotised amine and aniline often being the diazoamino compound. However, the presence of electron-donating substituents, such as methyl or methoxy groups, in the benzene nucleus makes coupling much easier and allows the introduction of an azo group into the 4-position of compounds such as 3-methylaniline (m-toluidine), 2,5-dimethylaniline (p-xylidine), 3-amino-4-methoxytoluene (cresidine) and 2,5-dimethoxyaniline. In the event of the 4-position being blocked, as in 2,5-dimethoxy-4-methylaniline, the azo group can be introduced into the unoccupied o-position [28]. Like the 4-arylazophenols, these 4-arylazoanilines display pH sensitivity, becoming protonated under acid conditions; they are therefore mainly of use as intermediates in the synthesis of disazo dyes.

N-Alkylation of primary aromatic amines increases their nucleophilic character, making them couple much more readily, the introduction of the azo group occurring in the 4-position. Thus, in contrast to aniline, N-methylaniline couples readily and N,N-dimethylaniline very readily with simple diazonium salts. Diphenylamine also couples in the 4-position, but less readily than N-methylaniline.

The increase in coupling power gained on *N*-alkylation can be exploited to bring about the coupling of primary arylamines by warming the base with an aqueous solution of one equivalent of sodium bisulphite and one equivalent of formaldehyde. The complex thus formed reacts with the arylamine, giving a clear solution of the methyl-ω-sulphonate derivative (4.12) which couples readily. The methyl-ω-sulphonate group is labile and can be conveniently removed by acid hydrolysis, affording a facile preparation of aminoazobenzenes not accessible by direct coupling (Scheme 4.16).

$$ArNH_2 \ + \ HOCH_2SO_3Na \longrightarrow ArNHCH_2SO_3Na \ + \ H_2O$$

Scheme 4.16   *4.12*

The *N,N*-dialkylanilines are of paramount importance in the synthesis of disperse dyes, the whole gamut of shades from yellow to greenish blue being obtainable from them by suitable choice of diazo component. If the 4-position in an *N,N*-dialkylaniline is blocked, as for example in *N,N*-dimethyl-4-methylaniline, steric hindrance prevents the diazonium ion approaching the *o*-position and coupling does not take place [30].

As with resorcinol, the 1,3-diamines of the benzene series are useful in the preparation of disazo dyes that can form the basis of brown shades. Generally the 2,4-disazo compound is the product of coupling with two equivalents of diazonium salt, but at higher pH values formation of the 4,6-isomer can be significant [31]. Again, the 1,2- and 1,4-diamines reduce diazonium salts on attempted coupling. 1,3,5-Triaminobenzene has been found to couple three times [32].

4.4.7 Aminophenols

3-Aminophenol is a useful dyestuff intermediate, capable of coupling in either the 2- or the 4-position. It is often used in preference to resorcinol or benzene-1,3-diamine (*m*-phenylenediamine) as a final coupling component in the preparation of complex dyes containing more than one azo group, typically trisazo direct dyes. Other aminophenols are of little interest in this context.

4.4.8 Naphthols

In this discussion of coupling components it is convenient to separate naphthalene compounds from their benzenoid analogues since important differences in behaviour exist between the two classes. Naphthalene, although formally containing two fused benzene rings, only possesses ten π-electrons, has much less than twice the resonance stabilisation energy of benzene and therefore has a lower level of aromaticity. The reason for this situation is related to the fact that in only one of the three limiting canonical forms (4.13a–c) are both rings 'benzenoid', the other two forms each containing one 'benzenoid' and one 'quinonoid' ring. A consequence is that the contribution of 4.13b to the overall structure of naphthalene is greater than that of the other two canonical forms; so that the bonds between adjacent α- and β-positions show a degree of double-bond character. This type of bond stabilisation has an effect on the coupling behaviour of naphthols and naphthylamines, as will be shown later.

4.13a   4.13b   4.13c
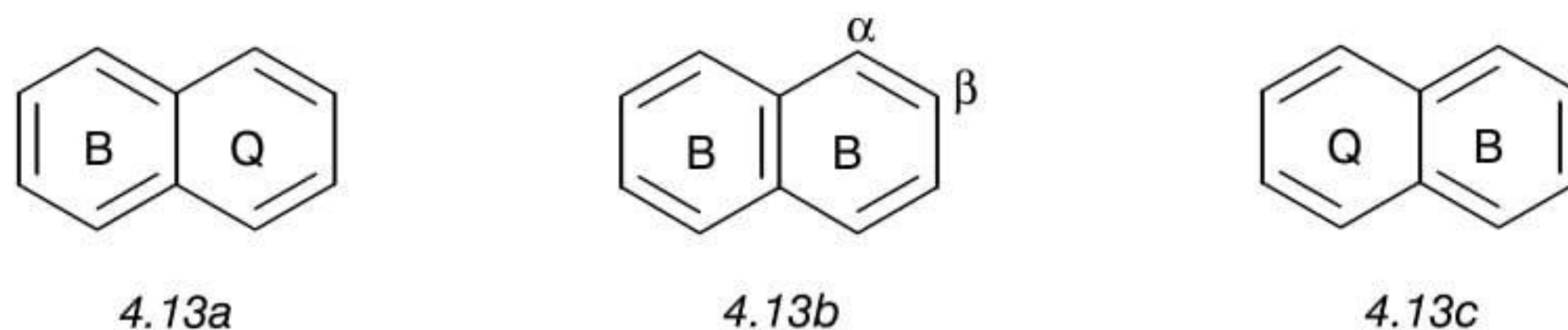
The two isomeric naphthols and some of their sulphonic acids are very widely used as coupling components in dye manufacture, generally giving orange hues when coupled with simple diazonium salts. 1-Naphthol (4.14) couples in both the 2- and 4-positions and, as with phenol, it is difficult to make the coupling selective. Highly reactive diazonium salts couple chiefly in the 4-position whilst weakly reactive ones, especially those derived from aminophenols and aminonaphthols, couple mainly in the 2-position. The position of coupling in 1-naphthols is, of course, also influenced by substituents; for example, a sulphonic acid group in the 3-, 4-, or 5-position inhibits 4-coupling and directs the diazonium ion to attack at the 2-position.

4.14
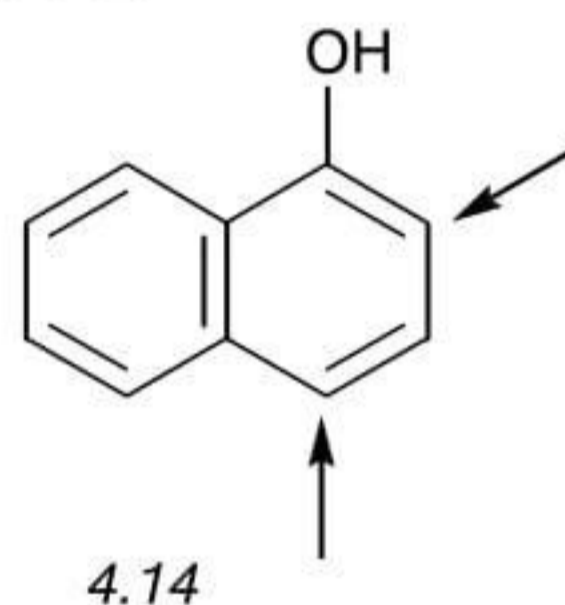
With 2-naphthol (4.15) the special characteristics of the structure of naphthalene mentioned above come into play and coupling is directed exclusively into the 1-position. When this position is blocked, as with 1-methyl-2-naphthol, no coupling occurs. The reason for this behaviour lies in the nature of the relevant resonance canonicals (4.15a–c) of the naphtholate ion (Scheme 4.17). In structure 4.15a the unsubstituted ring retains its benzenoid character and is therefore vastly preferred over structure 4.15c, in which the unsubstituted ring is forced to assume a quinonoid configuration. This difference localises the lone pair of electrons and the negative charge on the 1-position and leads to selective attack of the diazonium ion at this site.

4.15

4.15a   4.15b   4.15c
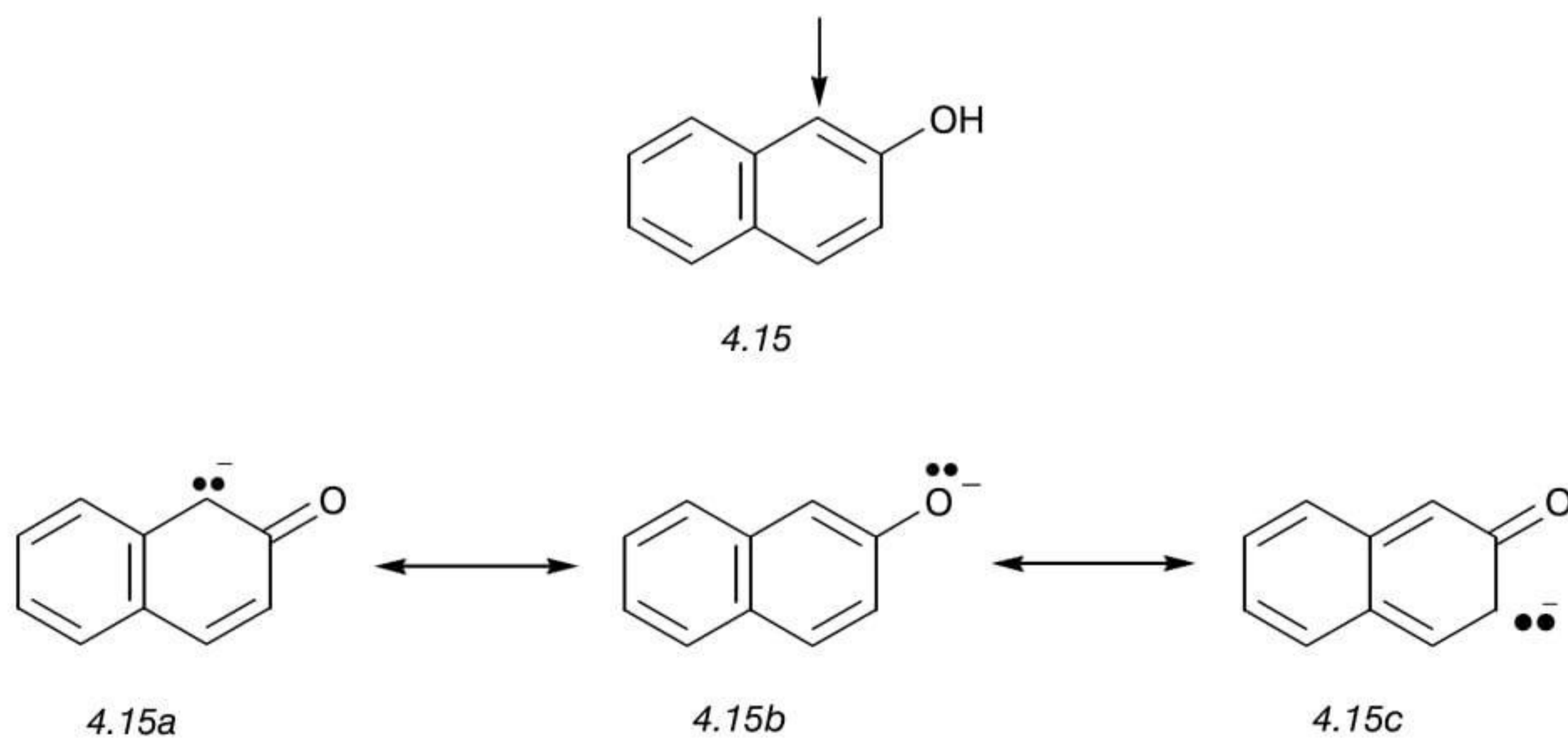
Scheme 4.17

4.4.9 Naphthylamines

The aminonaphthalenes couple much more easily than do the amines of the benzene series. This increased reactivity allows azo compounds to be prepared without the need to reinforce the effect of the amino group with additional electron-donating substituents. The resulting dyes have hues similar to those obtained from naphthol coupling components and the parent amines display directive influences similar to those shown by the naphthols in the coupling reaction. Thus with one equivalent of a diazonium salt 1-naphthylamine couples largely in the 4-position [33]. With two equivalents of diazonium salt the 2,4-disazo compound can be obtained [34,35]. 2-Naphthylamine, like 2-naphthol, couples exclusively in the 1-position [31] and derivatives with this position blocked by non-labile substituents fail to couple. When treated with powerful diazonium salts, 2-naphthylamines with labile substituents in the 1-position, such as 2-naphthylamine-1-sulphonic acid, couple by introducing the azo group into the 1-position with concomitant expulsion of the labile substituent.

In the distant past, 2-naphthylamine was an important intermediate for the synthesis of dyestuffs, but its recognition as a potent carcinogen resulted in its total withdrawal by reputable dye manufacturers. Stringent precautions also need to be taken when using 1-naphthylamine to ensure that the material is not contaminated with the 2-isomer. The naphthylaminesulphonic acids, however, remain amongst the most important dyestuff intermediates, finding wide-ranging applications as both diazo and coupling components. 4-Substituted 3-aminoacetanilides have been examined as replacements for 1-naphthylamine in monoazo dyes [36]. 3-Amino-4-methoxyacetanilide can be used as an effective substitute for 1-naphthylamine in the synthesis of disazo dyes [37].

4.4.10 Aminonaphthols

There are 14 isomers carrying both an amino group and a hydroxy group attached to a naphthalene nucleus, but only those in which the two groups are located in different rings are of use as coupling components. In these cases, each group exerts the major directive influence within its own ring, so that at pH 7 or below coupling occurs in the amino-substituted ring, whereas at alkaline pH coupling in the hydroxylated ring becomes important. Often there is still a choice of possible coupling sites, leading to mixtures of products. Very few of the aminonaphthol isomers have found use in dye manufacture, their value being determined by ease of manufacture, toxicological considerations and the properties of the derived dyes.

Of far greater importance are the sulphonated aminonaphthols, in which the versatility conferred by the presence of both an amino and a hydroxy group makes them among the most important group of azo intermediates. Three are outstanding, namely, 6-amino-1-naphthol-3-sulphonic acid (4.16; J acid), 7-amino-1-naphthol-3-sulphonic acid (4.17; γ acid) and H acid (4.2), which couple under the relevant conditions of pH at the arrowed positions.
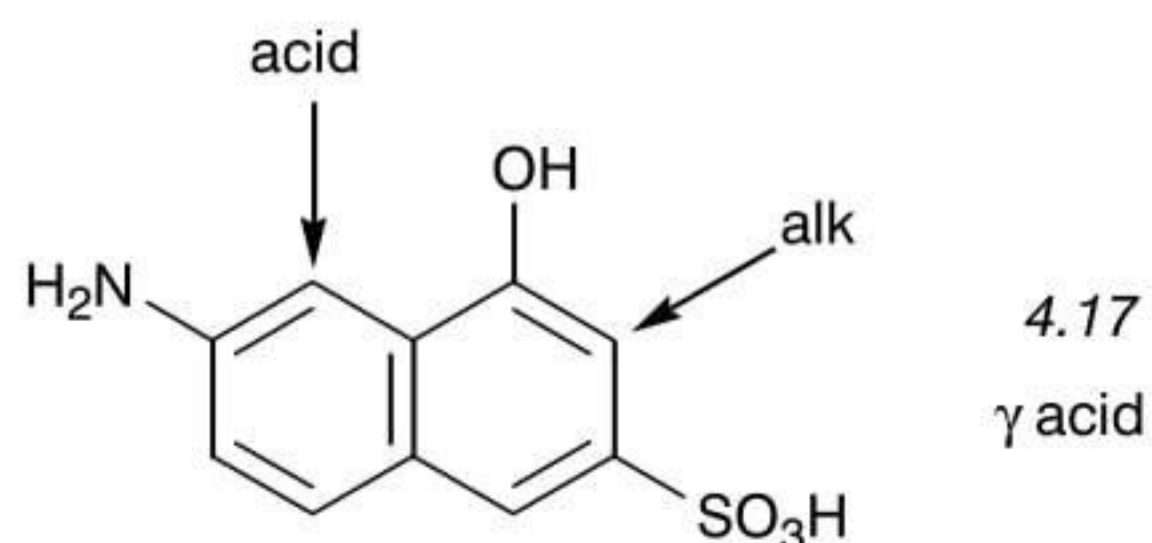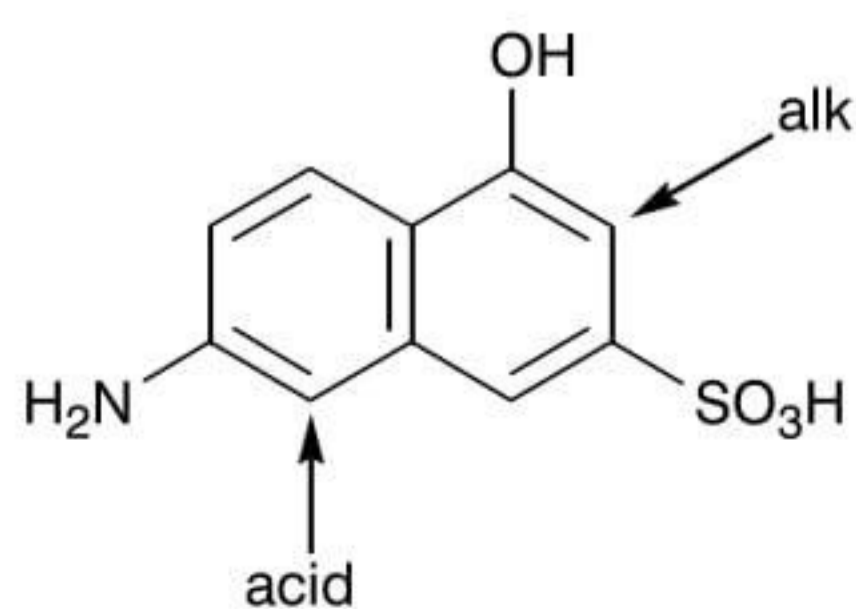
Particularly important dyes are produced when the *N*-acylated derivatives are coupled, bright orange hues resulting from the use of *N*-acyl J acid and bright reds from *N*-acyl γ acid and *N*-acyl H acid derivatives. Coupling of γ acid under acid conditions leads to red monoazo dyes that cannot be further coupled and have exceptional fastness to light. These characteristics result from hydrogen bonding between both the amino and the hydroxy groups and the azo linkage (4.18), thus preventing ionisation of the hydroxy group which is essential for coupling to occur and also protecting the azo linkage by involving both lone pairs of electrons in coordination.

4.18
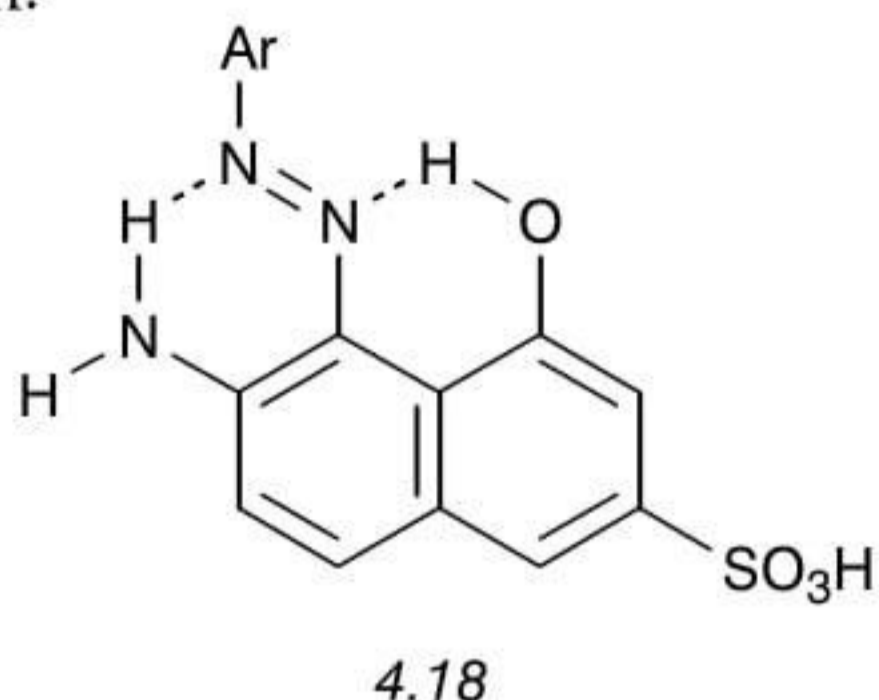
Other important dye classes are formed by coupling aminonaphtholsulphonic acids with two equivalents of diazonium salt, giving a disazo dyestuff. In the case of H acid it is essential that the acid coupling stage is carried out first, the products being navy blue in colour. With J acid, which again gives dark blue disazo dyes, the initial coupling should preferably be carried out under alkaline conditions.

4.5 STRUCTURE OF AZO DYES

4.5.1 Stereoisomerism

The simplest azo compound, azobenzene, exists as a mixture (Scheme 4.18) of a stable *trans* (4.19) and an unstable *cis* (4.20) form [38,39]. Formation of the *cis* isomer is induced by exposure to light, the quantum yield of the process depending upon the wavelength of the light employed [40]. The proportion of *cis* isomer can be appreciable in an equilibrium mixture. Thus a concentration of 24% of this unstable form builds up within a few hours when an acetic acid solution of azobenzene is exposed to sunlight in shallow white trays. Reversion to the *trans* form occurs readily on heating and is catalysed by a variety of substances that can function as electron donors or acceptors [41].

The two isomers display different properties and can be separated by exploiting differences in their distribution between immiscible solvents or by chromatography on alumina. The molecule of the *trans* form is very nearly planar, whereas in the *cis* isomer the


4.19

trans

4.20

cis
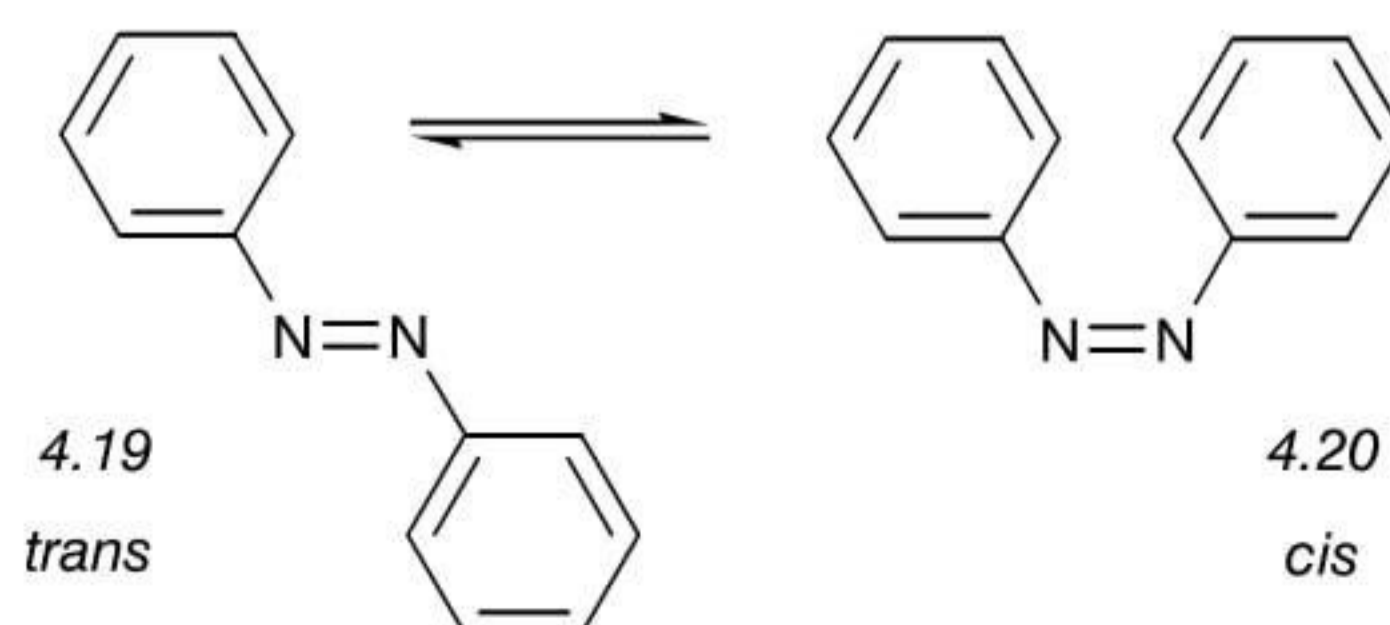
Scheme 4.18

benzene rings are inclined at an angle of about 56 degrees to one another [42,43]. The *trans* isomer forms monoclinic crystals, has no dipole moment and melts at 68 °C whereas the *cis* isomer forms orthorhombic bipyramidal crystals, has a dipole moment of 3.0 debye and melts at 71.4 °C. The two isomers also differ in hue. Some substituted azobenzenes display similar stereoisomerism but these are mainly simple structures, increasing molecular complexity causing steric factors to control the configuration exclusively in the *trans* form. Some simple azobenzene derivatives serve as disperse dyes, but in these the difference in hue between the *cis* and *trans* forms gives rise to the phenomenon of photochromism, manifested as a change in hue on exposure to light; this property is an undesirable feature of such dyes. The thermal *cis–trans* isomerisation of 4-diethylamino-3′-nitroazobenzene has been studied in various solvents. The conversion appears to involve an inversion mechanism passing through an sp-hybridised linear transition state [44].

4.5.2 Tautomerism

Whilst azo compounds prepared from diazonium salts and phenolic or keto–enol coupling components are often depicted in the hydroxyazo form (4.11), an alternative tautomeric structure can be drawn for such compounds (Scheme 4.19). This ketohydrazone tautomer (4.21) can, in cases where the azo and hydroxy groups are located on adjacent carbon atoms, exhibit hydrogen bonding between the two groups as shown. Similar pairs of structures, but without hydrogen bonding, can be drawn for *p*-hydroxyazo compounds.

4.11   4.21
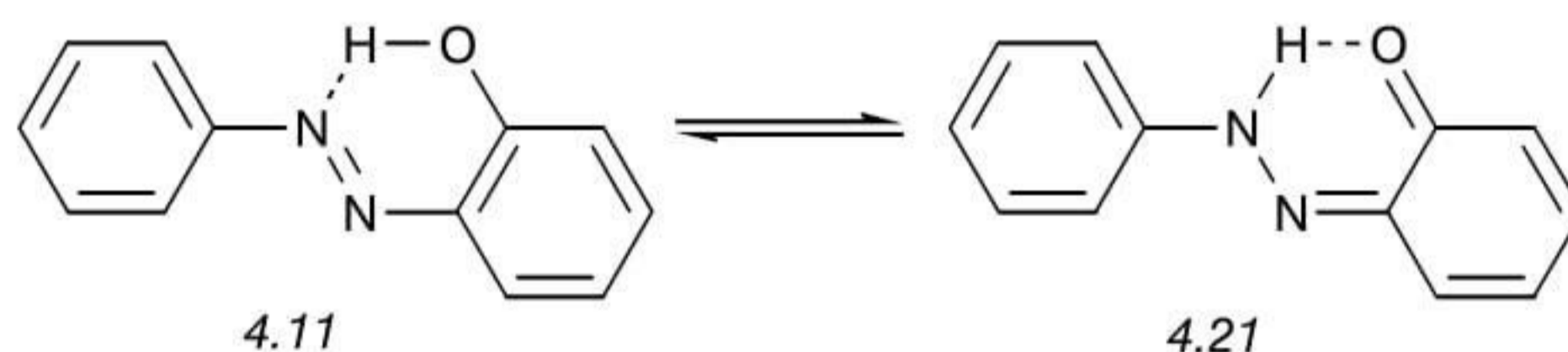
Scheme 4.19

The actual structure of any particular azo compound will depend on the relative energy levels of the two tautomers which can be drawn for that compound. Where one form has a much lower energy level than the other, then the lower-energy form will predominate; a tautomeric mixture will result when the energy levels of the two forms are similar. In the case of azo compounds derived from keto–enol coupling components (acetoacetarylamides, pyridones, pyrazolones and aminopyrazoles) the ketohydrazone form has a much lower energy level than the hydroxyazo alternative and represents the true structure of these compounds. Physical measurements support this conclusion. For example, spectroscopic evidence shows that azo compounds derived from acetoacetarylamides have structure 4.22 [45]. This finding is confirmed by n.m.r. evidence, which indicates that pyrazolone-based azo compounds have the structure 4.23 [46,47]. Substituted phenylazopyridones favour the ketohydrazone form in solution [48]. The most appropriate representation of tautomeric colorants has been discussed [49].

The converse of this situation is presented by diazotised arylamines coupled to phenols, where assumption of a ketohydrazone structure (4.21) would necessitate loss of the aromatic character of the phenolic ring. Consequently, these compounds exist solely in the hydroxyazo form.
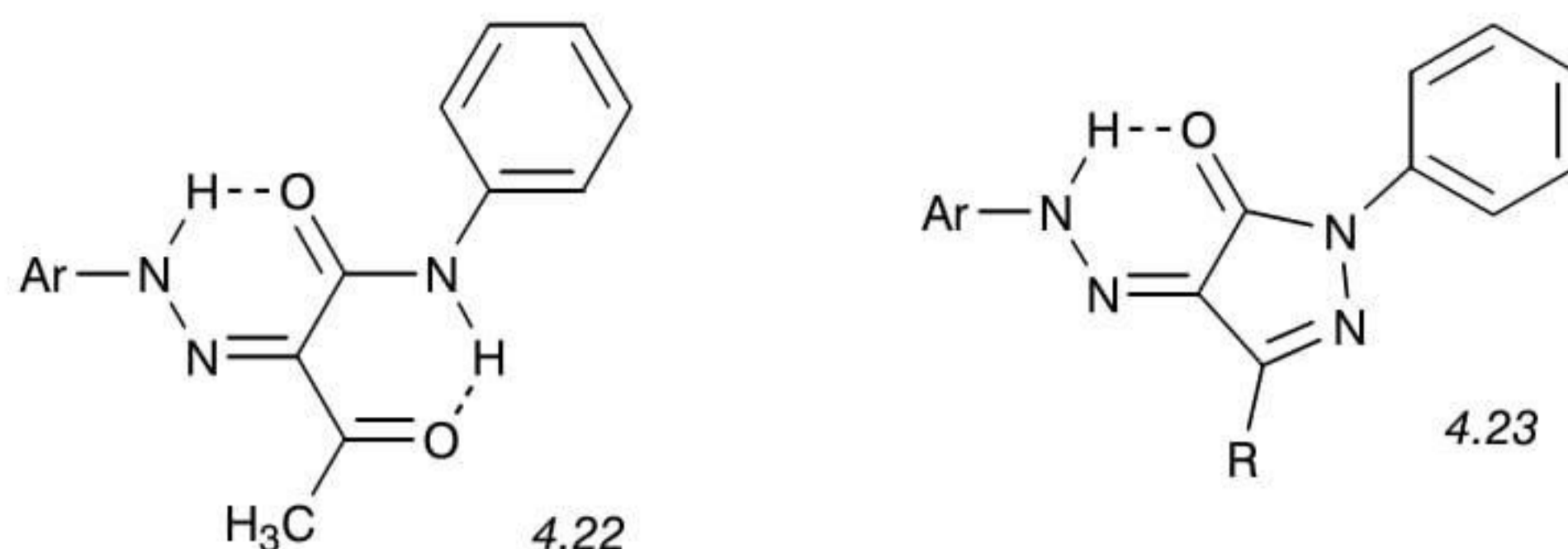
The phenylazonaphthols present a particularly interesting series. Despite the partial loss of aromaticity in the hydrazone structures that can be drawn for 1-phenylazo-2-naphthol, 2-phenylazo-1-naphthol and 4-phenylazo-1-naphthol, these structures are not much higher in energy than the azo forms [50], so that there should be no significant preference for one form over the other. When the visible absorption curves of 4-phenylazo-1-naphthol are measured in a variety of solvents, they all pass through a common point (isosbestic point) as in Figure 4.1 [51,52]. 1-Phenylazo-2-naphthol shows similar behaviour. This finding is clear evidence that in solutions of these compounds both tautomers are present.

The solvent effect on the azo–hydrazone equilibrium of 4-phenylazo-1-naphthol has been modelled using *ab initio* quantum-chemical calculations. The hydrazone form is more stable in water and in methylene chloride, whereas methanol and iso-octane stabilise the azo form, The calculated results were in good agreement with the experimental data in these solvents. Similar studies of 1-phenylazo-2-naphthol and 2-phenylazo-1-naphthol provided confirmation. Substituent effects in the phenyl ring were rationalised in terms of the HOMO–LUMO orbital diagrams of both tautomeric forms [53].

Tautomerism both in the solid state and in solution is confirmed by infrared spectroscopic measurements on all three compounds [54,55]. The highest content of ketohydrazone form within the three isomeric phenylazonaphthols occurs, in solution, with 2-phenylazo-1-naphthol [56]. A ^{15}N-n.m.r. study of some azo dyes derived from H acid and related intermediates has confirmed the dominance of the ketohydrazone tautomer [57]. Similar findings have been obtained using high-field [1]H- and ^{13}C-n.m.r. spectroscopy [58].
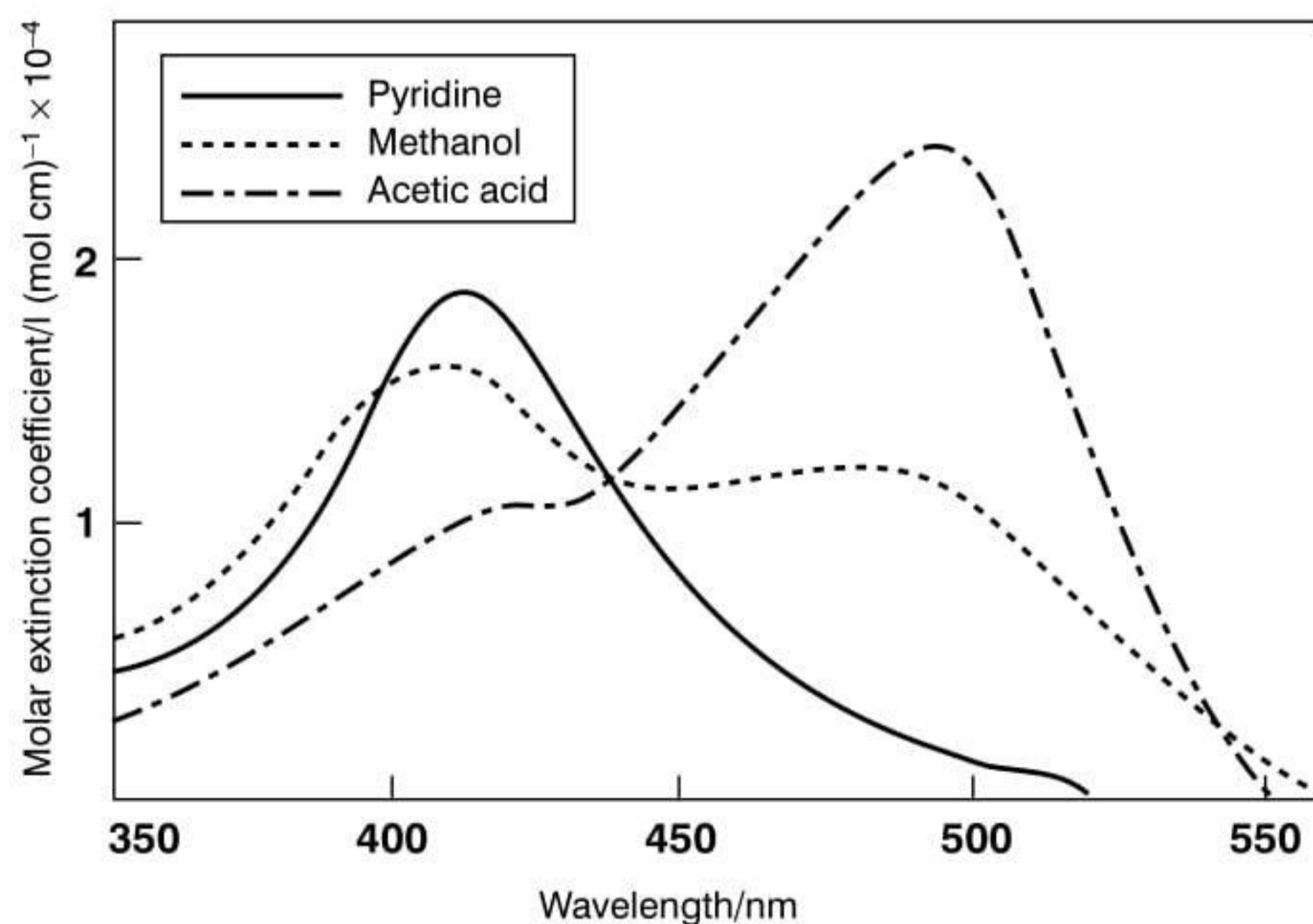
Figure 4.1 Effect of solvent on 4-phenylazo-1-naphthol spectrum

A totally different picture is presented by 3-phenylazo-2-naphthol. This unusual isomer cannot be prepared by a normal coupling procedure but has been obtained by reaction of 3-amino-2-naphthol with thionyl chloride to give the *N*-sulphinylamine (4.24), condensation of which with *N*-phenylhydroxylamine yields the desired product [59]. Here, assumption of a ketohydrazone form would entail loss of aromatic character in both rings of the naphthalene nucleus and the energetic unfavourability of this situation ensures that the compound exists solely in the hydroxyazo form.

In the case of phenylazonaphthylamines, the aminoazo tautomer is very much favoured relative to the iminohydrazone form [57,60].
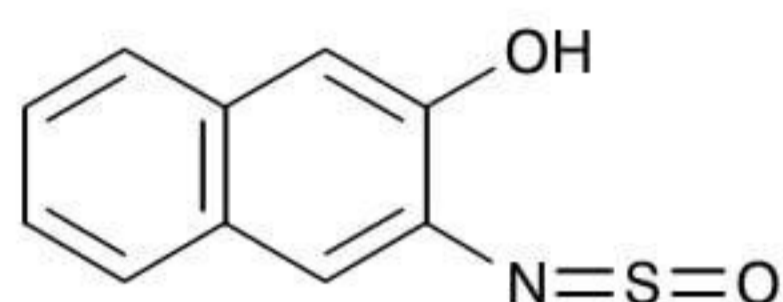
4.24

4.6 PREPARATION AND IMPORTANCE OF NAPHTHALENE INTERMEDIATES

4.6.1 Importance of naphthalene

When purely benzenoid intermediates are employed in the preparation of azo dyes, the products exist solely in the hydroxyazo form since the energy level of this tautomer is significantly lower than that of the ketohydrazone form. The position changes when a naphthalene intermediate is used, for here the two tautomers are of comparable energy and so coexist. The ketohydrazone form generally possesses a higher extinction coefficient than does the hydroxyazo alternative. The practical consequence is that the former has a greater tinctorial strength – in crude terms, more colour value per unit mass. The participation of the ketohydrazone form in naphthalene-based dyes allows them to gain this strength advantage which, together with the ready availability of naphthalene and its convenient processing to yield ideally substituted derivatives, has made this hydrocarbon of great importance as a primary starting material in the manufacture of intermediates for the dyestuffs industry.

Naphthalene intermediates [61] are always built up by substitution reactions starting from the cheap and plentiful hydrocarbon using, in the main, only seven basic reactions. Most of these reactions are generally familiar from benzene chemistry but with some modification, since naphthalene has two different possible positions of substitution. These positions are often designated α and β, the four α-positions being *ortho* and the four β-positions *meta* to the nearest carbon atom of the central bond. A further modifying influence is the lower level of aromaticity of naphthalene compared with benzene, leading to increased reactivity.

The main reactions used in the manufacture of dyestuff intermediates from naphthalene are described in sections 4.6.2 to 4.6.8.

4.6.2 Sulphonation

Treatment of naphthalene with concentrated sulphuric acid [62] results in substitution at one of the α-positions (4.25) if the temperature is below about 60 °C, but the reaction is

reversible (Scheme 4.20) and at higher temperatures rearrangement occurs, involving desulphonation and resulphonation, yielding the thermodynamically stable β-isomer (4.26).

Under more forcing conditions, such as the use of higher operating temperatures or of oleum (sulphur trioxide dissolved in anhydrous sulphuric acid), more than one sulphonic acid group can be introduced. This approach can lead to mixtures of isomers and, in practice, the reaction conditions must be carefully controlled if the desired isomer is to be produced in maximum yield.
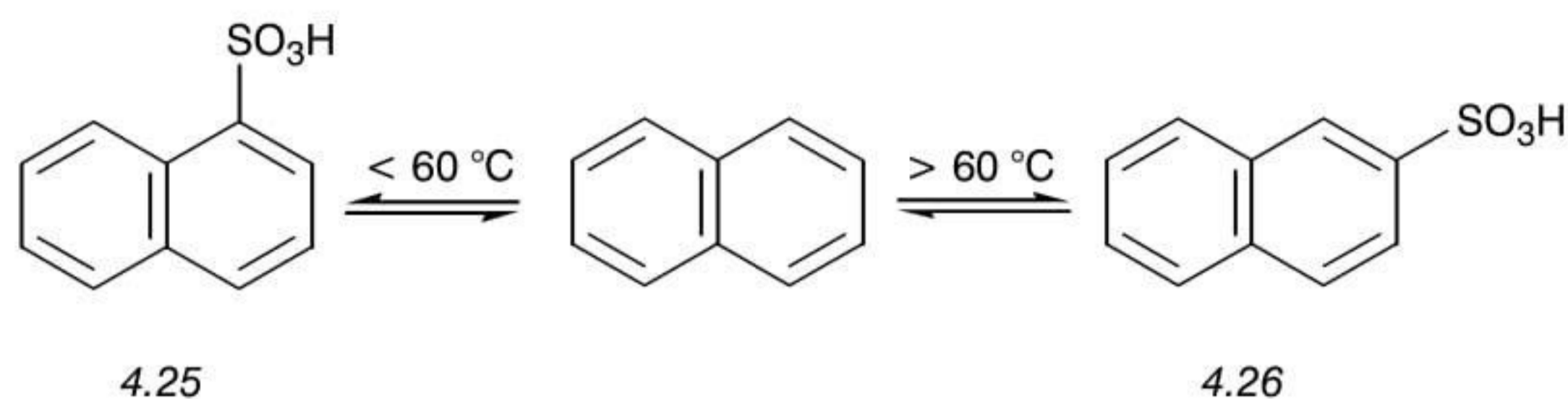
Scheme 4.20

4.6.3 Nitration

Nitration [63], unlike sulphonation, is not reversible and results very largely in α-substitution, yielding 1-nitronaphthalene (4.27).

4.27
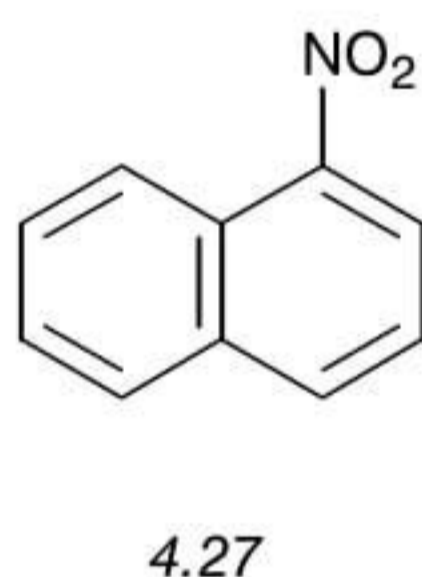
4.6.4 Reduction

Reduction of a nitro compound to the corresponding naphthylamine proceeds exactly as in the benzene series. A batch process using iron and hydrochloric acid is traditional but has been somewhat superseded by catalytic hydrogenation.

4.6.5 Replacement of a sulphonic acid group by a hydroxy group

This displacement is accomplished by heating the sulphonated derivative at a high temperature with sodium or potassium hydroxide [64]. Typical is the preparation of 2-naphthol (4.15) from naphthalene-2-sulphonic acid (Scheme 4.21). Displacement of the sulphonic acid group occurs more readily when it is located at the α- rather then at the β-position, the former requiring a fusion temperature of about 200 °C and the latter one of about 250 °C. This difference in reactivity can be exploited to prepare naphtholsulphonic acids by fusion of suitable naphthalenedisulphonic acids.

Scheme 4.21   4.26   4.15
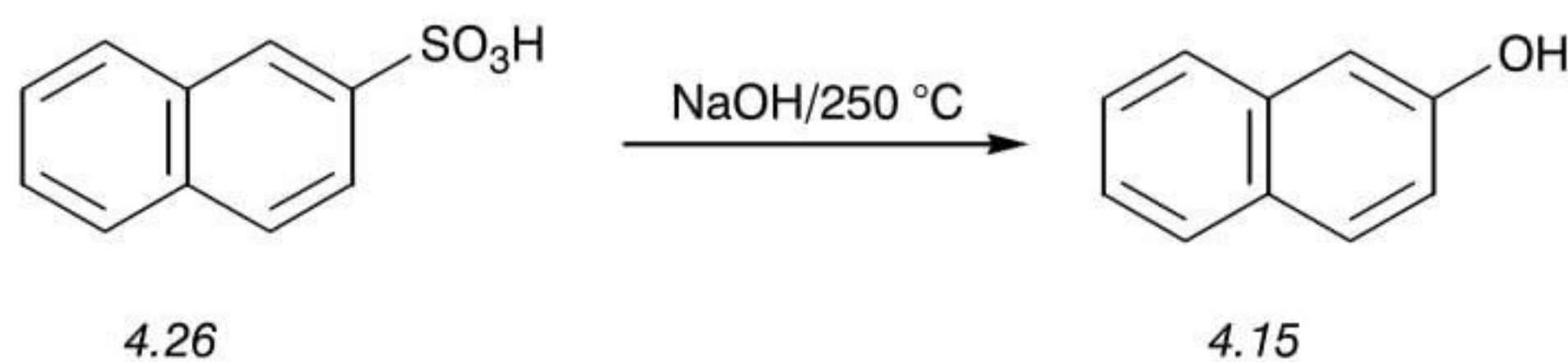
4.6.6 Bucherer reaction

This reaction [65–67] is only rarely encountered in the benzene series but is extremely useful for appropriate derivatives of naphthalene, where the mechanism of the reaction has been investigated extensively. The reaction allows a hydroxy group to be exchanged for an amino group or vice versa. When a hydroxy group is to be converted into an amino group, the naphthol is heated under pressure with ammonium bisulphite (often produced *in situ* by introduction of ammonia liquor and sulphur dioxide into a sealed autoclave) at a temperature of 100–150 °C; the naphthol is thereby converted into the corresponding naphthylamine. The mechanism of the reaction is outlined in Scheme 4.22.
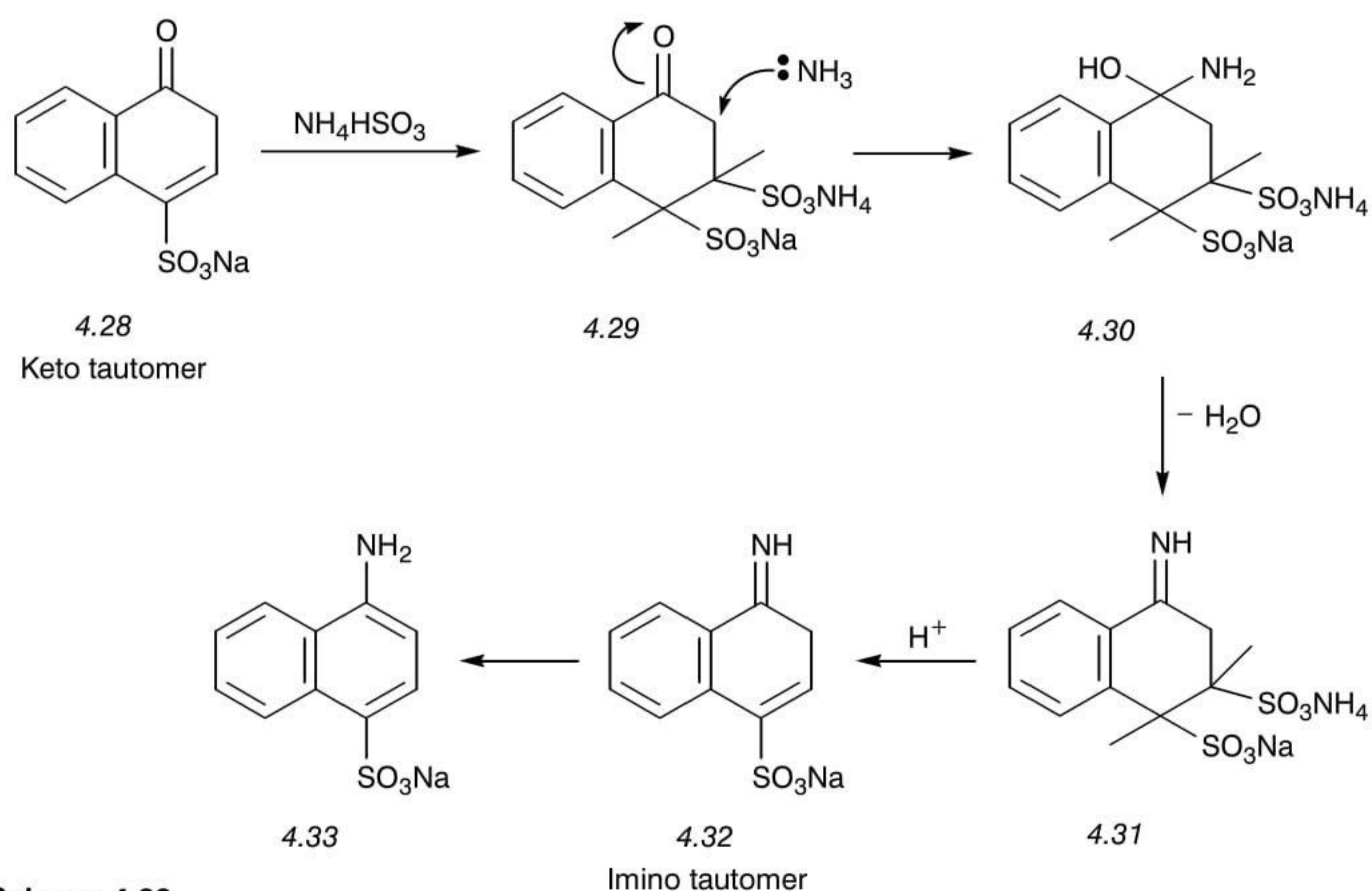
Scheme 4.22

In the initial step the naphthol reacts in its keto tautomeric form (4.28), adding ammonium bisulphite across the isolated double bond in the sulphonated ring. Nucleophilic attack by ammonia on the tetralonesulphonic acid (4.29) is followed by a proton shift from nitrogen to oxygen, producing an intermediate (4.30) which then loses water to give the imine (4.31). After cooling and discharging the autoclave, the reaction mixture is acidified and boiled. The added bisulphite is thereby eliminated from the molecule and rearrangement of the imine tautomer (4.32) so produced completes the conversion into the naphthylamine (4.33).

The reverse of this reaction, which allows a naphthylamine to be converted into the corresponding naphthol, is similarly carried out by heating the amine with sodium bisulphite and finally acidifying the mixture; the mechanism is outlined in Scheme 4.23.

The Bucherer reaction can also be used in the preparation of substituted naphthylamines. Carrying out the reaction on a naphthol but employing an alkylamine in place of ammonia results in the production of the corresponding *N*-alkylnaphthylamine. Alternatively, a

naphthylamine can be used as starting material, whereupon the excess of alkylamine employed results in the amino group being displaced by the alkylamino group. Of greater importance is the preparation of N-aryl naphthylamines by heating a naphthol (or a naphthylamine) with sodium bisulphite and an arylamine, whereupon the hydroxy (or amino) group in the starting material is exchanged for the arylamino group.

In the above reaction mechanisms it is noteworthy that the sulphonic acid group introduced has been shown to enter at the 3-position and not the 4-position as previously postulated. A consequence of this situation is that an attempted Bucherer reaction on a naphthol (or a naphthylamine) carrying a sulphonic acid group located *meta* to the hydroxy (or amino) group would require a second sulphonic acid group to be introduced at this position. Since it is impossible to locate two sulphonic acid groups on the same carbon atom, these compounds cannot undergo the transformation.
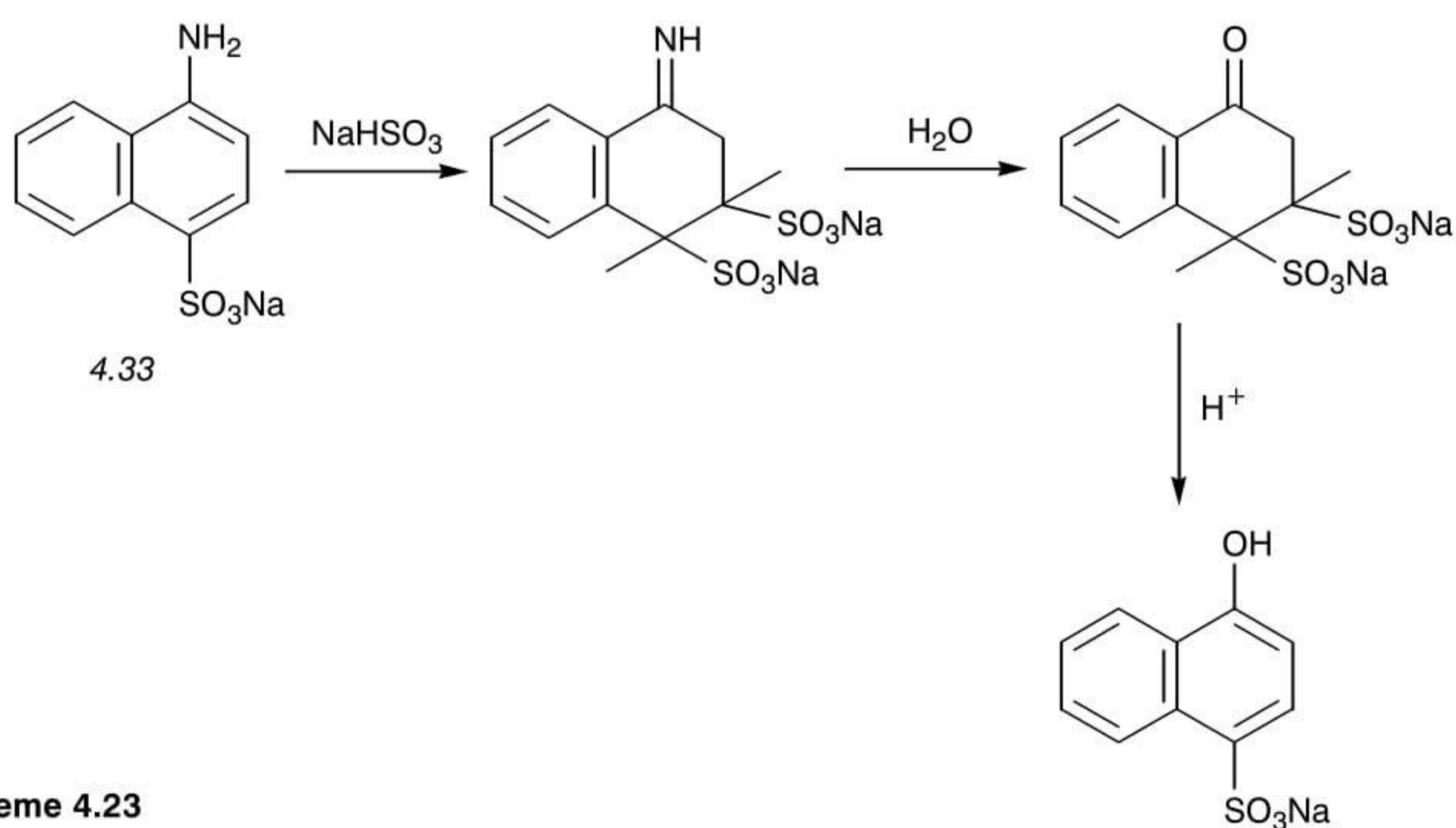
Scheme 4.23

4.6.7 Arylation

In some cases where it is difficult to carry out the Bucherer reaction successfully, it is easier to prepare N-arylnaphthylamines by heating together a naphthylamine and an arylamine. In particular, this reaction is useful in the preparation (Scheme 4.24) of 1-phenylaminonaphthalene-8-sulphonic acid (4.34; N-Phenyl Peri acid) and its N-4-methylphenyl analogue (Tolyl Peri acid), both of which intermediates are valuable components for the production of navy blue dyes.
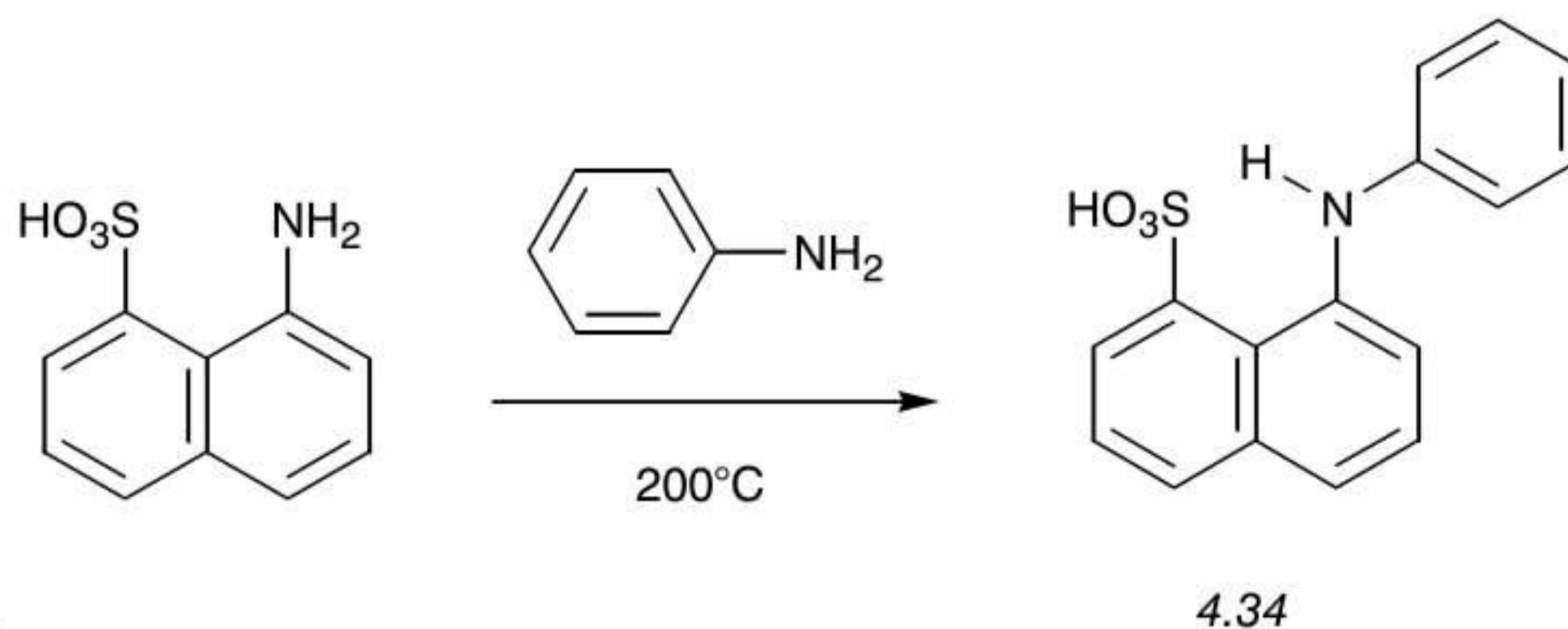
Scheme 4.24

4.6.8 Kolbe-Schmitt reaction

This carboxylation reaction is of importance mainly for the manufacture from 2-naphthol of β-oxynaphthoic acid (BON) acid, the parent acid of sodium 3-hydroxy-2-naphthoate (4.35). The carboxylation is achieved by heating the sodium salt of 2-naphthol under pressure in an atmosphere of carbon dioxide (Scheme 4.25). Under these conditions an equilibrium mixture of the naphthol and its carboxylated derivative is established, the mixture containing about 30% of the carboxylic acid. The desired product is extracted from the reaction mixture and the unchanged 2-naphthol is recycled.
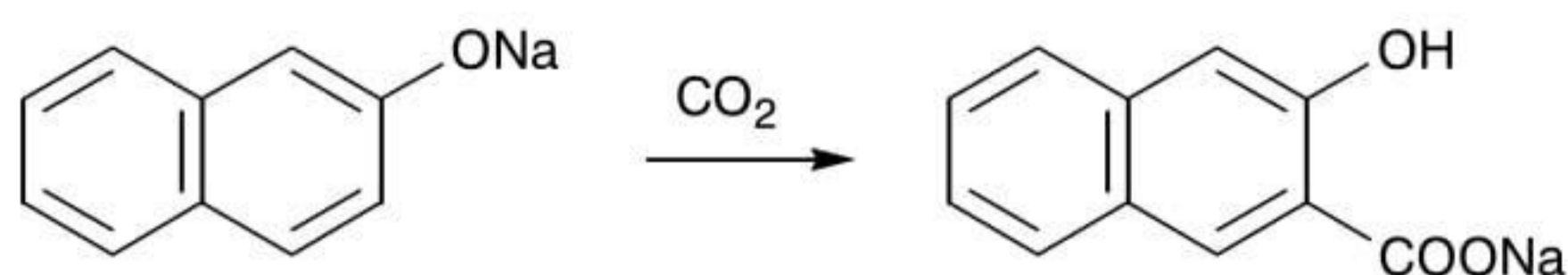
Scheme 4.25

4.35

4.6.9 Preparation of specific intermediates

The above reactions can be used to prepare a variety of multi-purpose intermediates that are of great value in dyestuffs manufacture. Many of these intermediates were prepared and found to be of value in dye manufacture before the orientation of their substituents was established. This early lack of basic knowledge resulted in these intermediates being given trivial names that have persisted in the dyestuffs industry.

In the preparation of naphthalene intermediates the reactions must be employed in the correct sequence to achieve a desired orientation in the final product. A further crucial consideration can be the need to avoid steps that would result in the formation of carcinogenic materials. These points are illustrated in the following examples.

Naphtholsulphonic acids and γ acid

The preparation of 2-naphthol by high-temperature sulphonation of naphthalene followed by alkali fusion of the resulting naphthalene-2-sulphonic acid has been mentioned previously. Further sulphonation of 2-naphthol yields several useful naphtholsulphonic acids and conditions can be chosen to make one or other of these compounds the main product. The initial product is the unstable 2-naphthol-1-sulphonic acid, which readily rearranges to 2-naphthol-6-sulphonic acid (4.36; Schaeffer's acid). Further sulphonation leads to 2-naphthol-6,8-disulphonic acid (4.37; G acid) at low temperature and 2-naphthol-3,6-disulphonic acid (4.38; R acid) at higher temperature.

| *4.36* | *4.37* | *4.38* |
| Schaeffer's acid | G acid | R acid |
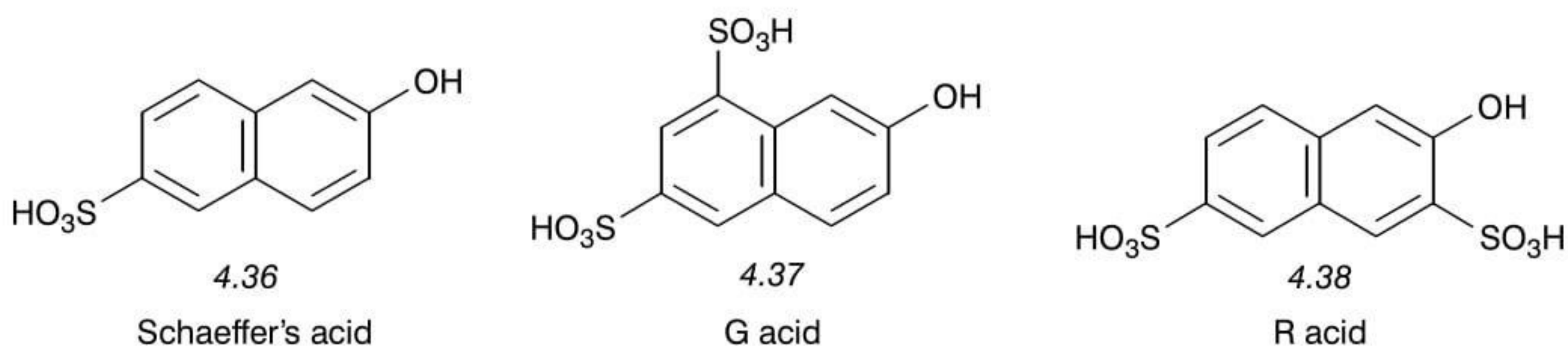
Fusion of 2-naphthol-6,8-disulphonic acid with sodium hydroxide yields naphthalene-1,7-diol-3-sulphonic acid (4.39), the more readily displaced α-sulphonic acid group being replaced. When this compound is subjected to a Bucherer reaction only the 7-hydroxy group is exchanged for an amino group, yielding γ acid (4.40), as in Scheme 4.26. This selectivity arises because the 1-hydroxy group is unable to form the intermediate addition product necessary for the Bucherer reaction to proceed, the sulphonic acid group being located in the *meta* position.
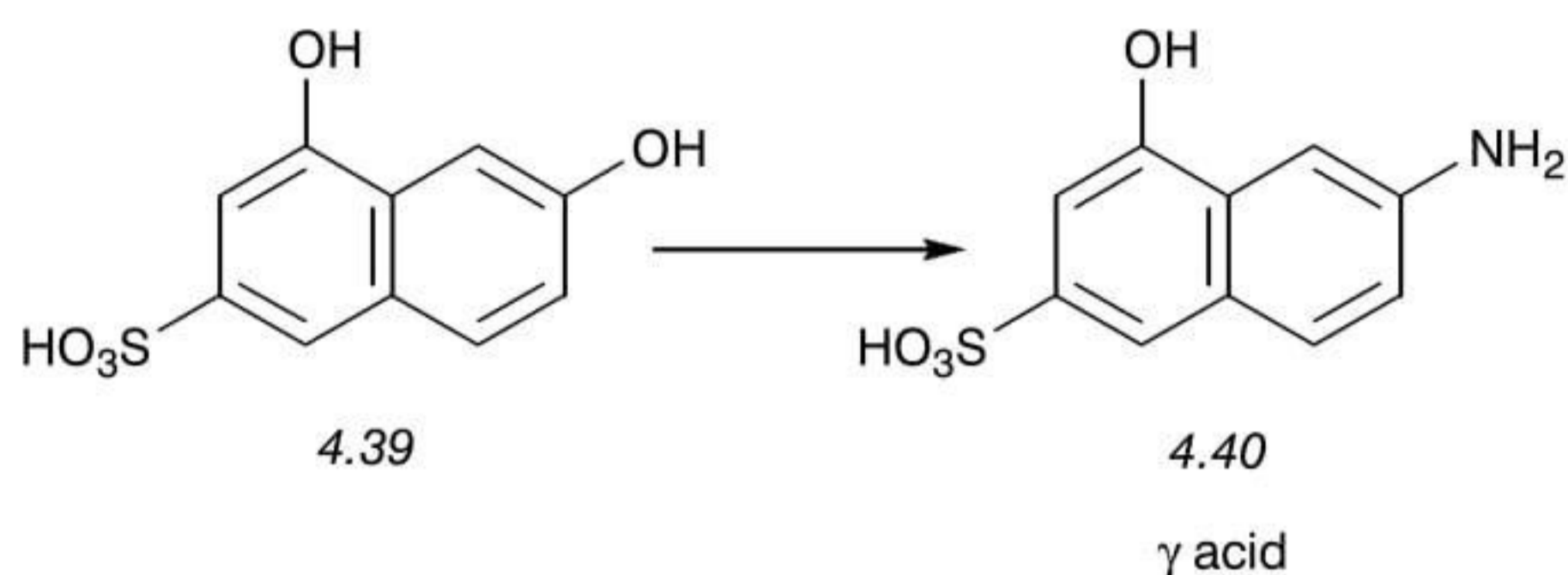
Scheme 4.26

H acid

H acid (4.2) is possibly the most important single naphthalene-based intermediate. The preparation of this intermediate starts with a high-temperature sulphonation of naphthalene using 65% oleum (anhydrous sulphuric acid in which 65% by mass of sulphur trioxide has been dissolved) to give mainly naphthalene-1,3,6-trisulphonic acid, the nitration product from which is purified by selective isolation. Reduction of the nitro group followed by hydrolysis of the 1-sulphonic acid substituent by heating with sodium hydroxide solution at 180 °C completes the process (Scheme 4.27).

Use of a higher temperature (280 °C) at the final stage results in more extensive hydrolysis, with the amino group also being replaced by a hydroxy group, leading to the formation of naphthalene-1,8-diol-3,6-disulphonic acid (chromotropic acid).
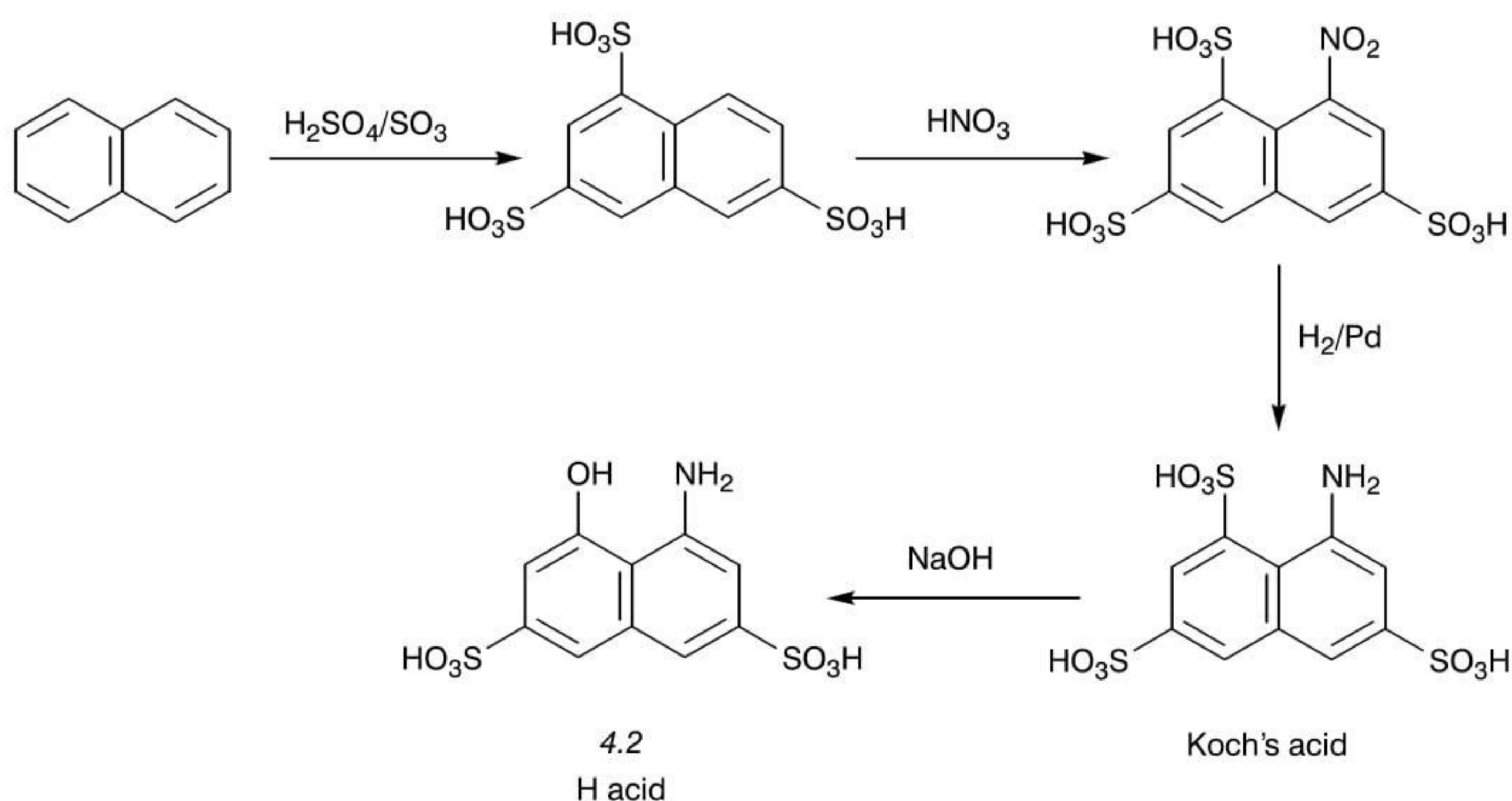
Scheme 4.27

J acid

Of particular interest is the chain of reactions leading to J acid (4.43), since several of the compounds that feature at intermediate stages in the chain are themselves useful as dyestuff intermediates. The starting point for this chain is 2-naphthol which, in early syntheses, was converted by means of a Bucherer reaction into 2-naphthylamine, this then being sulphonated to yield 2-naphthylamine-5,7-disulphonic acid (4.42; Amido J acid). The recognition that 2-naphthylamine is a potent carcinogen caused this route to be abandoned. In the method of preparation now in use (Scheme 4.28), a sulphonic acid group is introduced into the 1-position of the naphthalene nucleus and is carried through the early stages, so that 2-naphthylamine-1-sulphonic acid (4.41; Tobias acid) rather than the unsulphonated amine figures in the preparation.
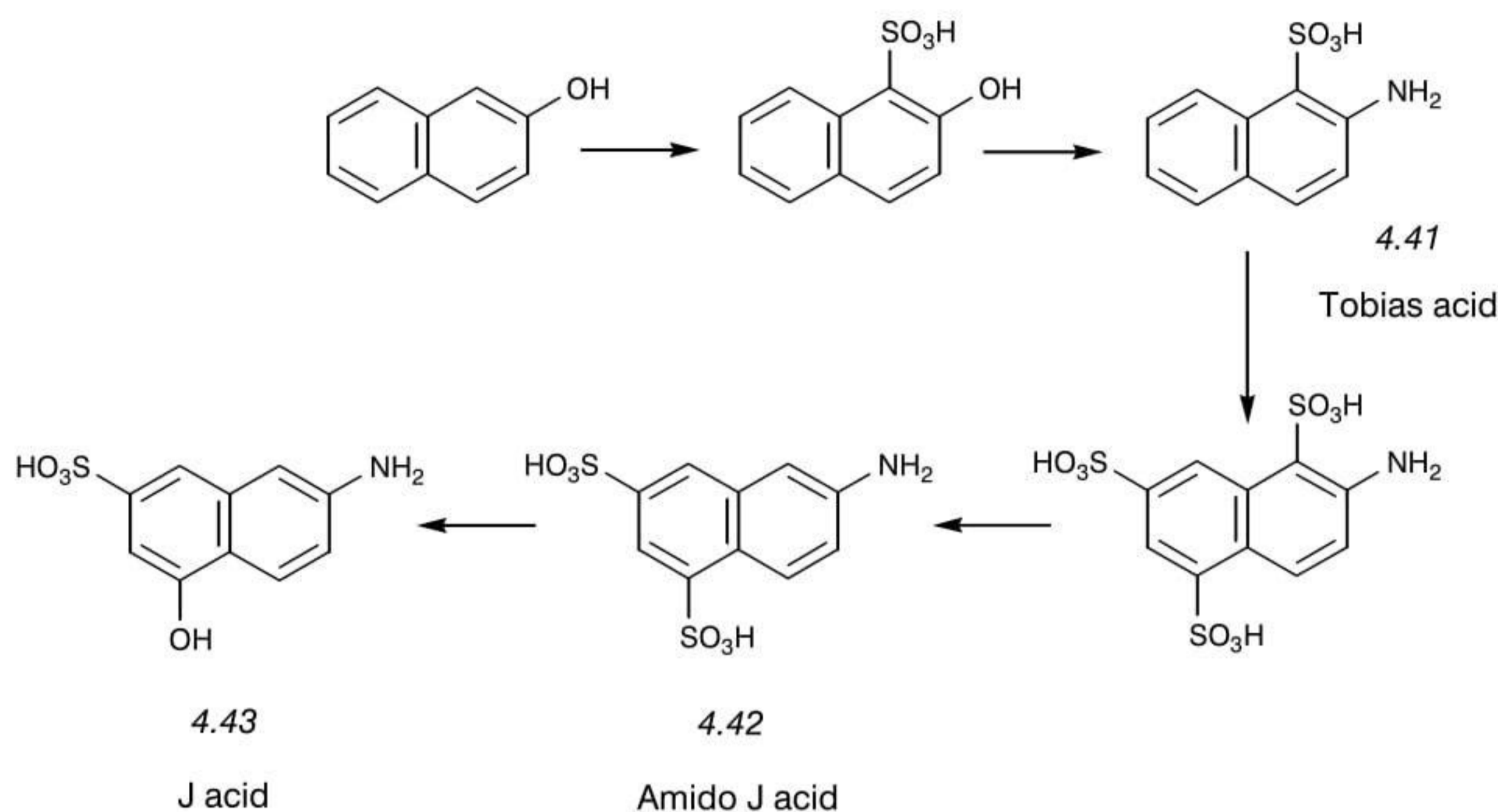
Scheme 4.28

After sulphonation to 2-naphthylamine-1,5,7-trisulphonic acid, the labile 1-sulphonic acid substituent, which has now served its purpose, is eliminated by diluting the sulphonation mixture and heating. Fusion of the resulting disulphonic acid (4.42) with sodium hydroxide replaces the more labile 5-sulphonic acid group by a hydroxy group, forming J acid.

2-Naphthylamine-5,7-disulphonic acid and 2-naphthylamine-1-sulphonic acid, which are intermediate products in Scheme 4.28, as well as 2-naphthylamine-1,5-disulphonic acid (obtained by careful low-temperature sulphonation of Tobias acid), are all used in the synthesis of azo dyes.

1-Naphthylaminesulphonic acids

Nitration of naphthalene-1-sulphonic acid produces two isomeric nitronaphthalenes that have very similar solubilities. It is convenient to reduce the mixture without separation, giving a mixture of 1-naphthylamine-8-sulphonic acid (4.44; Peri acid) and 1-naphthylamine-5-sulphonic acid (4.45; Laurent's acid), as in Scheme 4.29. These two

compounds can be readily separated since the former has a much lower solubility. The isomers also differ markedly in their value as intermediates, Peri acid being a very useful dye component whilst Laurent's acid finds little use.

In all the above sequences, single isomers are produced by careful control of the reaction conditions combined with purification by selective isolation at various points in the synthesis. Occasionally two isomers are produced which give dyestuffs that have very similar properties; in these cases it is often quite acceptable and economically beneficial not to separate the individual components but to use the total mixture in dye preparation. An example is the mixture of 1-naphthylamine-6- and 7-sulphonic acids (4.46; mixed Cleve's acids), which arises by nitration and reduction of naphthalene-2-sulphonic acid (Scheme 4.30).
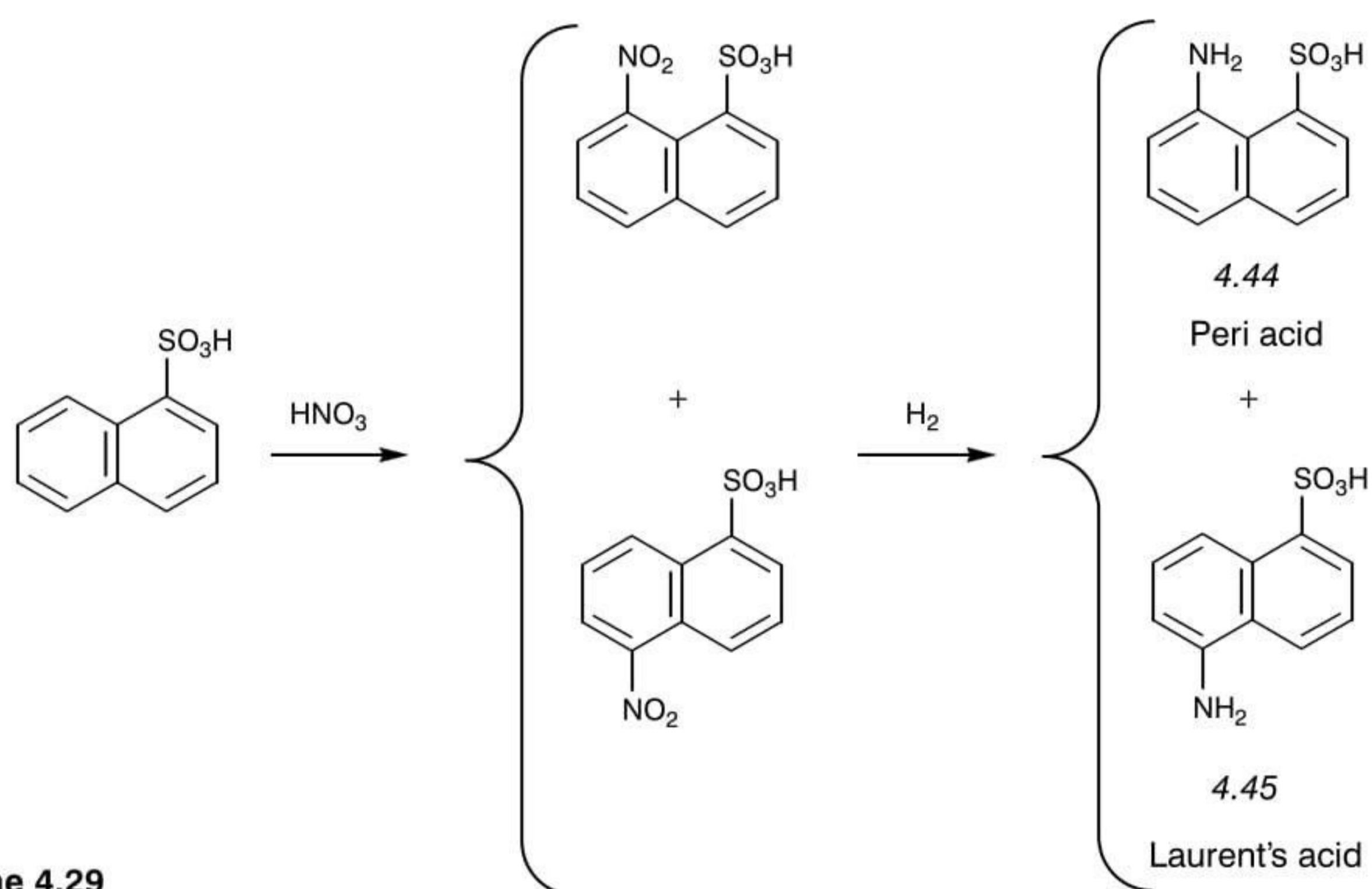
Scheme 4.29
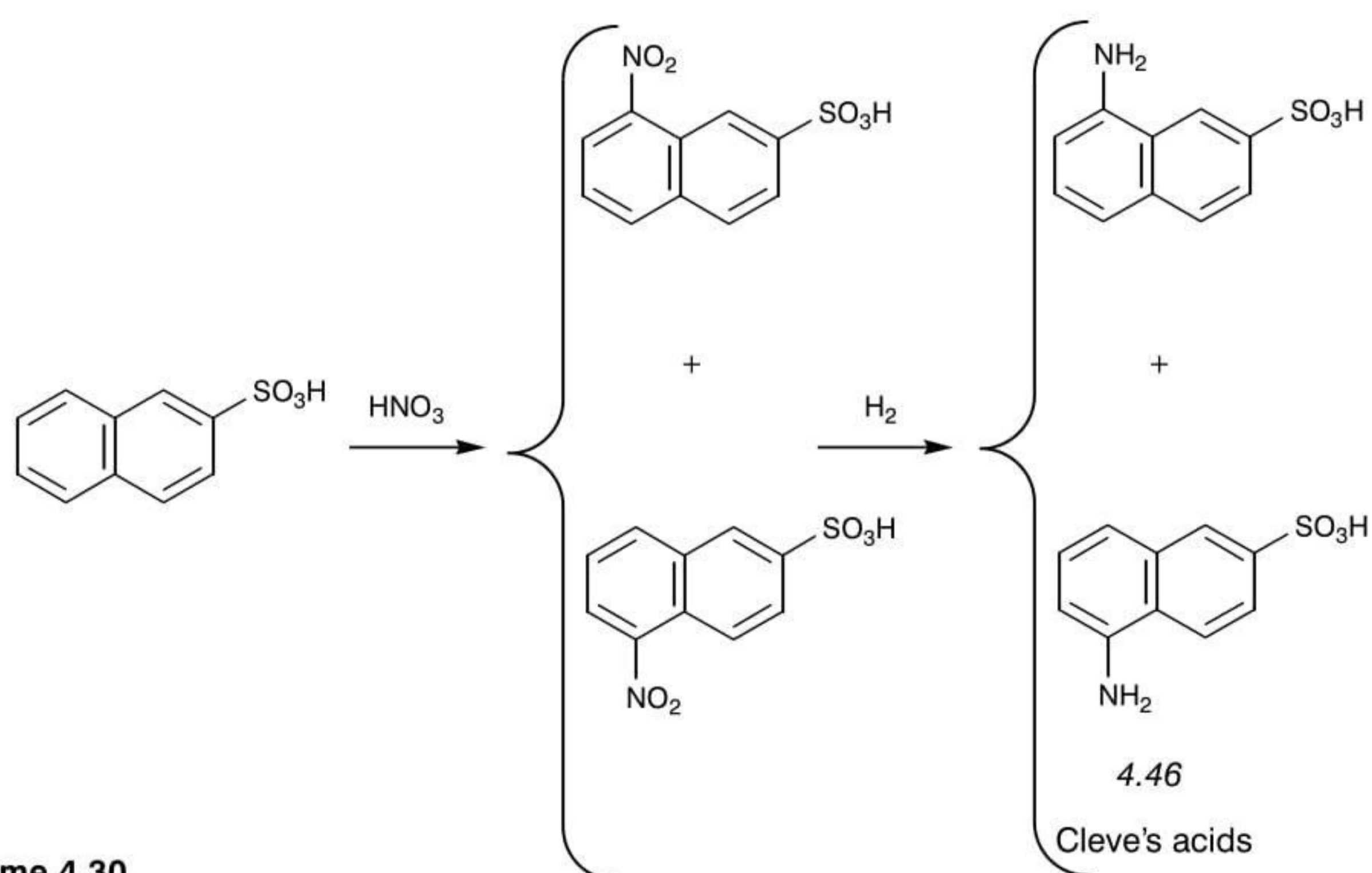
Scheme 4.30

4.7 SCHEMATIC REPRESENTATION OF COUPLING

The simple process of diazotising an amine and joining the resulting diazonium salt with a coupling component produces a monoazo dye, that is, a dye containing a single azo group. Such dyes are often represented as A→E dyes, A standing for the amine, E the end coupling component and the arrow symbol meaning 'diazotised and coupled with'. The certainty with which diazotisation and coupling proceed, together with the wide variety of components available, allows more complex dye structures to be built up by combining two or more diazotisation and coupling sequences. A convenient shorthand way of classifying these more complex products has gained common acceptance. This shorthand, known as Winther symbols, uses arrows combined with the following capital letters to indicate the nature of the components:

- A: an amine that is diazotised
- E: an end coupling component
- D: a diamine that is tetrazotised (both amino groups are diazotised)
- M: an amine that is first coupled with a diazotised amine and then is itself diazotised
- Z: a coupling component that can couple twice.

Using this nomenclature, disazo dyes (dyes containing two azo groups) fall into one or other of the three classes represented thus:

$$E_1 \leftarrow D \rightarrow E_2 \quad A_1 \rightarrow Z \leftarrow A_2 \quad A \rightarrow M \rightarrow E$$
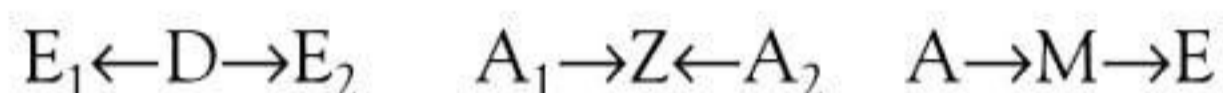
4.8 SULPHONATED AZO DYES

In the majority of dyeing processes the dye is transferred from aqueous solution onto the fibre, so that adequate aqueous solubility is a desirable property in a dye. The sulphonic acid group provides the cheapest way of solubilising a dyestuff and does not generally cause any diminution in the light fastness of the chromogen to which it is attached. Consequently, dyes containing sulphonic acid groups find use in the dyeing of cellulosic fibres (section 3.2.1) and amide fibres (section 3.2.2). In the ranges of dyes available for the dyeing of these fibres, sulphonated monoazo structures provide many of the dyes in the yellow to red sector as well as a few of the more bathochromic hues. As indicated previously, the coupling component is of prime importance in determining the hue, with the diazo component merely modifying it, although when the diazo component contains powerful electron-withdrawing or -donating substituents this modification can be profound. Pyridone and pyrazolone coupling components are generally used in yellow dyes and naphthol, naphthylamine, aminonaphthol or acylaminonaphthol coupling components to cover the orange to red region. Disazo dyes span the spectrum from yellow to greenish blue and find use mainly on cellulosic fibres but also on wool and silk. Trisazo and polyazo dyes are restricted to duller hues on cellulosic fibres.

The actual structures chosen vary according to the particular fibre as well as the end use to which the dyed material will be put. It is appropriate to divide the discussion of the structures of these dyes according to the fibres on which they are used.

4.8.1 Acid dyes for wool

Simple monoazo dyes containing one or two sulphonic acid groups are used to dye wool, the dye being retained on the fibre by electrostatic bonding. Pyrazolones, naphthols, naphthylamines and acylaminonaphthols are commonly used coupling components. These 'levelling acid' dyes are typified by tartrazine (4.47; CI Acid Yellow 23) and CI Acid Orange 20 (4.48). These simple dyes are markedly hydrophilic in character and this necessitates them being applied to the substrate from a strongly acidic dyebath. Under these conditions the dyes readily penetrate the wool fibres and distribute themselves evenly, but their highly hydrophilic character makes them easily desorbed and thus limits their fastness to washing. A higher level of wash fastness can be achieved by using disazo dyes of larger molecular size, usually carrying two sulphonic acid groups. These 'milling acid' dyes are typified by CI Acid Yellow 42 (4.49), CI Acid Red 151 (4.50) and CI Acid Blue 116 (4.51). 4-Amino-2'-nitrodiphenylamine has been used as the A component in disazo dyes based on structure 4.51 [68].

4.47
CI Acid Yellow 23

4.48
CI Acid Orange 20

4.49
CI Acid Yellow 42

4.50
CI Acid Red 151

4.51
CI Acid Blue 116
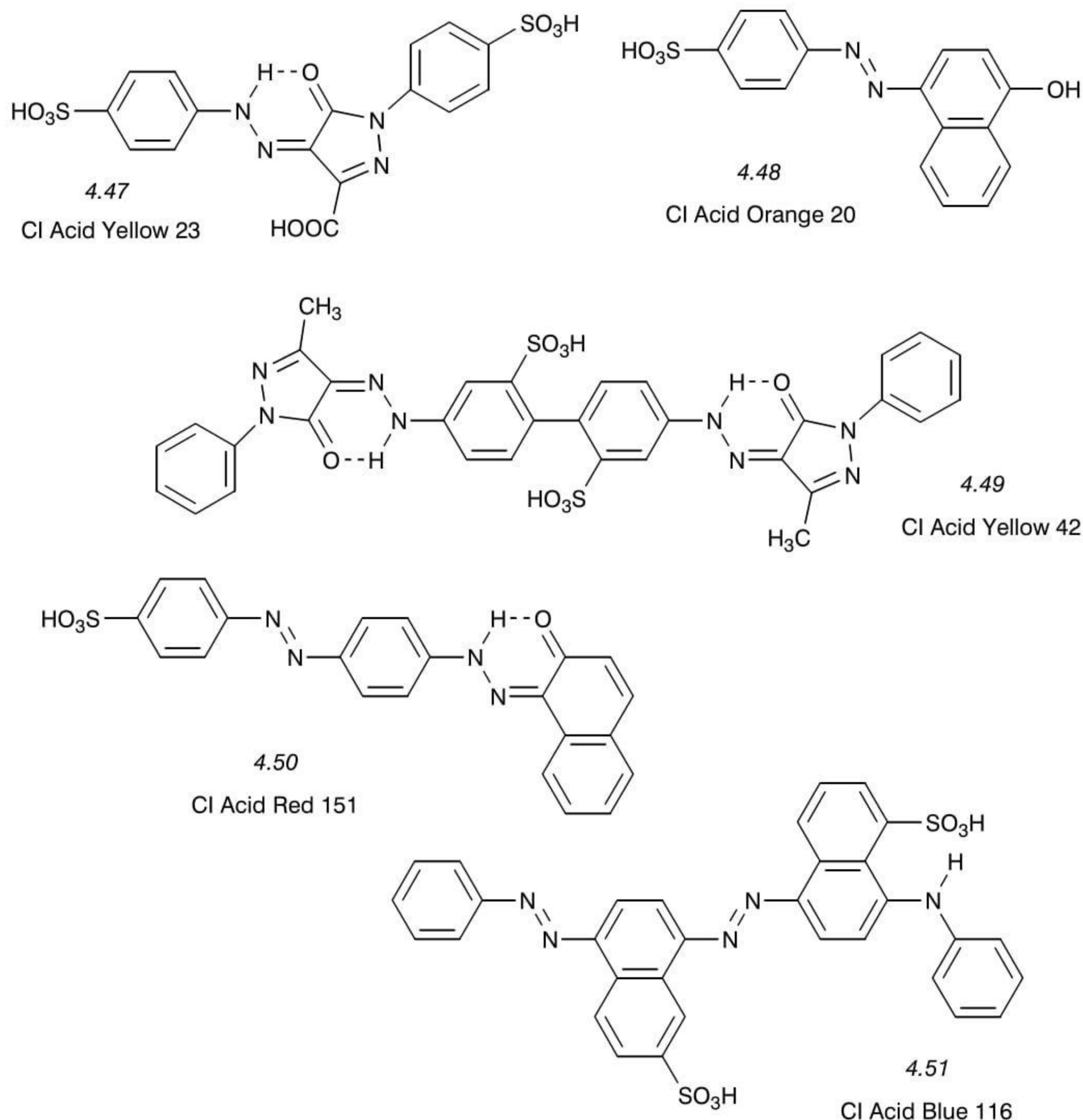
Much superior wet fastness can be achieved by incorporating a highly hydrophobic weighting group into the dye molecule [69]. Non-polar bonding between this group and hydrophobic side chains in wool imparts neutral-dyeing affinity to these 'super-milling' dyes (section 3.2.2). A typical example is CI Acid Red 138 (4.52). Confirmation of the ketohydrazone structure has been obtained by spectroscopic and PPP-MO techniques [70].
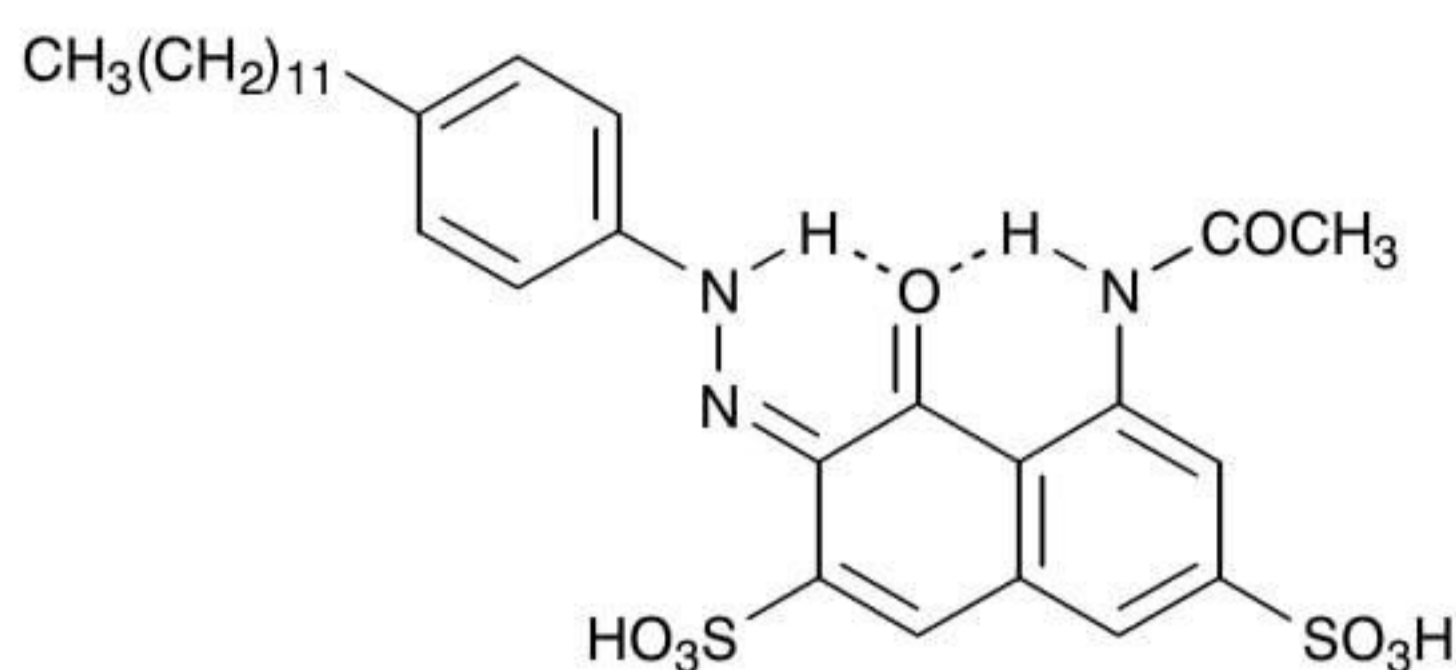
4.52

CI Acid Red 138

Of particular interest are the light-fast red dyes obtained by coupling onto γ acid under acid conditions. In this latter type, an example of which is CI Acid Red 32 (4.53), both the amino group and the hydroxy group are hydrogen bonded to the azo linkage [71]. This double hydrogen bonding prevents the tautomerism that is normally a feature of naphthalene-based azo dyes by locking the dye in the hydroxyazo form, leading both to the red hue and to the high level of light fastness.

Strongly electron-withdrawing or -donating substituents in the diazo component can have a profound effect on the hue, producing a large bathochromic shift (section 1.4). The use of diazo components of the naphthalene series produces a similar but less marked effect. These effects are exploited in CI Acid Blue 92 (4.54), prepared by coupling diazotised O-tolylsulphonyl H acid with N-Phenyl Peri acid and hydrolysis of the product. Here the proximity of the *peri*-sulphonic acid group to the secondary amino group prevents any marked pH sensitivity, removing the need to stabilise the hue by acylation. Again the hydroxy group on the diazo component is hydrogen bonded onto the azo linkage, resulting in excellent light fastness.
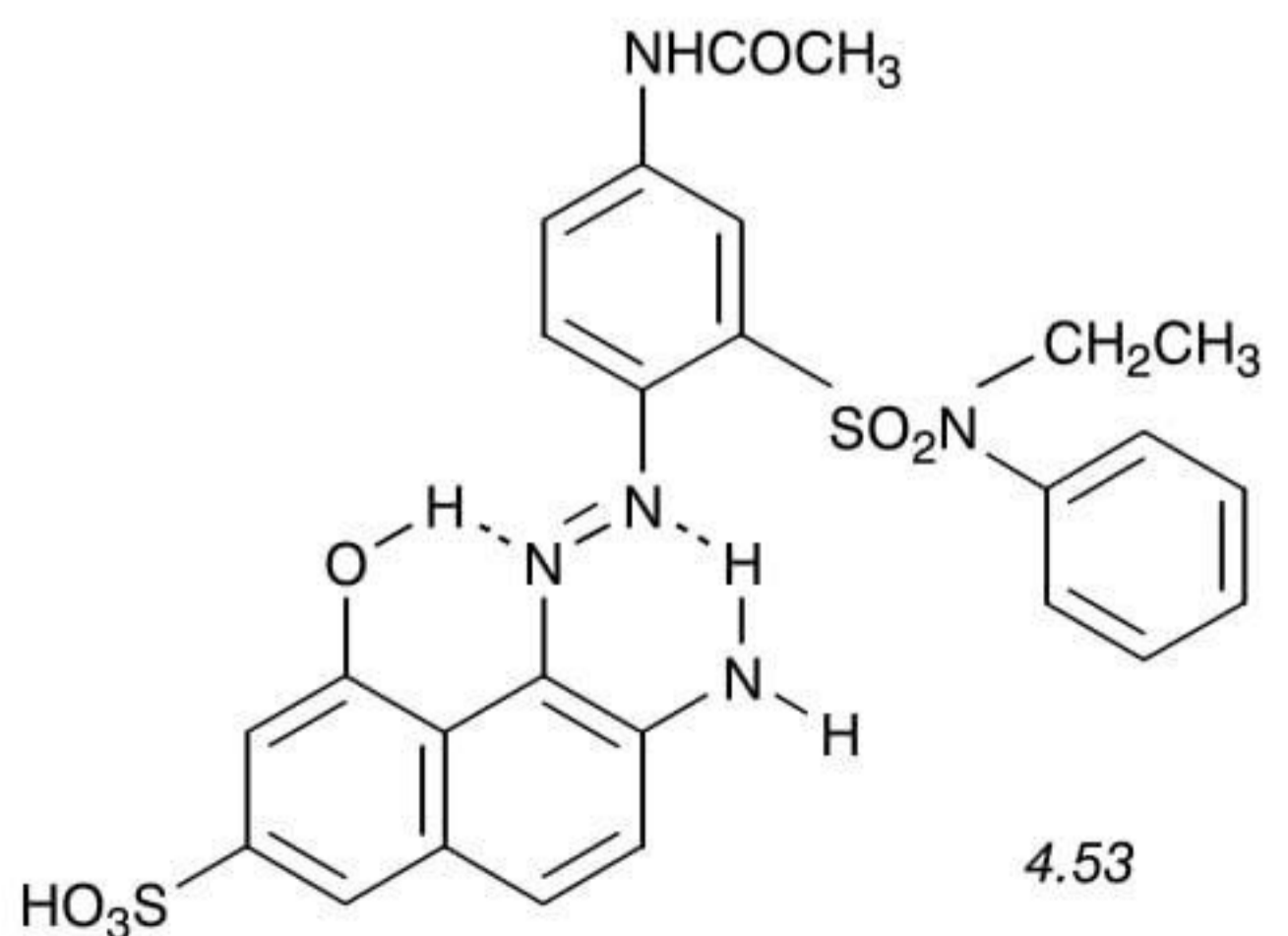
4.53

CI Acid Red 32
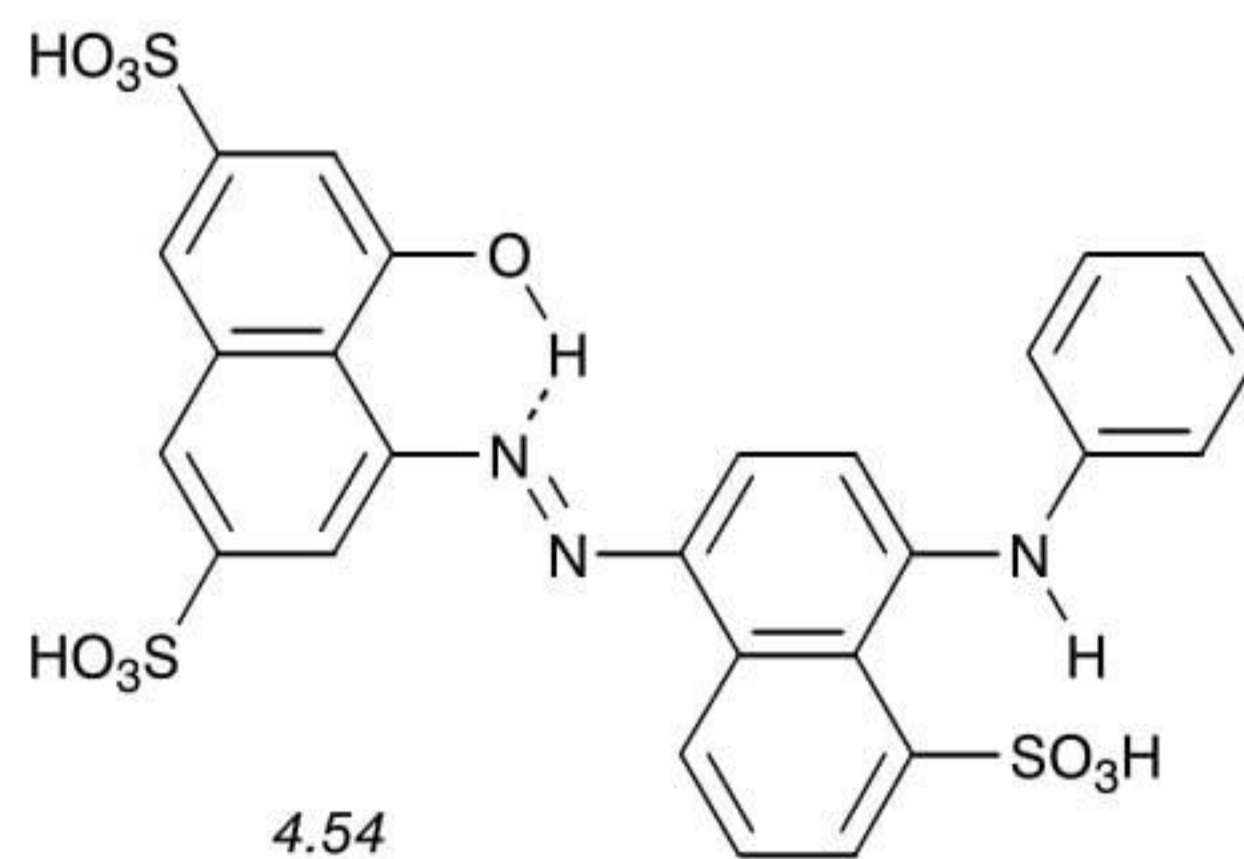
4.54

CI Acid Blue 92

4.8.2 Acid dyes for nylon

The synthetic polyamide fibre nylon can be dyed with either acid dyes or disperse dyes, the former giving better fastness and the latter better levelling properties. The types of acid dye used are broadly similar to those for wool, that is, monosulphonated levelling acid dyes with relative molecular mass (M_r) in the 300–500 region and disulphonated milling acid dyes with M_r of 600–900. Dyes of small molecular size are often deficient in wet fastness and those of M_r higher than about 800 tend to give unlevel dyeings. Within these crude guidelines certain structural features exert specific effects; for instance, hydrogen bonding substituents such as hydroxy and acylamino groups boost fastness to washing but may impair level dyeing behaviour.

Monoazo dyes containing a single sulphonic acid group conveniently fall into the levelling acid group. A typical structure is CI Acid Red 266 (4.55).

Monosulphonated levelling acid dyes are mainly yellow or red in colour, whilst the larger molecular size that can be tolerated with a disulphonated milling acid dye allows the use of disazo compounds, such as CI Acid Blue 118 (4.56), to cover more bathochromic hues such as navy blue.

4.55

CI Acid Red 266

4.56

CI Acid Blue 118
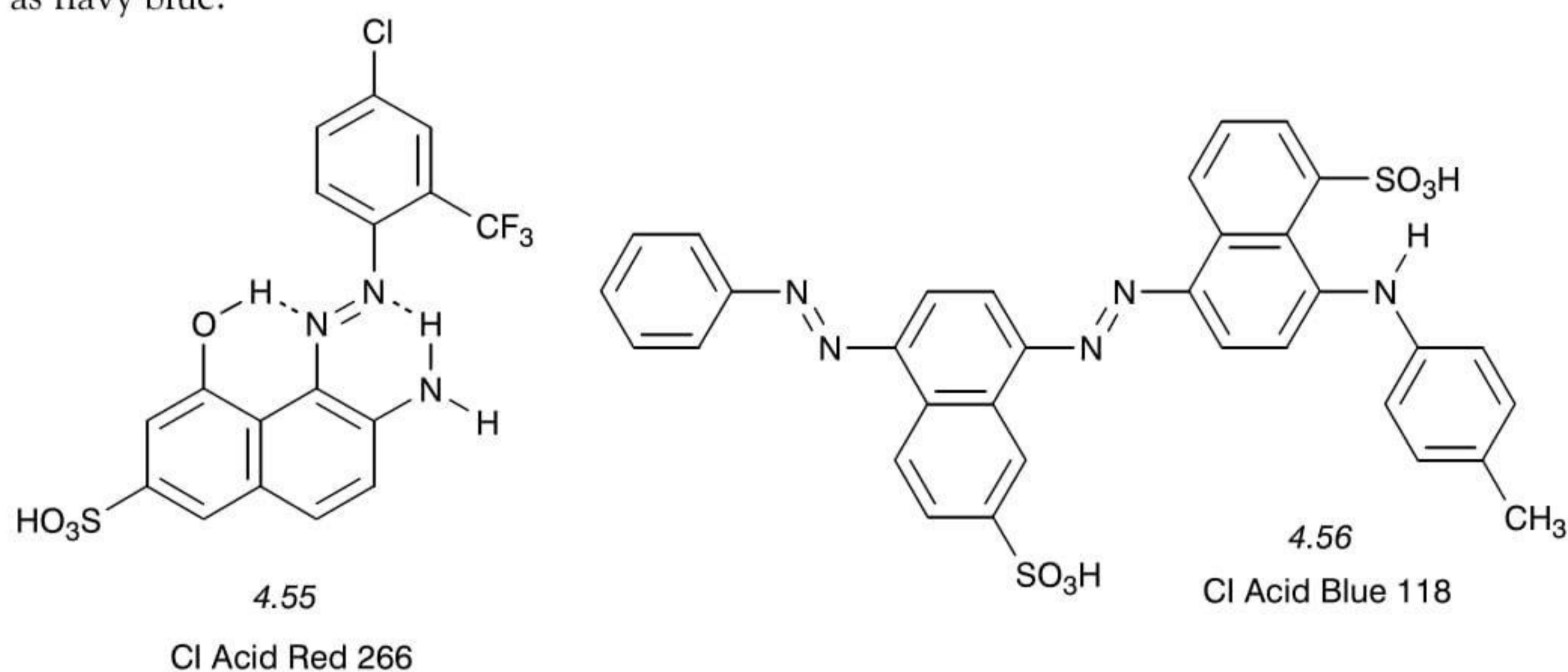
4.8.3 Direct dyes

Certain water-soluble dyes are directly adsorbed onto cotton that has not been pretreated with a mordant (section 3.2.1). The first dye in which this phenomenon was observed was Congo red (4.57; CI Direct Red 28), discovered in 1884 by Böttiger. The extreme pH sensitivity of this dye now restricts its use to that of an indicator, but it deserves mention as the forerunner of the direct dye class.


4.57

CI Direct Red 28
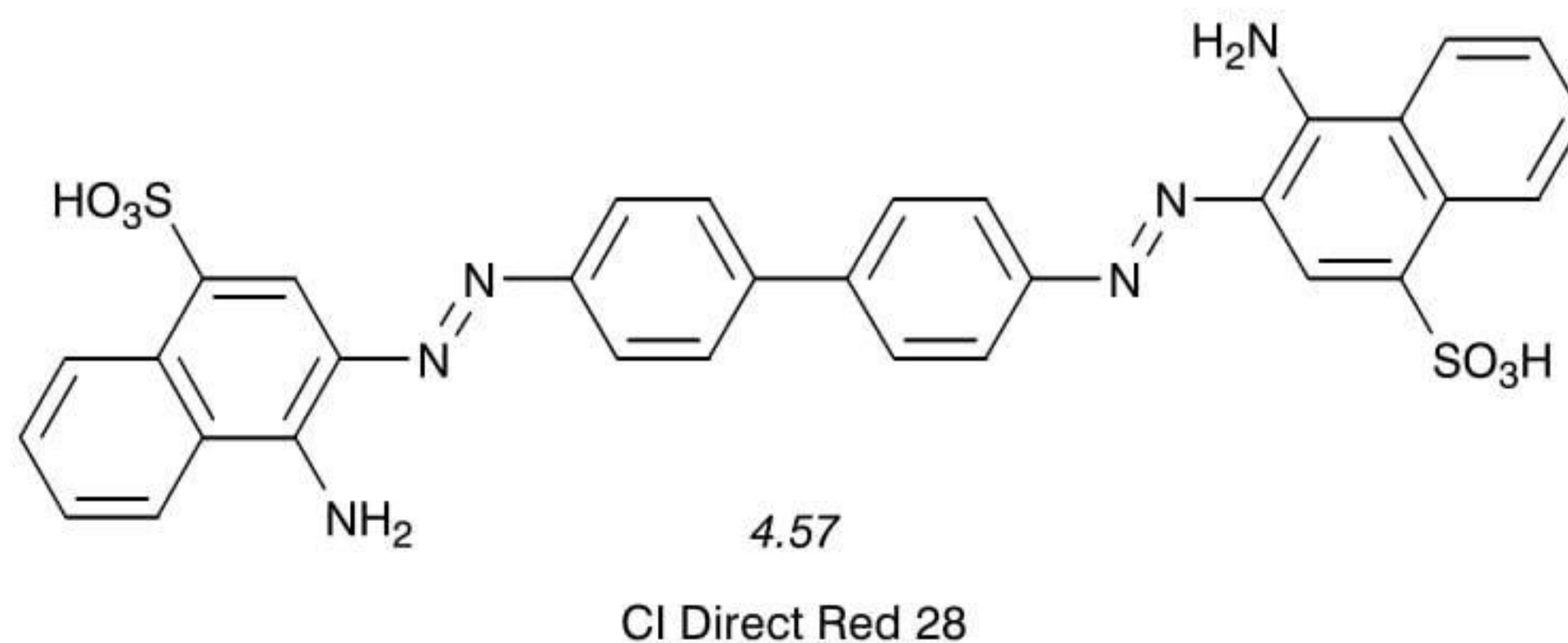
If the solubility of dyes of this type is kept to an acceptable minimum, adequate wash fastness can be achieved. This low solubility requirement is met by the use of the minimum number of solubilising groups consistent with the need to prepare an aqueous dyebath. Hydrogen bond formation with the fibre depends upon having numerous groups containing electron-rich atoms, such as oxygen and nitrogen, positioned at intervals along an extended planar molecule. Suitable features conferring substantivity include amino and acylamino groupings, hetero atoms in aromatic rings and the azo group itself.

The simplest monoazo dyes fail to meet these requirements, but by choosing intermediates known to confer substantivity and by building up the molecule to provide the necessary length and coplanarity (section 3.2.1), direct dyes can be produced from this class. Thus the highly substantive character of the benzothiazole nucleus is exploited in CI Direct Yellow 8 (4.58), as is the alignment of the azo, ureido and acylamino groups in the substituted J acid coupling component of CI Direct Red 65 (4.59).

4.58

CI Direct Yellow 8

4.59

CI Direct Red 65
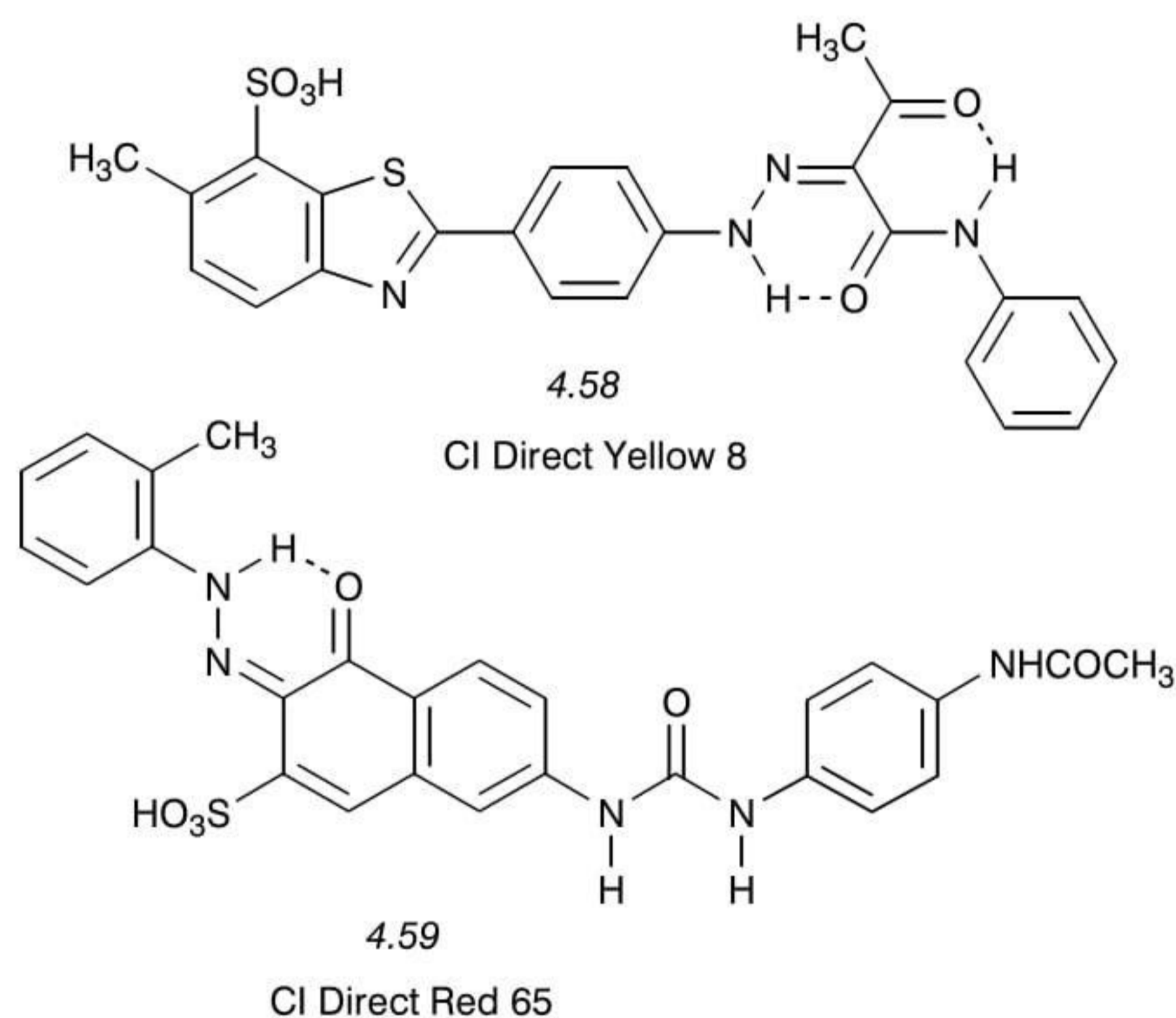
The required long planar shape is more readily supplied by simple disazo structures such as CI Direct Blue 1 (4.60). Copper complexes of such disazo compounds are important and are dealt with elsewhere (section 5.5.3). A widely used method of producing A→Z←A type disazo dyes relies on treating J acid with phosgene (COCl$_2$) to give the bis-coupling component carbonyl J acid (4.61).

4.60

CI Direct Blue 1
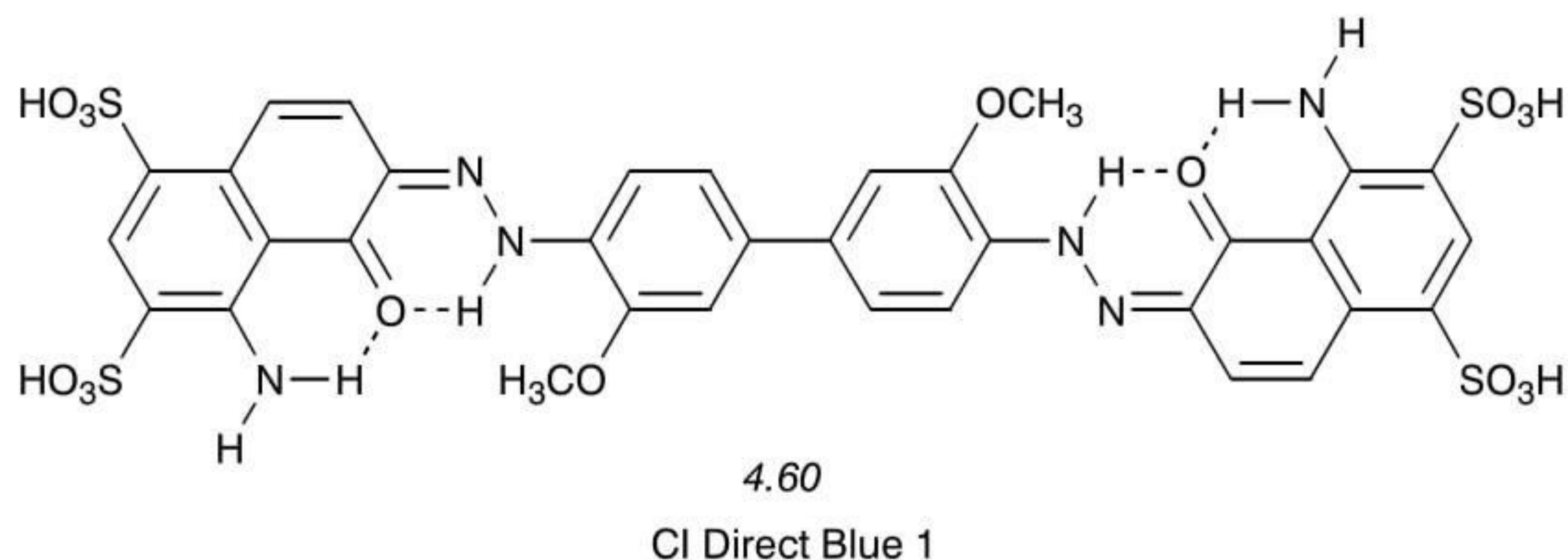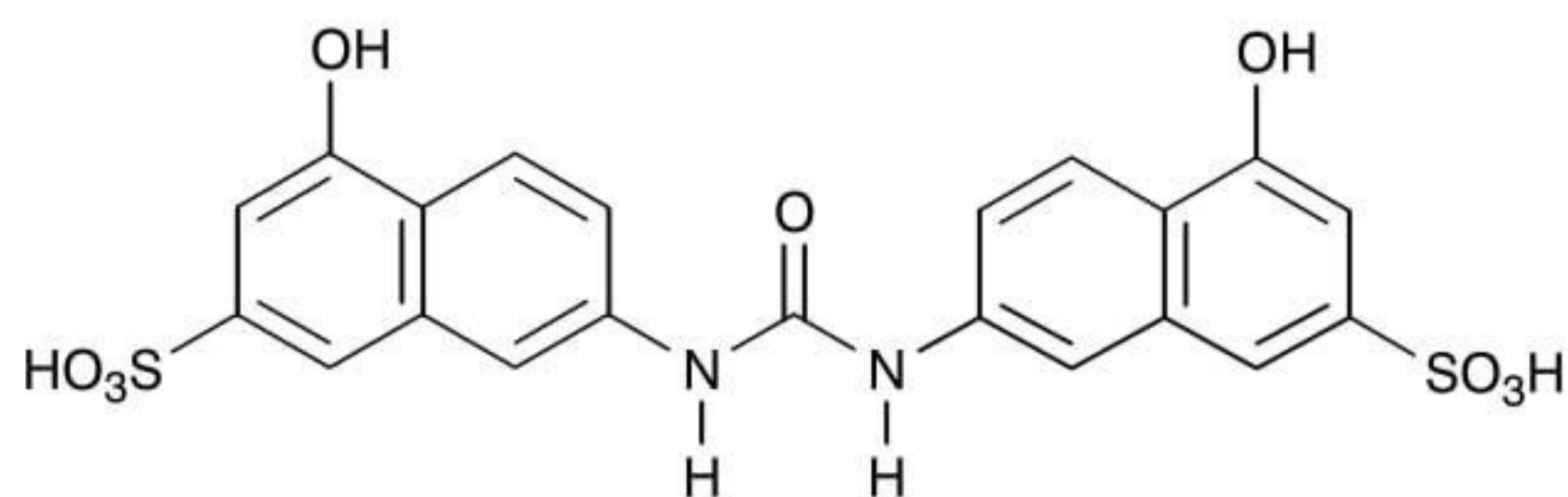
4.61

Carbonyl J acid

Disazo dyes can also be prepared by phosgenating suitable amino monoazo dyes. The phosgenation technique for building up direct dye molecules by joining together sub-units generally produces symmetrical structures. However, the use of cyanuric chloride (4.62) allows different sub-units to be joined together and this intermediate has been employed to link non-substantive anthraquinone structures to substantive azo moieties in green direct dyes, such as CI Direct Green 28 (4.63).

4.62

Cyanuric chloride
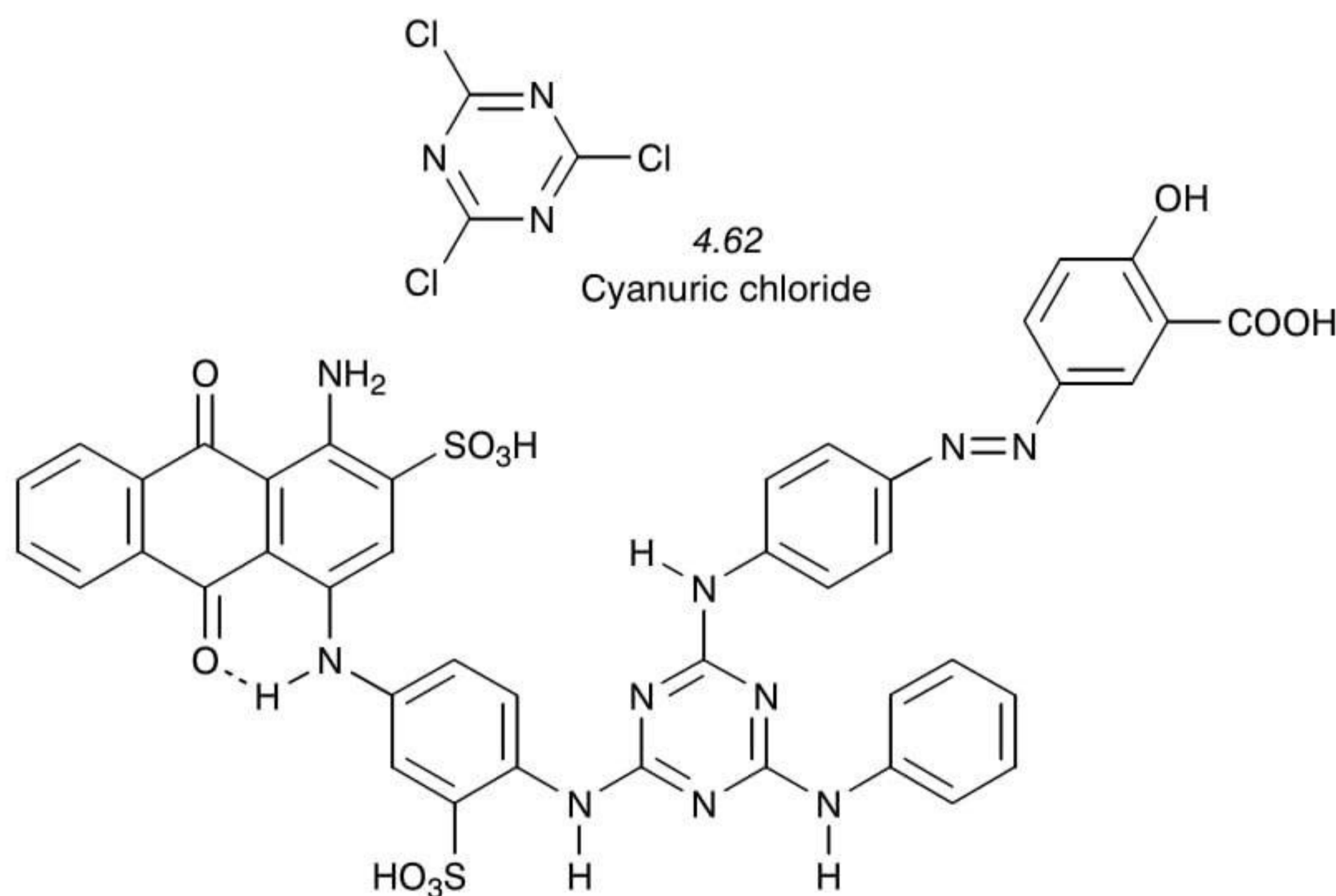
4.63

CI Direct Green 28

It is in the direct dye class that the more complex polyazo dyes come into their own, and trisazo structures such as CI Direct Blue 78 (4.64), CI Direct Brown 222 (4.65) and CI Direct Black 38 (4.66) are classic examples of this type of dye. The last-named dye is now known to be carcinogenic [72]. Generally, the A→M$_1$→M$_2$→E type (such as 4.64) afford reasonably bright blue shades whilst dyes prepared according to other sequences, such as the E←D→Z←A type (examples 4.65 and 4.66) yield drab shades.

The last of this trio highlights an area of concern in direct dye chemistry. Many dyes of this type relied on the extremely useful intermediate 4,4′-diaminobiphenyl (benzidine). In the tetrazonium salt prepared from this diamine, the two diazonium groups are conjugated and strongly activate one another. This activation makes the first coupling proceed very readily, but after completion the second diazonium group is no longer subject to the

4.64

CI Direct Blue 78

4.65

CI Direct Brown 222

4.66

CI Direct Black 38
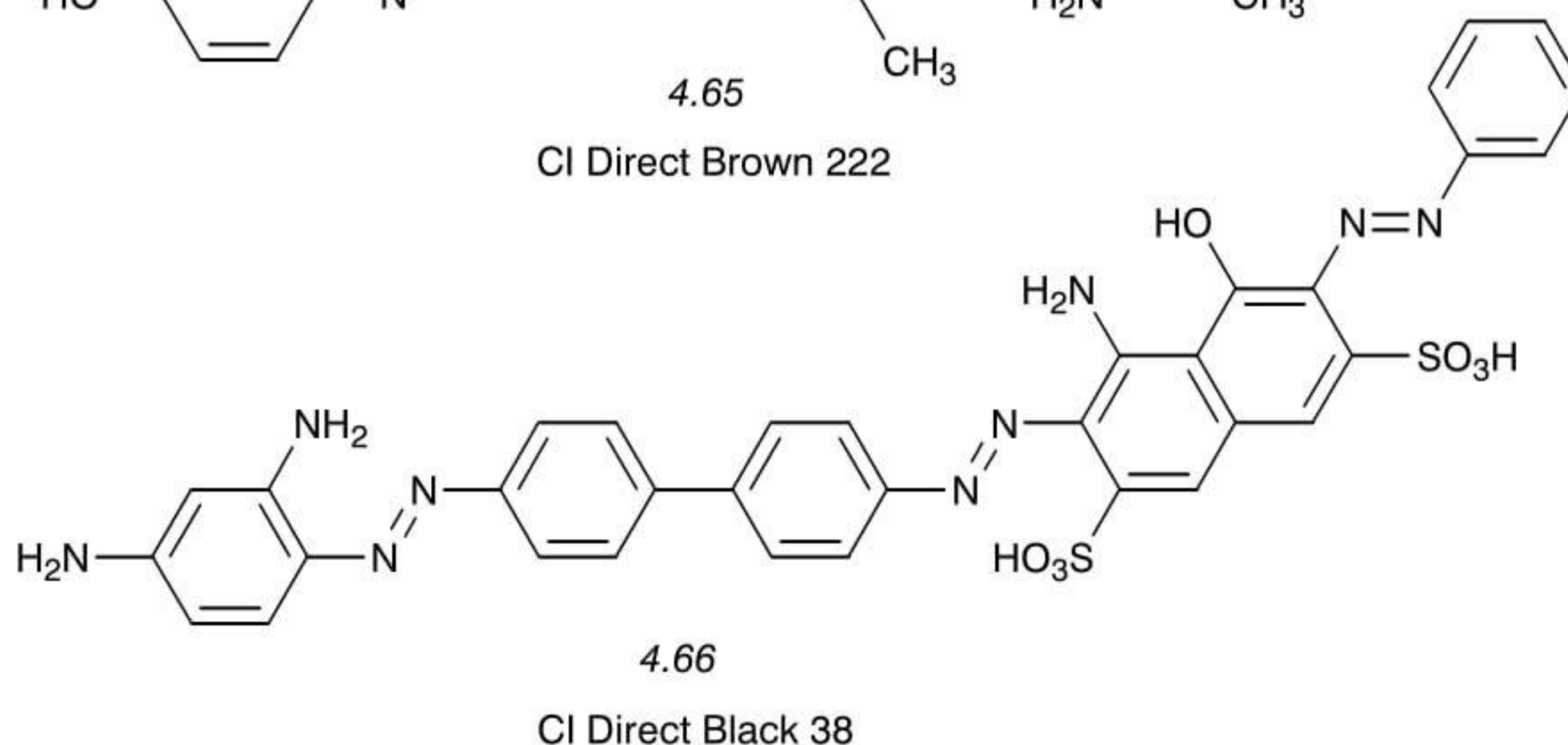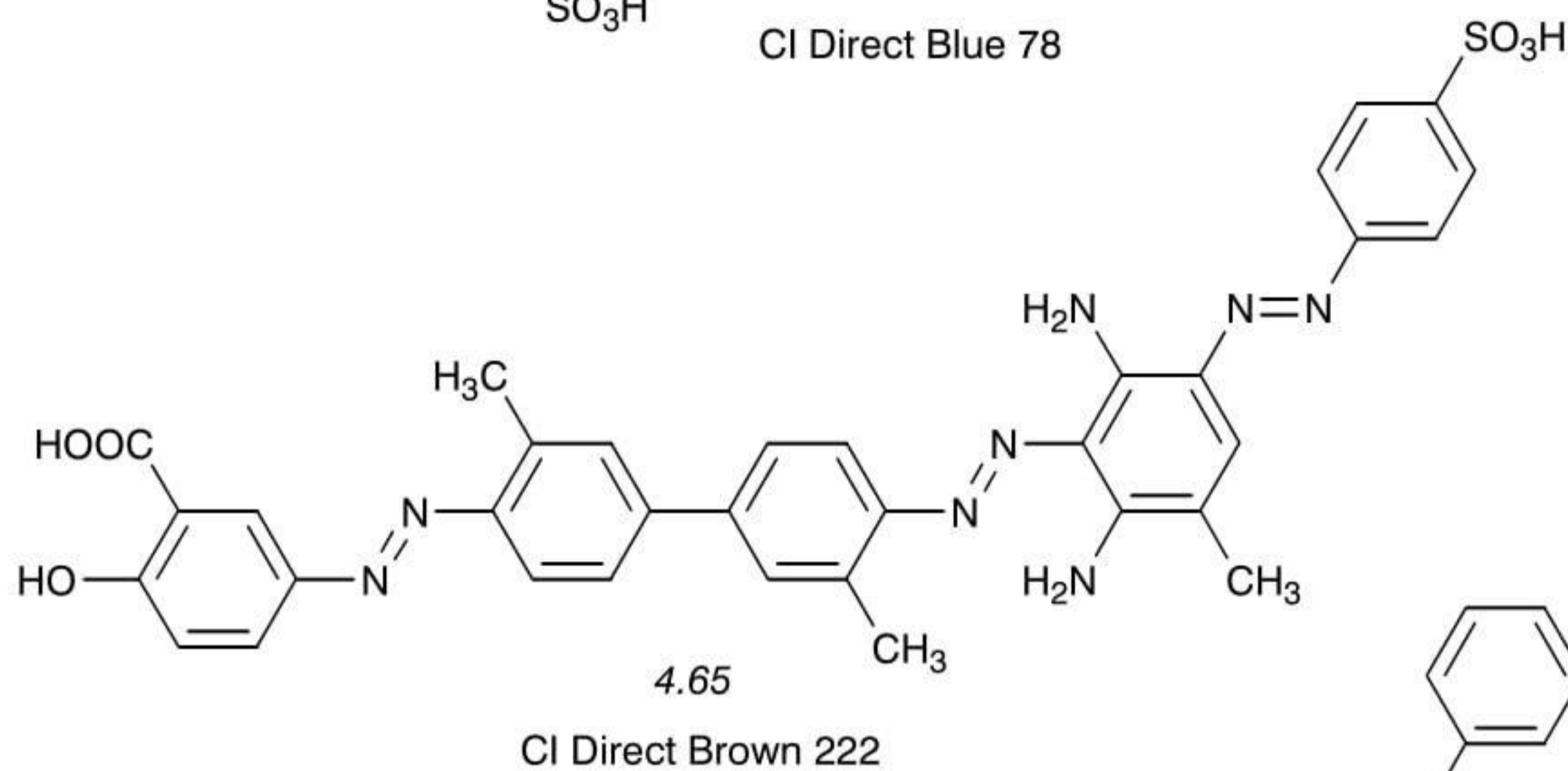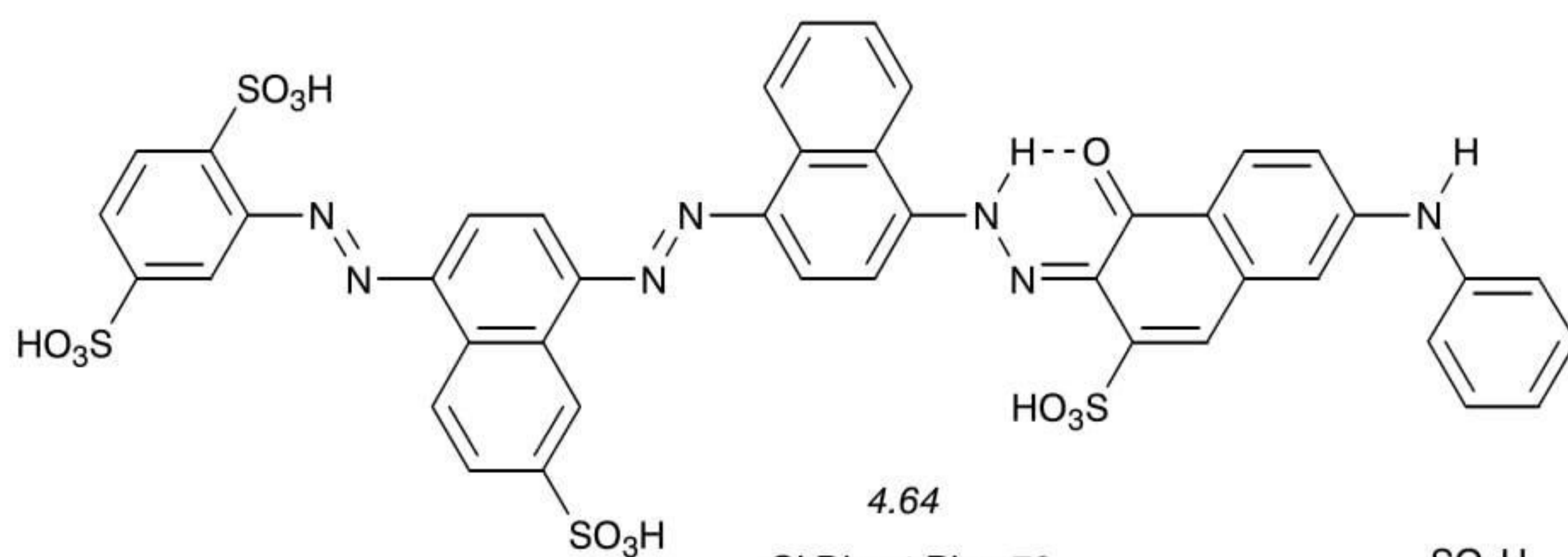
powerful activating influence of a conjugated diazonium group and it couples far more sluggishly. The two diazonium groups can thus be coupled selectively in a stepwise manner to produce a host of useful products. In the preparation of CI Direct Black 38, for example, one diazonium grouping in tetrazotised benzidine undergoes coupling at low pH with H acid and diazotised aniline is then added. On raising the pH, the benzenediazonium chloride couples next to the hydroxy group on the H acid unit. Finally, *m*-phenylenediamine is added and the second benzidinediazonium grouping couples slowly to produce the third azo linkage. The withdrawal of the notorious carcinogen benzidine by major dyestuff manufacturers in the 1970s led to an extensive search for replacements for these dyes. One product that has emerged from this effort is CI Direct Black 166 (4.67), in which 4,4′-diaminobenzanilide is used as a benzidine replacement. Sulphonated diaminobenzanilides have also been examined [73]. Other alternative diamines have been reported [74,75]. Interesting examples include 5,5′-diamino-2,2′-bipyridyl [76] and 3,8-diaminophenanthridone [77], a benzidine analogue in which the biphenyl rings are linked by an amide group. The genotoxicity of azo dyes has been reviewed [78].
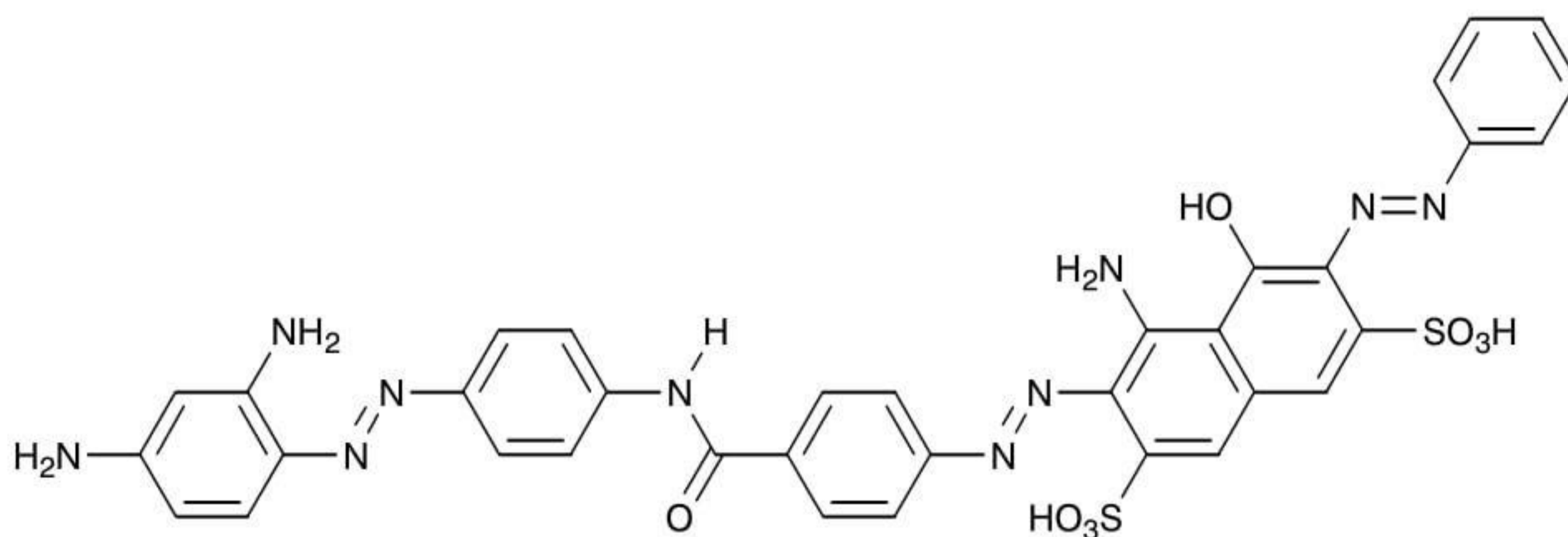
4.67

CI Direct Black 166

Tetrakisazo dyes (dyes containing four azo groups) are less common but some do find use, these products often arising from the phosgenation of an amino disazo dye.

Direct dyes have only modest fastness to washing, which may be improved by after-treatments such as metal-complex formation (section 5.5.3) or by diazotisation of the dye on the fibre and further coupling of the diazonium salt with an insoluble coupling component (section 1.6.14). In addition to their use on cotton and viscose, direct dyes are important in the dyeing of leather. The cheapest members of this class are also used in the coloration of paper, since for this purpose fastness properties are largely irrelevant and price is all-important.

4.9 UNSULPHONATED MONOAZO DYES

4.9.1 Solvent-soluble dyes

These dyes, already described in section 2.12, require adequate solubility for the coloration of various organic solvents and must be cheap [79]. The simplest and least polar dyes of this class are used for the coloration of petrol and ball-pen inks, with more polar types being used in lacquers, stains and varnishes. Some products of lower solubility are used in mass coloration.

These unexacting requirements make the simplest unsulphonated azo structures, often monoazo types, quite acceptable [80]. Typical of the least polar members of this class are CI Solvent Yellow 2 (4.68), CI Solvent Orange 1 (4.69) and CI Solvent Red 17 (4.70). Simple azo structures carrying sulphonamide, sulphone or carboxylate ester groups are used where a somewhat more polar, less soluble dye is needed. Simple disazo compounds (4-amino-azobenzene→2-naphthol, for example) are used as red solvent dyes. Probably the only structural feature worthy of note in this class is the occasional adoption of structures carrying long alkyl chains to enhance solubility, as in the case of the disazo dye CI Solvent Yellow 107 (4.71).
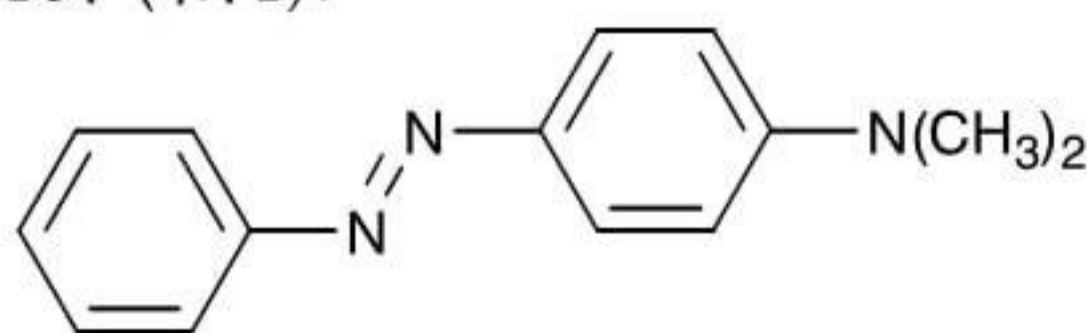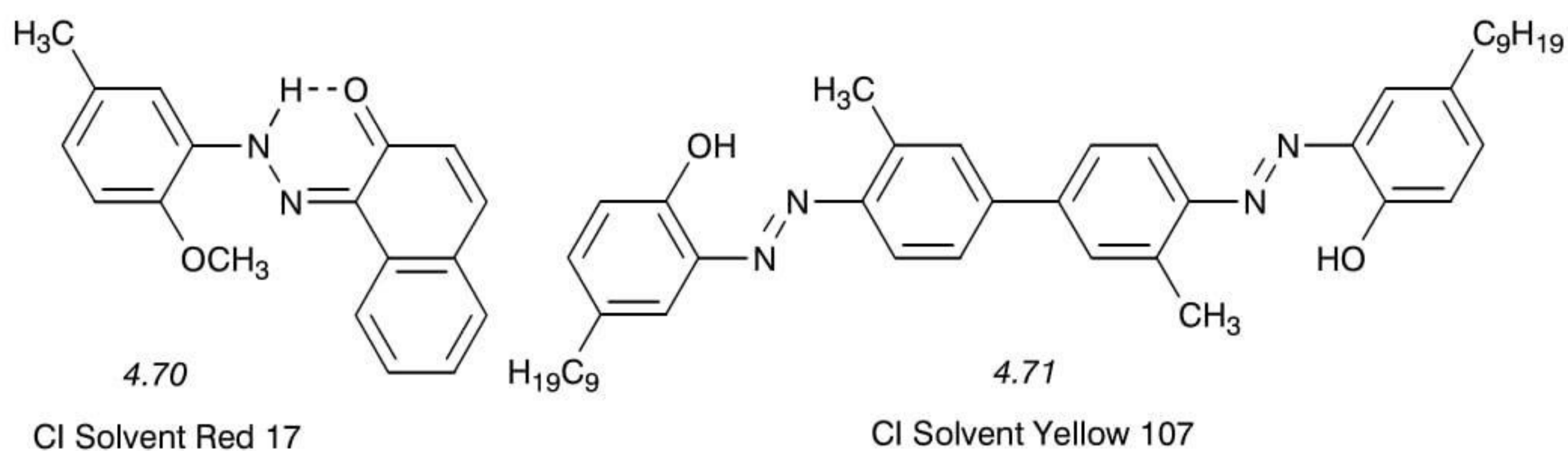

4.68

CI Solvent Yellow 2

4.69

CI Solvent Orange 1

4.70

CI Solvent Red 17

4.71

CI Solvent Yellow 107
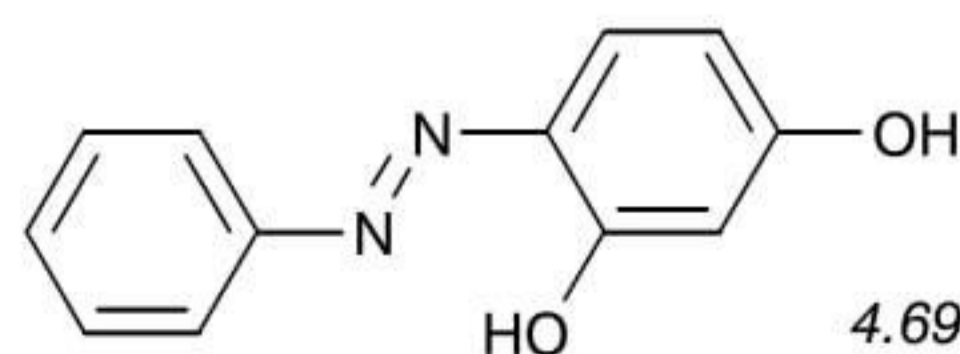
4.9.2 Disperse dyes

The introduction of the man-made fibre cellulose acetate in the early 1920s posed a new problem for the dyestuff chemist, an initial solution to which was supplied by Green and Saunders in 1923 with the launch of the Ionamine range [81,82]. These dyes carried, as sole solubilising group, an ω-methanesulphonate grouping, which was incorporated into the molecule by coupling onto an arylamine ω-methanesulphonate. During the dyeing process this grouping was hydrolysed, leaving a fine dispersion of a water-insoluble dye as the dyebath. This type of dye, known as a disperse dye [83,84], is now used for the dyeing of cellulose acetate, triacetate and polyester fibres as well as offering an alternative to acid dyes for the dyeing of nylon.

In order to facilitate satisfactory dye uptake, the molecular size of a disperse dye must be kept small; monoazo structures are therefore exceptionally important, particularly in the coloration of polyester and cellulose triacetate. In the yellow shade area, molecular size generally poses no problem and the various available coupling components can all be used without making the molecule too large. A very simple example of the type of structure employed using a phenolic coupling component is CI Disperse Yellow 3 (4.72). This dye is known to cause skin sensitisation when on nylon [85] and can also provoke an allergic reaction [86].

4.72

CI Disperse Yellow 3

4.73

CI Disperse Yellow 8
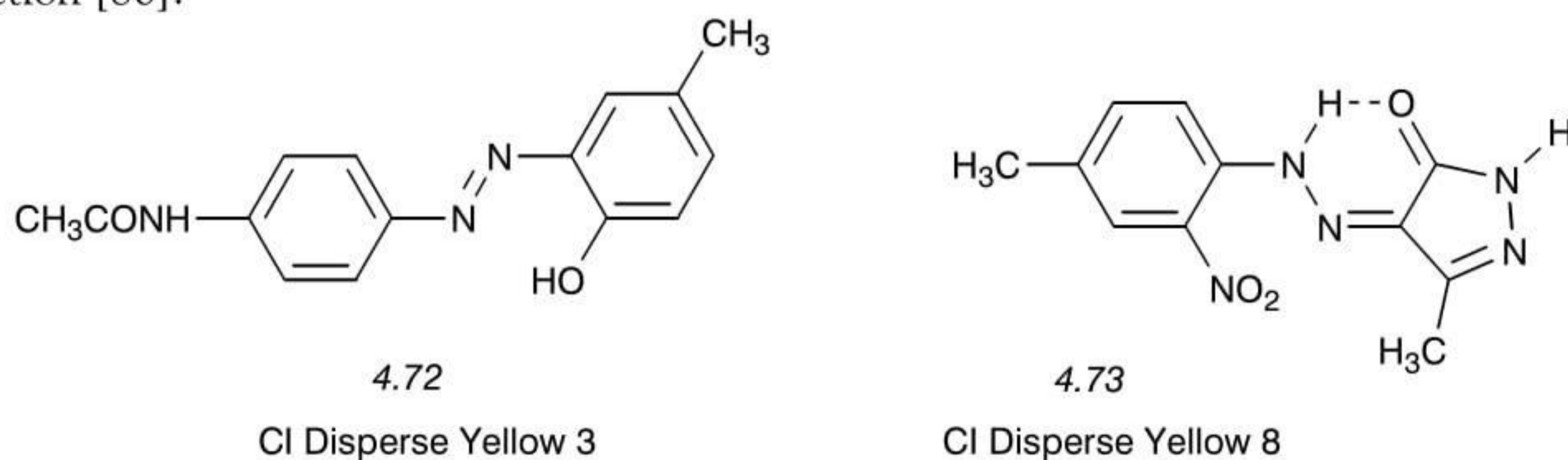
Heterocyclic coupling components are widely used in the disperse dye field for the production of yellow dyes. Numerous conventional dyes are based on simple pyrazolones, often combined with an *o*-nitroaniline diazo component, the *o*-nitro group being particularly favourable in ensuring good light fastness. CI Disperse Yellow 8 (4.73), which uses a very simple pyrazolone coupling component, is an example.

A very noticeable feature has been the use of a wider range of heterocyclic coupling components than in water-soluble azo dyes. An early example of this trend was CI Disperse Yellow 5 (4.74), which used 4-hydroxy-1-methylcarbostyril as coupling component. It was in

this field that the pyridones made their first impact. A typical example is CI Disperse Yellow 211 (4.75). These compounds are now the most important yellow-producing coupling components, giving exceptionally bright greenish yellow hues. Their success has stimulated the investigation of other compounds, with the particular aim of extending the range of hues available from such simple coupling components. Thus, derivatives of 2,6-diaminopyridine with simple diazo components yield orange dyes, such as 4.76.
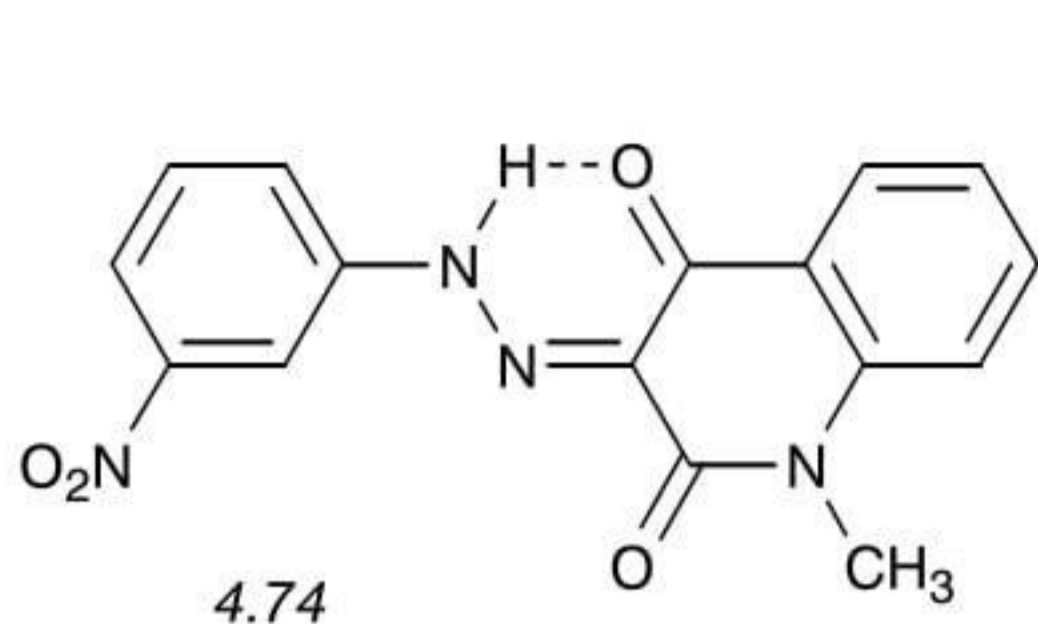
4.74

CI Disperse Yellow 5
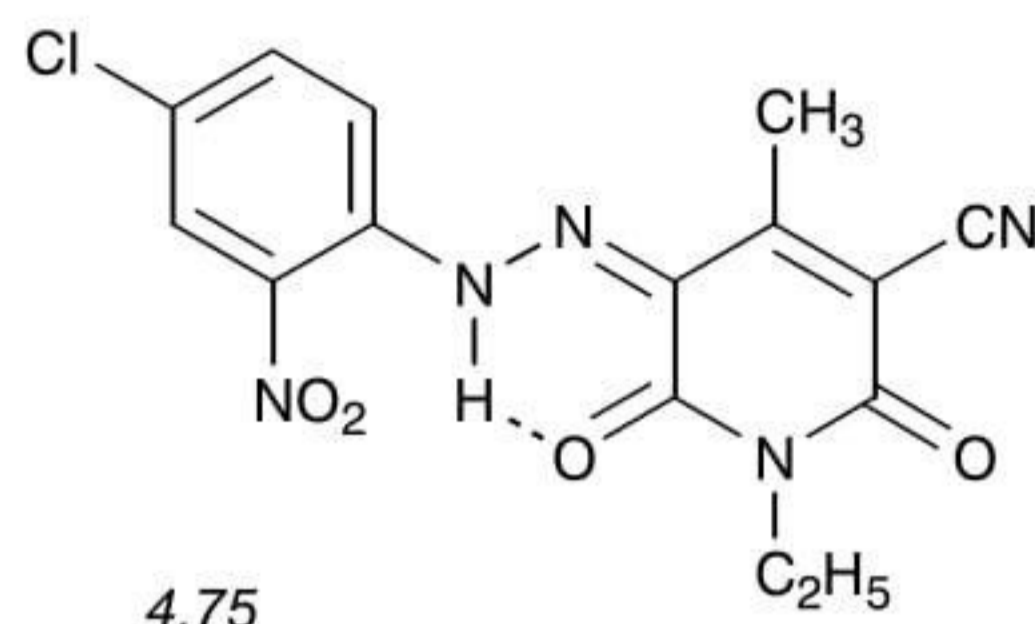
4.75

CI Disperse Yellow 211
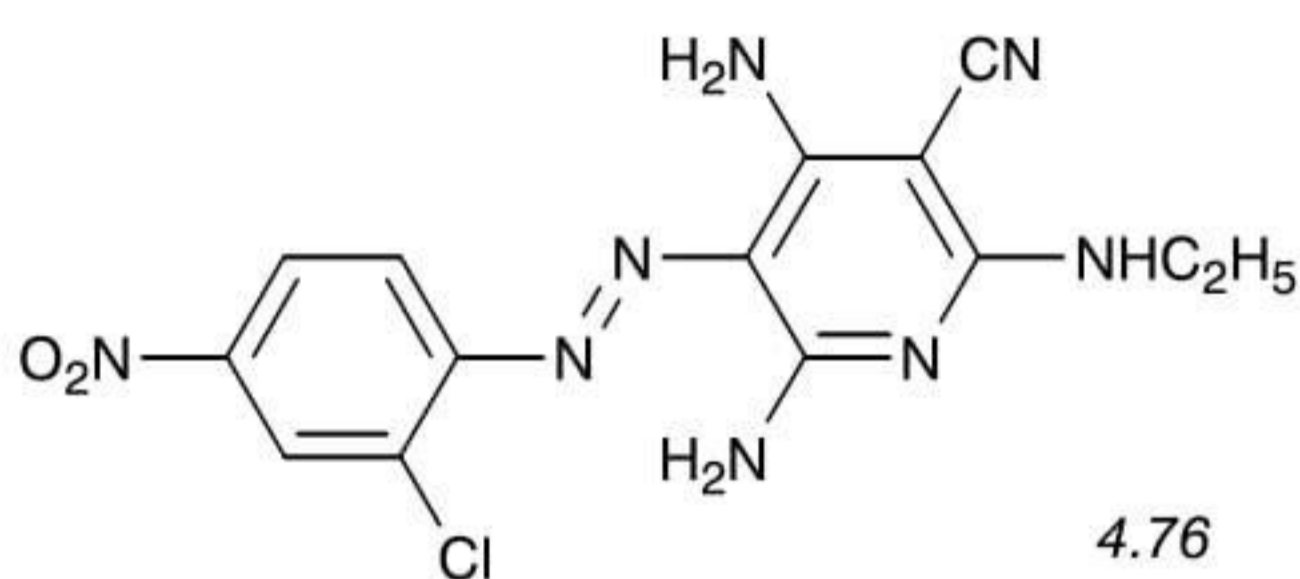
4.76

With the more bathochromic hues, the restriction posed by the requirement for small molecular size can only be overcome by using ω-substituted *N,N*-dialkylaniline coupling components and allying the powerful dialkylamino auxochrome with electron-attracting groups in the diazo component. This arrangement, with electrons being donated from one end of the molecule and attracted to the other, produces highly polar structures, with hues varying from yellow to red to blue as the polarity increases. Examples are CI Disperse Red 72 (4.77) and CI Disperse Blue 183 (4.78). In this latter dye the polarity is further increased by incorporating an amide group in the coupling component to reinforce the electron-donating effect of the dialkylamino group.
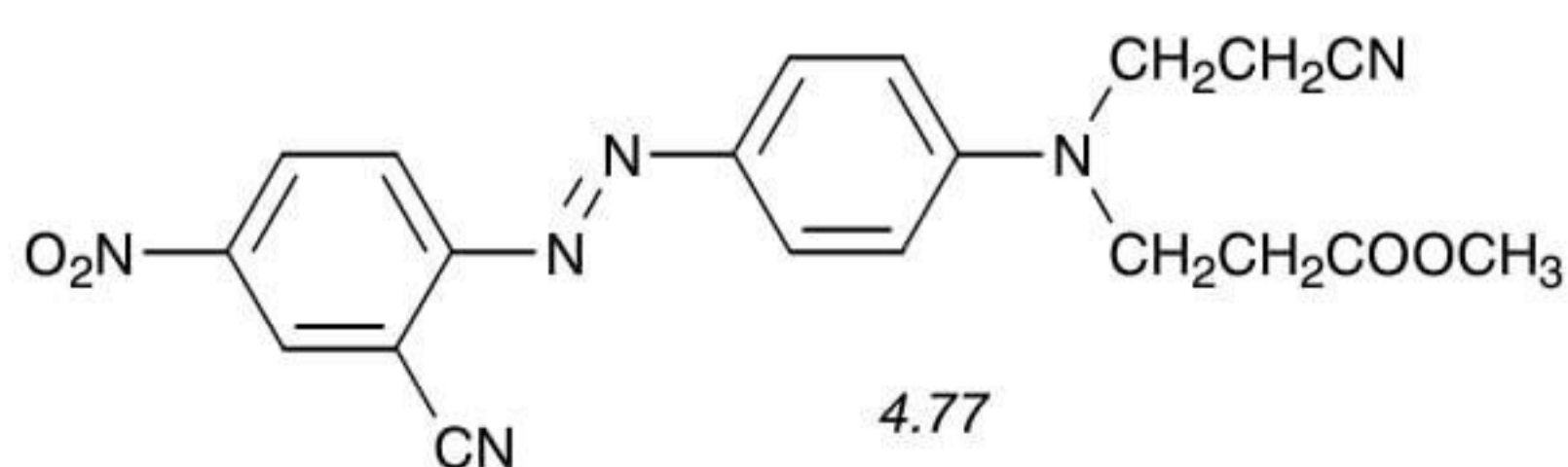

4.77

CI Disperse Red 72
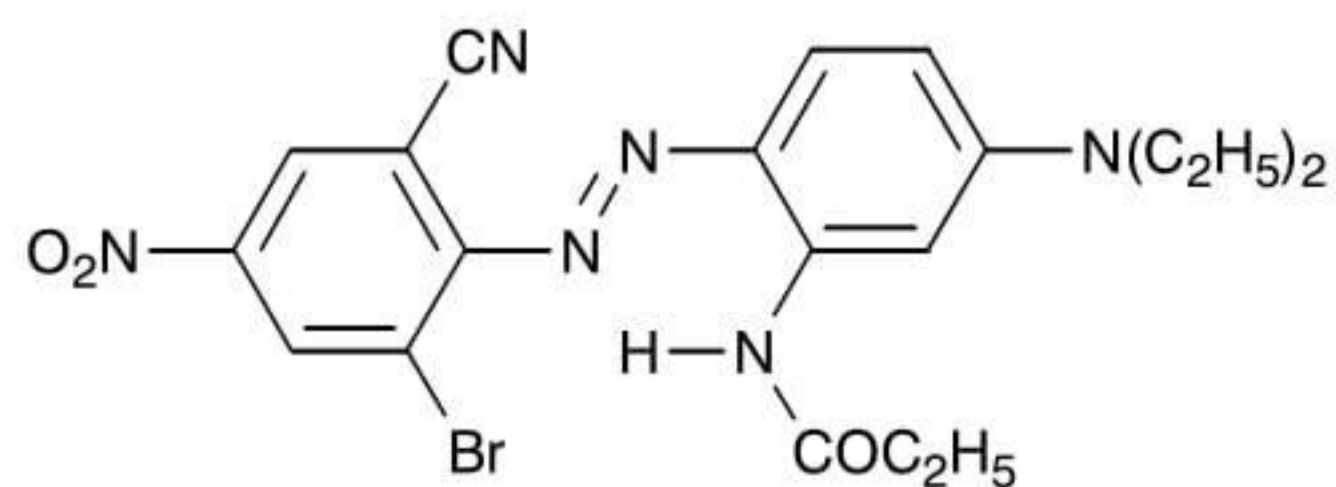
4.78

CI Disperse Blue 183

The coupling component in CI Disperse Red 72 is a complex tertiary amine, carrying cyano and methoxycarbonyl groups on the alkyl chains. Such a coupling component is prepared by reaction of the primary amine with acrylonitrile (H$_2$C=CHCN) and methyl acrylate (H$_2$C=CHCOOCH$_3$), the amino group adding across the activated double bond. The reason for incorporating these substituents is to enhance the fastness properties of the dye. Thus, the use of a cyanoethyl substituent in preference to a simple ethyl group in the tertiary amine coupling component generally improves fastness to light and sublimation.

In addition to benzenoid diazo components, diazotised heterocyclic amines in which the amino group is attached to a nitrogen- or sulphur-containing ring figure prominently in the preparation of disperse dyes [87,88], since these can produce marked bathochromic shifts. The most commonly used of these are the 6-substituted 2-aminobenzothiazoles, prepared by the reaction of a suitable arylamine with bromine and potassium thiocyanate (Scheme 4.31). Intermediates of this type, such as the 6-nitro derivative (4.79), are the source of red dyes, as in CI Disperse Red 145 (4.80). It has been found that dichloroacetic acid is an effective solvent for the diazotisation of 2-amino-6-nitrobenzothiazole [89]. Subsequent coupling reactions can be carried out in the same solvent system. Monoazo disperse dyes have also been synthesised from other isomeric nitro derivatives of 2-aminobenzothiazole [90]. Various dichloronitro derivatives of this amine can be used to generate reddish blue dyes for polyester [91].
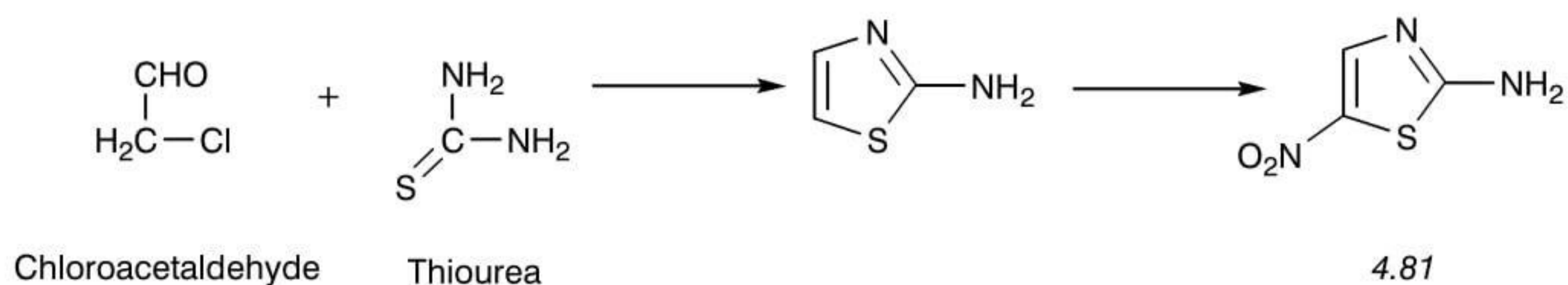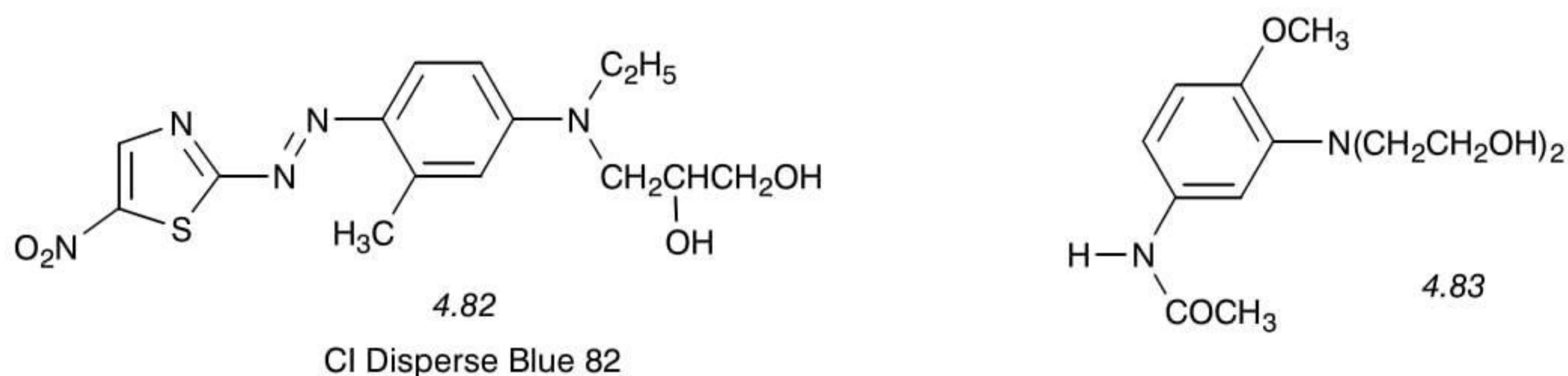

Scheme 4.31

4.79

4.80
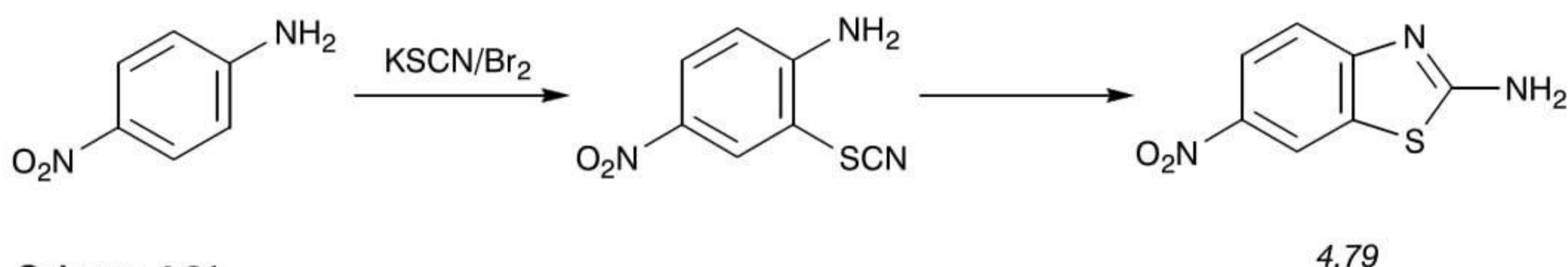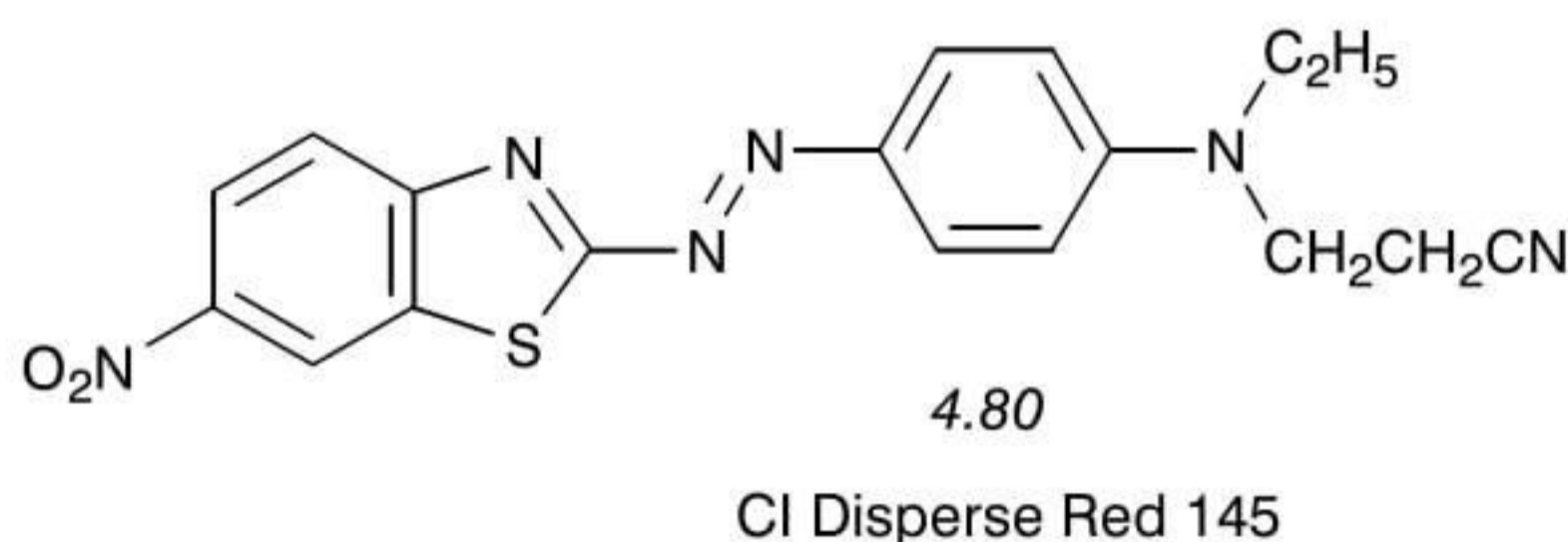
CI Disperse Red 145

The use of heterocyclic diazo components is particularly important in the preparation of blue disperse dyes. It is often difficult to prepare, diazotise and/or couple the highly electronegatively substituted diazo components of the benzene series needed to achieve blue hues, and feebly basic aminoheterocycles offer a convenient alternative. The small molecular size of these heterocyclic amines, compared with that of heavily substituted anilines, is another factor favouring their use.

One of the earliest diazo components of this type to be introduced was 2-amino-5-nitrothiazole (4.81), prepared by condensation of thiourea with chloroacetaldehyde and nitration of the resultant 2-aminothiazole (Scheme 4.32). This component yields bright dischargeable blues, such as CI Disperse Blue 82 (4.82), which have outstanding build-up, very high extinction coefficients and good fastness to burnt gas fumes. Use of diazo component 4.81 with coupling component 4.83 yields a greenish blue dye.
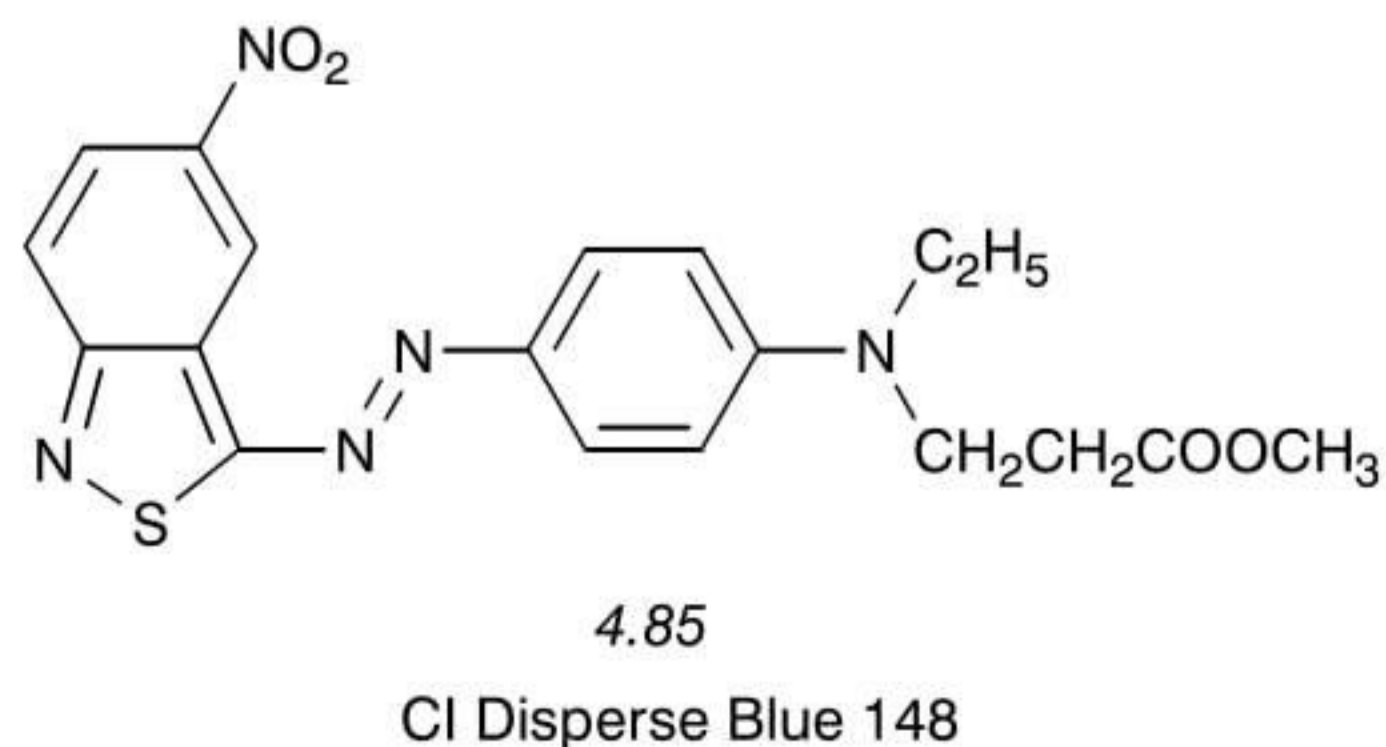
Scheme 4.32

4.82

CI Disperse Blue 82

4.83

Other examples include 3-aminobenzisothiazoles, especially the 5-nitro-derivative (4.84)[92] (synthesised as shown in Scheme 4.33) and electronegatively substituted 2-aminothiophenes (Scheme 4.34). Both of these amines, when diazotised, are capable of giving blues with arylamine coupling components. The non-benzenoid intermediate 4.84 has a strong bathochromic effect, as in CI Disperse Blue 148 (4.85). Diazotised 5-acetyl-2-amino-3-nitrothiophene (4.86) gives a greenish blue dye when coupled with compound 4.83 [93]. The corresponding dye from the diacetyl derivative of 4.83 and 2-amino-3,5-dinitrothiophene is green on polyester. An extensive range of thiophene-based monoazo disperse dyes has been examined [94].


Scheme 4.33

4.84

4.85

CI Disperse Blue 148
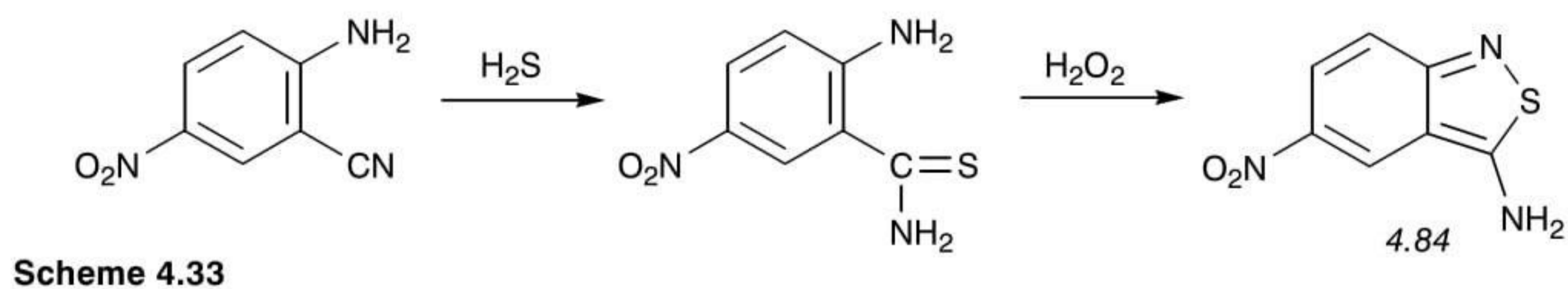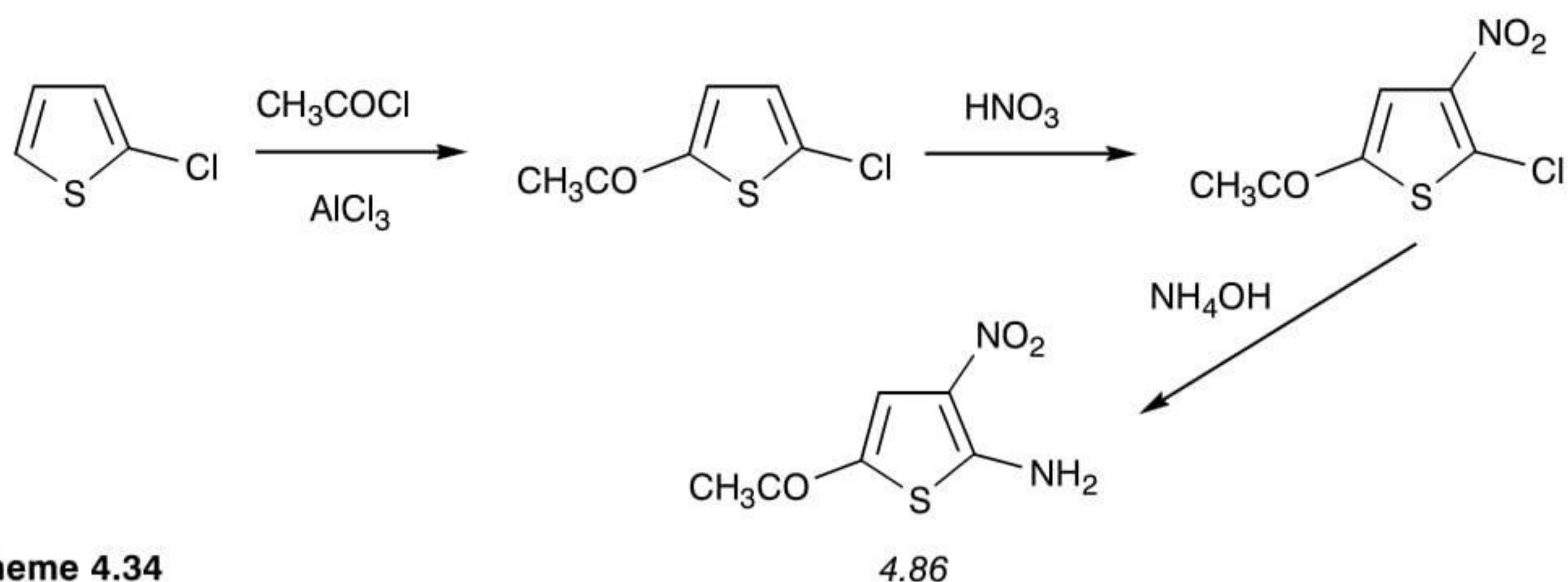
Scheme 4.34   *4.86*

Whilst monoazo dyes of small molecular size dominate the disperse dye field, the use of high-temperature dyeing and printing methods for the coloration of polyester has permitted some relaxation in the necessity for limiting molecular size. This flexibility has allowed the use of monoazo dyes such as CI Disperse Red 220 (4.87), employing a typical azoic coupling component, particularly as disperse dyes in processes for the dyeing of polyester/cotton blends. A novel development in the dyeing of such blends has been the introduction of disperse dyes such as CI Disperse Red 167 (4.88), in which the tertiary amine coupling component contains ester groupings. These groups can be hydrolysed in an alkaline clearing bath to facilitate removal of loose dye at the end of the dyeing process, thus minimising staining of the cellulosic portion of the blend.

4.87   *4.88*

CI Disperse Red 220   CI Disperse Red 167
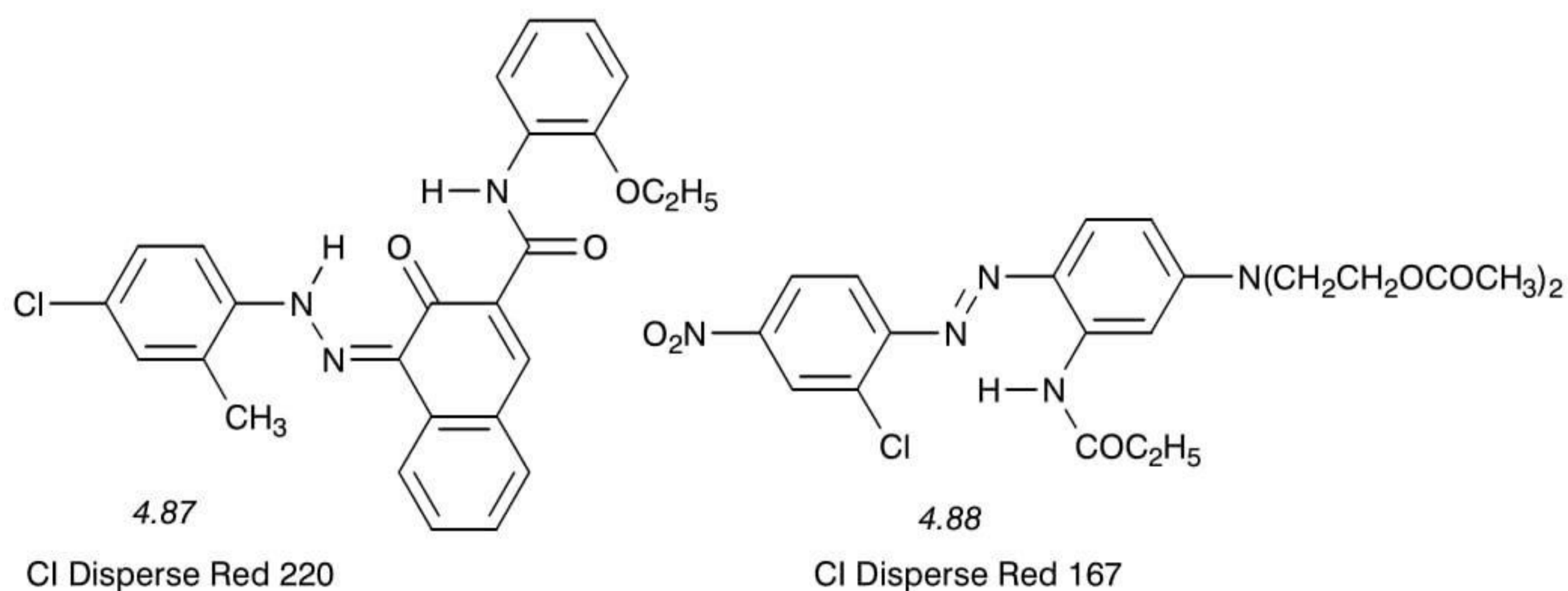
The widespread adoption of high-temperature dyeing methods has also allowed the use of simple disazo structures, such as CI Disperse Orange 13 (4.89) and CI Disperse Orange 29 (4.90), as economic dyes giving chiefly yellow and orange hues. The latter dye is known to exist in the *syn* conformation in the crystal [95]; the unsubstituted parent dye prefers the *anti* conformation. A few monoazo and disazo disperse dyes have absorption bands in the near infrared [96].

Considerable research effort has been devoted to developing a new generation of disperse dyes designed to optimise fastness to washing and minimise cross-staining of the cellulosic component of polyester/cellulosic blends [97,98]. Diester-containing monoazo disperse dye structures (4.91) that yield a dicarboxylic acid on hydrolysis and certain thienylazo blues

(4.92) that are capable of being rendered soluble by a mild alkaline aftertreatment offer considerable benefits when dyeing polyester/cellulosic blends, including:
(1) minimal cross-staining of the cellulosic fibre
(2) minimal processing time because the alkaline fixation for reactive dyes clears the disperse dye stain
(3) avoidance of a reduction clear with dithionite
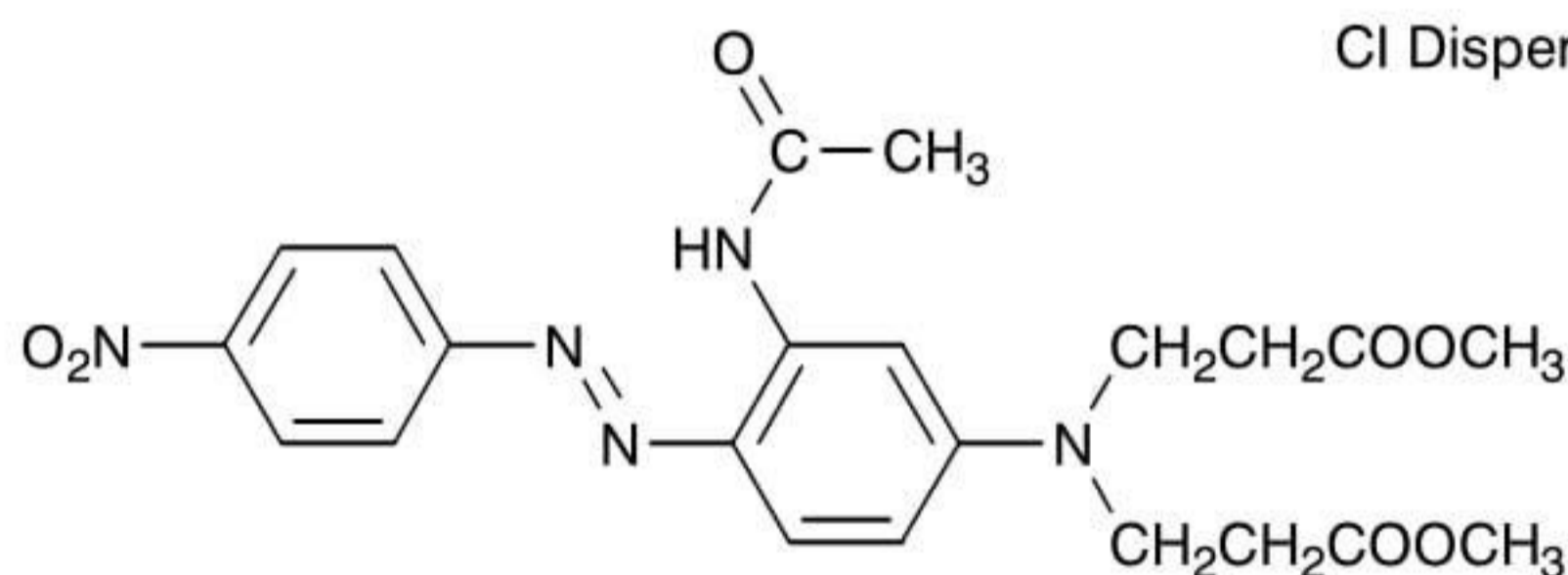(4) good washing fastness performance after heat setting during finishing.
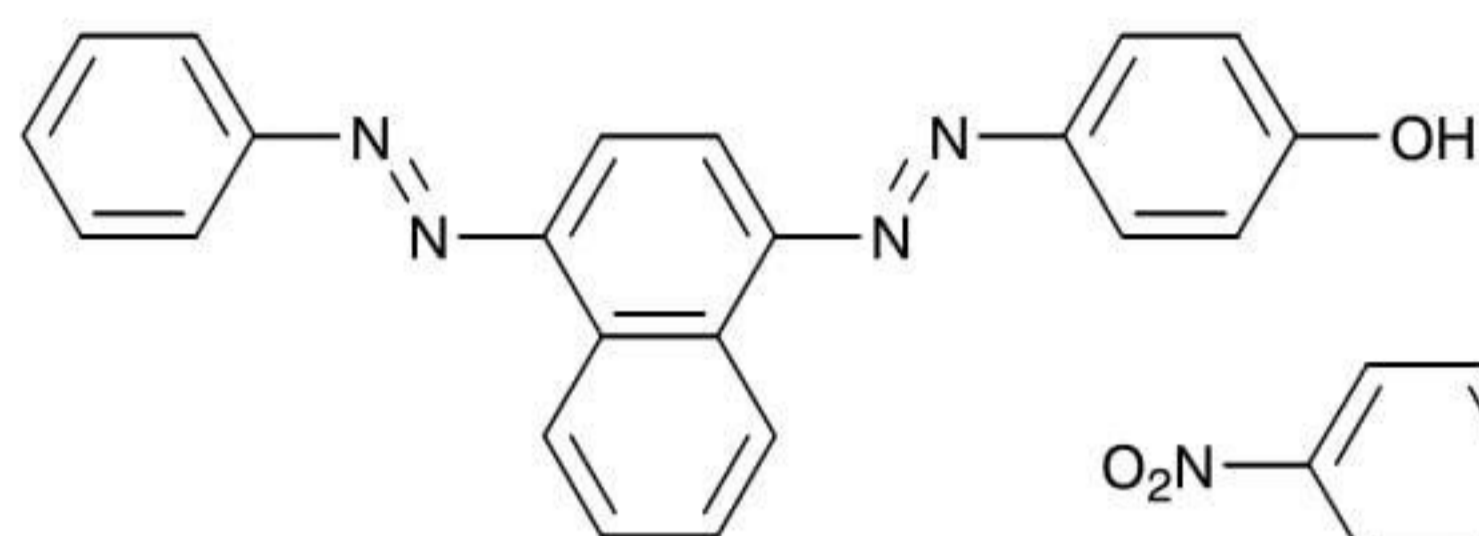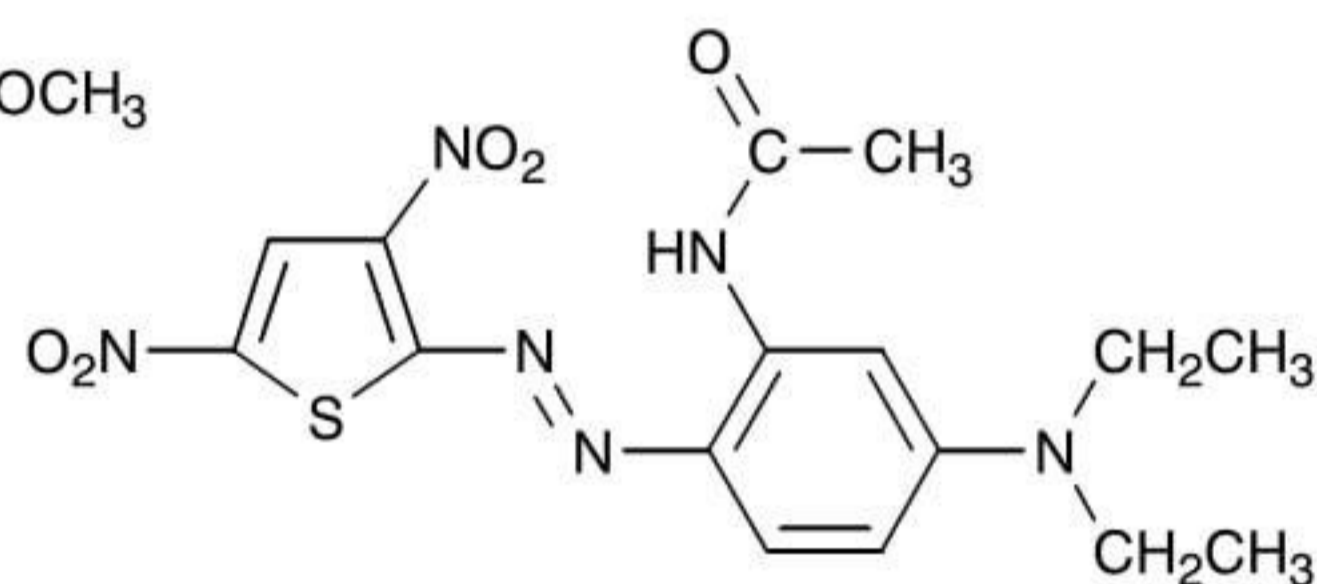
4.89

CI Disperse Orange 13
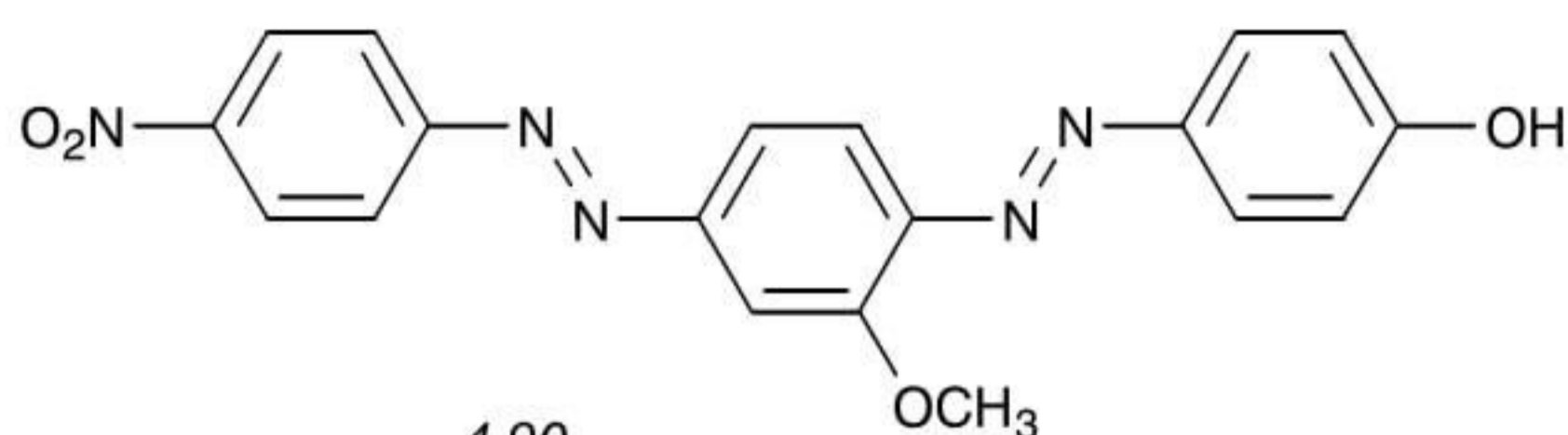
4.90

CI Disperse Orange 29

4.91

4.92

An investigation of more than twenty blue monoazo structures, mostly derived from 2-amino-3-carboxymethyl-5-nitrothiophene (4.93; X = COOCH$_3$) or its 2-amino-3,5-dinitro analogue (4.93; X = NO$_2$) and some containing hydrolysable ester groupings in the coupling component, was reported recently [99]. Depending on the dye structure, applied depth and conditions of heat setting, alkali clearing of these dyeings was as effective as a reduction clear in most instances. Comparisons between dyes containing either acetoxy (OCOCH$_3$) or carboxymethyl (COOCH$_3$) ester groups demonstrated that the lability of the thienyl ring system contributes more to alkali clearing efficiency than the nature of these hydrolysable esters.
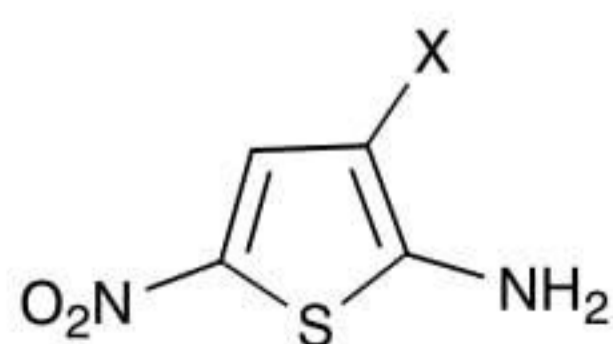
4.93

A different approach to the incorporation of a hydrolysable grouping is to synthesise monoazo derivatives of 4-aminophthalimide (4.94; R = Me or Et). This diazo component undergoes ring opening under relatively mild alkaline conditions (Scheme 4.35) to give a water-soluble structure containing a 3,4-dicarboxyphenyl grouping (4.95) without affecting the azo group present [100]. Therefore these dyes display good alkali-clearing properties, thus avoiding the need for a reduction clearing step that can result in the liberation of carcinogenic amines.
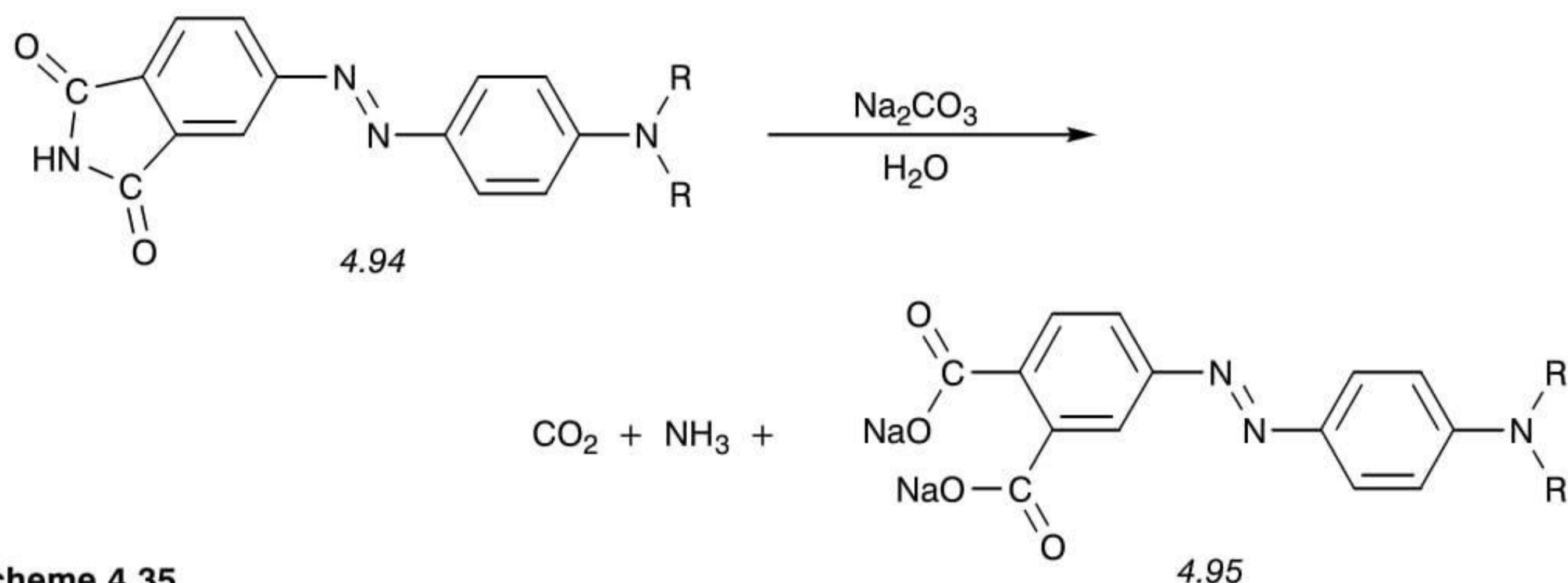

Scheme 4.35

4.10 BASIC AZO DYES

This class of dyes [101] includes some old-established products such as chrysoidine (4.96; CI Basic Orange 2) that have been of importance in the past due to their bright, strong, economical colours. Nowadays the main area of application of basic azo dyes is on acrylic fibres. The more advanced dyes developed for this purpose differ from the older ones in that the positive charge is supplied by a quaternary ammonium group rather than merely by a protonated amine. In the dyeing of acrylic fibres problems arise because the levelling properties of the adsorbed dye are poor, since the electrostatic attraction of a basic dye to the acidic centres in the fibre provides extremely strong binding, resulting in excellent fastness properties.

CI Basic Orange 2
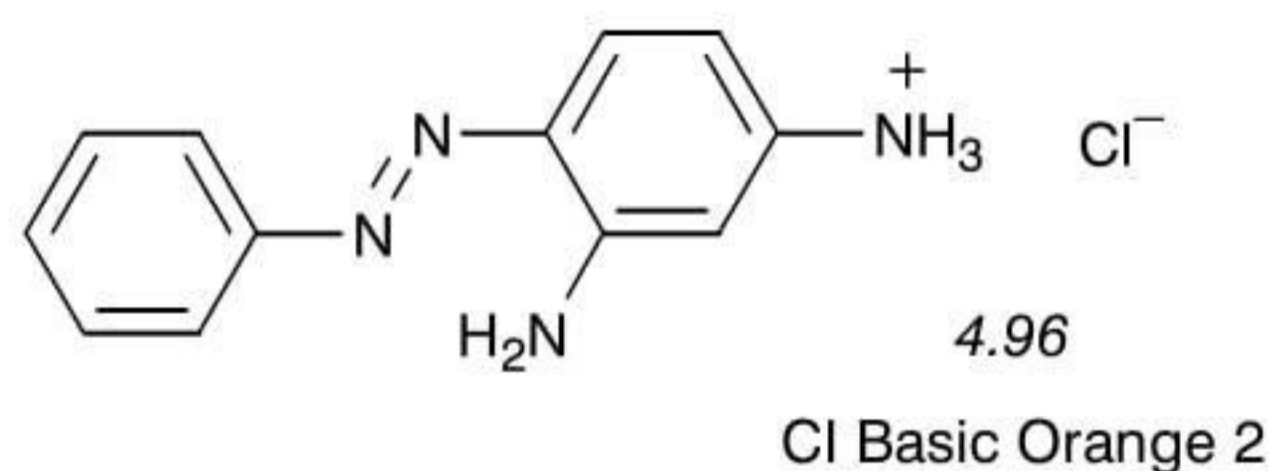
The two main classes of basic dyes vary in the way in which the basic centre is built into the molecule. The use of pendant quaternary ammonium groups, where the charge is insulated from the chromogen, allows disperse dyes to be given a cationic character. Alternatively, the cationic charge is delocalised within the chromogen.

Typically, CI Basic Red 24 (4.97) has a structure reminiscent of a disperse dye, except that a quaternary ammonium group is carried on the pendant alkyl chain in the coupling component. This coupling component is prepared by reaction of N-ethylaniline with ethylene oxide followed by conversion of the resulting β-hydroxyethyl derivative into the β-

4.97

CI Basic Red 24

4.98
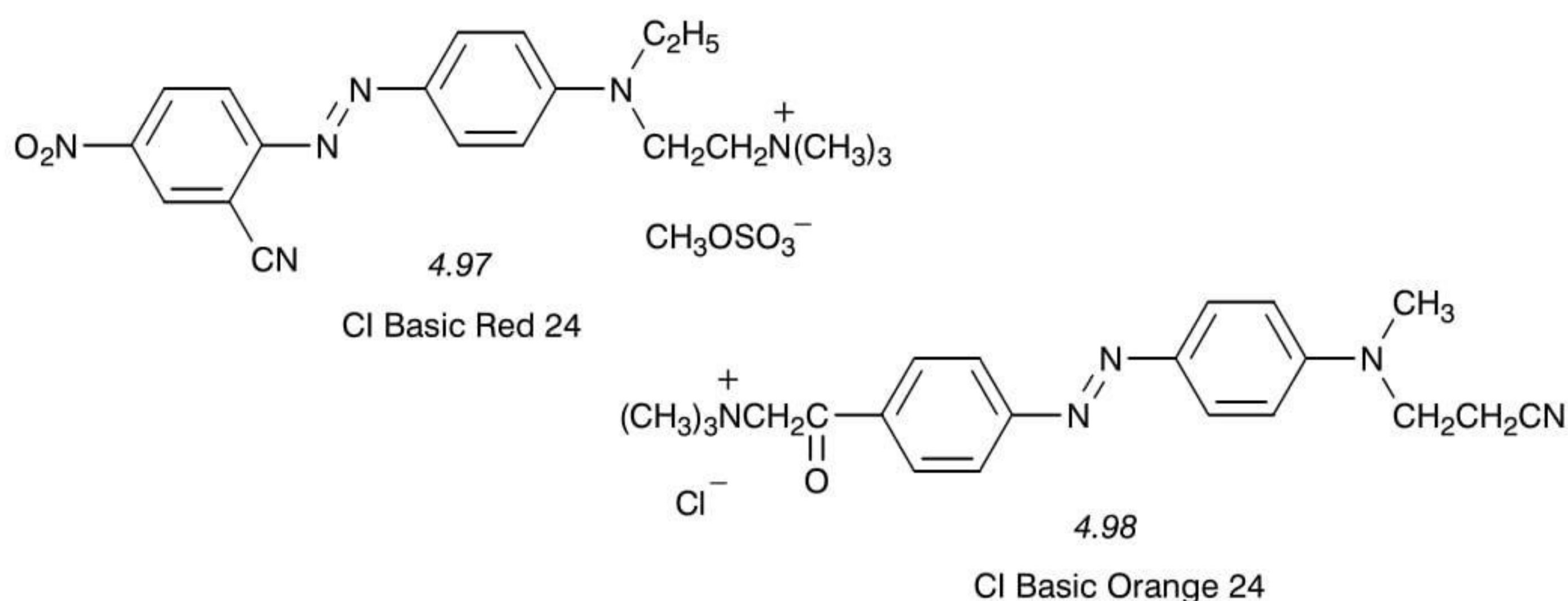
CI Basic Orange 24

chloroethyl compound, which is then treated with trimethylamine. By contrast, in CI Basic Orange 24 (4.98) the basic site is located in the diazo component.

Basic dyes in which the positive charge is supplied by a quaternised heterocyclic ring that forms part of the chromogenic system often have particularly bright, strong hues. The intermediates used here are again typical disperse dye components, quaternisation being carried out after coupling by treating the dye with an alkylating agent such as dimethyl sulphate. Using typical tertiary amine coupling components, bright blue dyes, such as CI Basic Blue 41 (4.99), are readily obtained.

4.99

CI Basic Blue 41
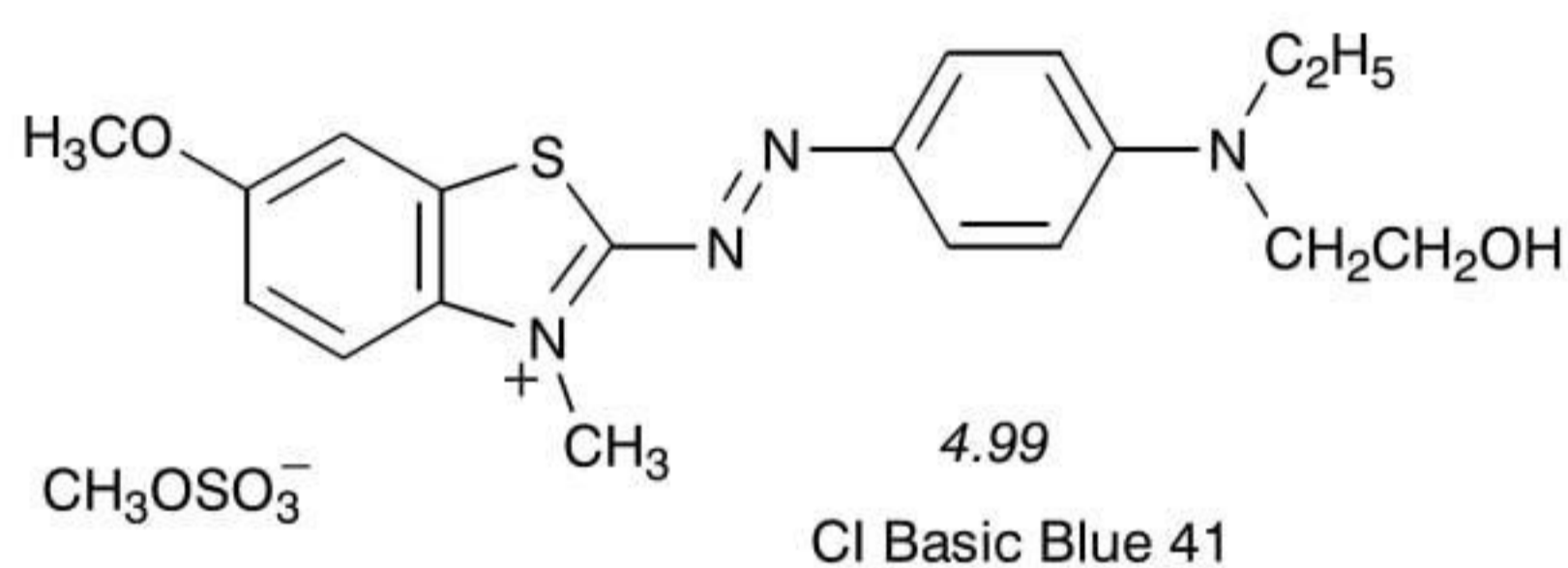
Considerable difficulties are often experienced in the preparation of basic dyes from quaternised heterocyclic diazo components. An alternative technique is to use an oxidative coupling procedure, in which a mixture of a hydrazone and a coupling component is treated with a mild oxidising agent, such as a hexacyanoferrate(III) [102]; an azo compound is then produced as shown in Scheme 4.36 for the synthesis of CI Basic Red 30 (4.100) [103]. Quaternisation of heterocyclic derivatives can lead to the formation of mixtures of isomers, as in the case of CI Basic Red 22 (4.101). As well as the 2,4-dimethyl derivative shown, the product contains about 15% of the 1,4-dimethyl isomer [104].

4.100

CI Basic Red 30

Scheme 4.36

4.101

CI Basic Red 22
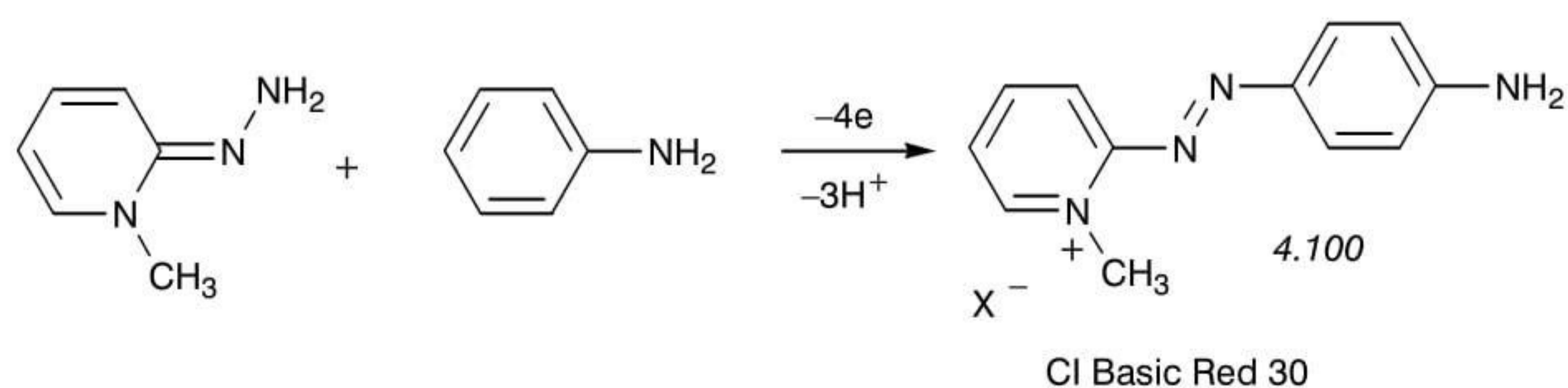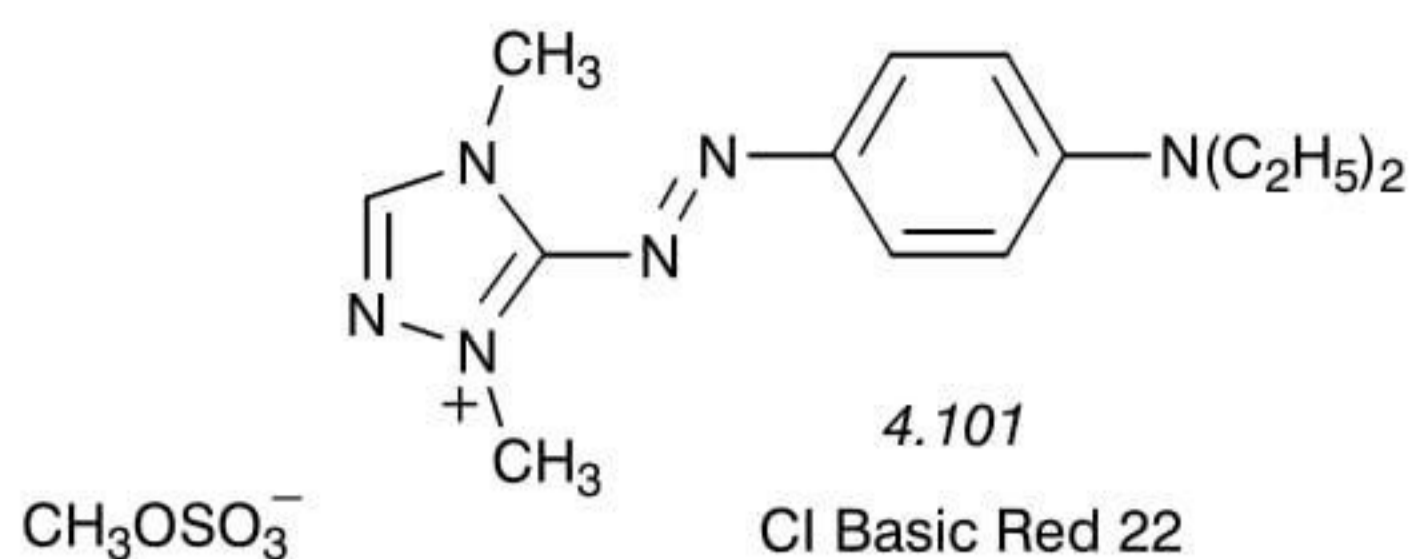
It is convenient to include in this class certain tautomeric structures that can exist either in the azo form or in the alternative hydrazone form. These dyes are the diazatrimethinecyanines, which can be viewed as being derived from the trimethinecyanines (R–CH=CH–CH=R) by replacement of two of the CH units by nitrogen atoms (R–N=N–CH=R). Such dyes are important in achieving yellow and red shades and they are often most conveniently prepared by an oxidative coupling procedure using coupling components peculiar to basic dyes. CI Basic Red 29 (4.102) and CI Basic Yellow 24 (4.103) are typical of this group.

4.102

CI Basic Red 29

4.103

CI Basic Yellow 24
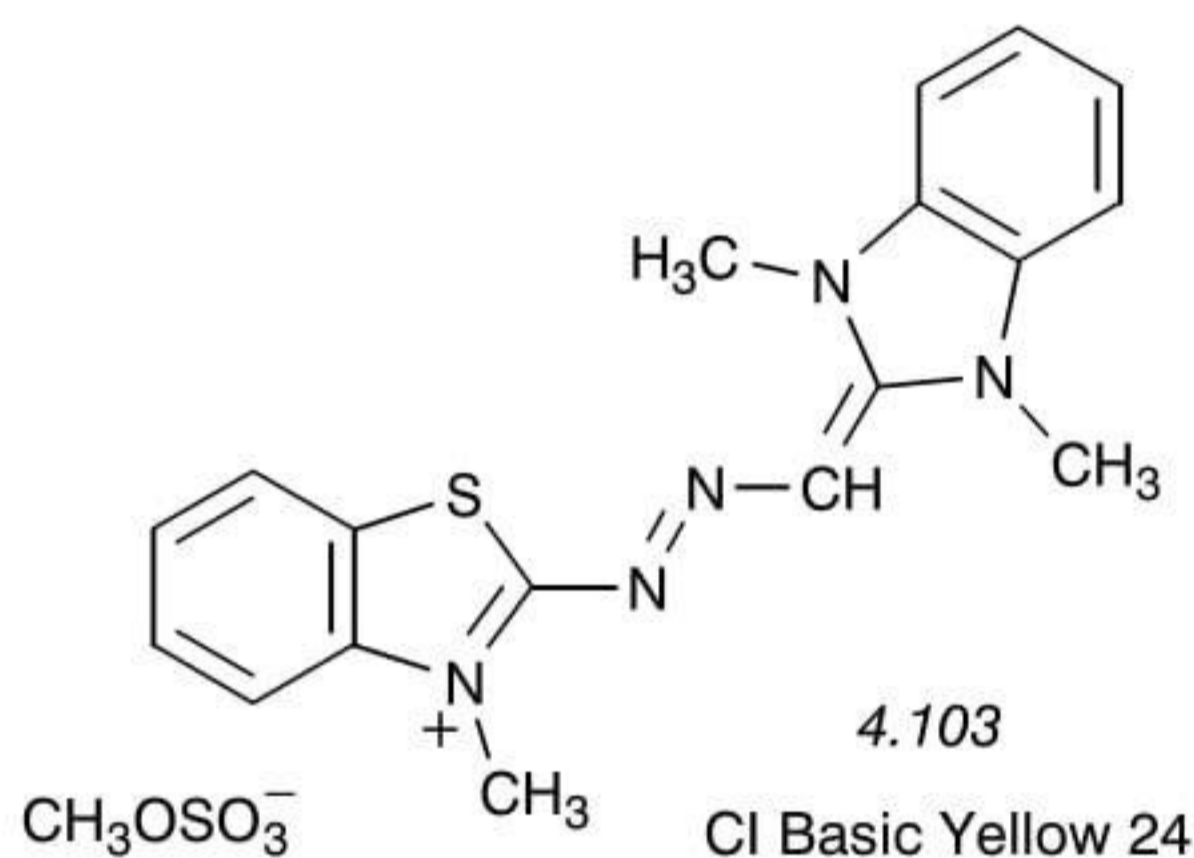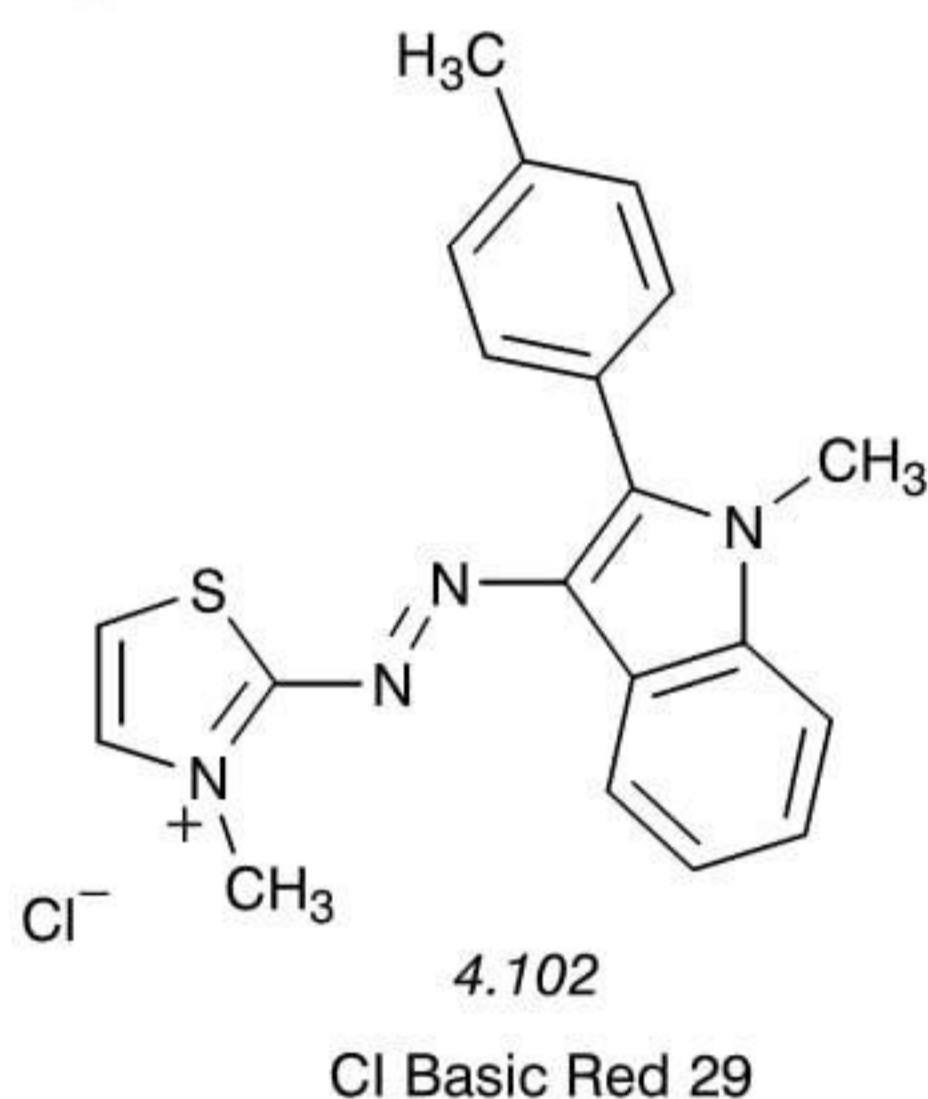
4.11 AZOIC DIAZO AND COUPLING COMPONENTS

In 1880 a process for the coloration of cotton by initial impregnation with an alkaline solution of 2-naphthol and subsequent treatment with a solution of a diazonium salt was patented by Thomas and Robert Holliday. In this process a water-insoluble monoazo dye of good fastness to washing was formed within the fibre pores. The dyer's need to diazotise the arylamine component at low temperature led to these dyes becoming known as 'ice colours' and the product obtained using diazotised 4-nitroaniline became known as Para Red. Over the next thirty years minor improvements in the process were introduced, but a major step forward was made in 1912 when Griesheim-Elektron introduced a new type of coupling component, 3-hydroxy-N-phenylnaphthalene-2-carboxamide (4.104; 3-hydroxy-2-naphthoic anilide), under the trade name Naphtol AS (CI Azoic Coupling Component 2). The guiding principle behind this advance was that the new intermediate was substantive towards cellulose and therefore was better held in place on the fibre prior to and during the treatment with a diazonium salt. Furthermore, the increased substantivity and diminished solubility of the resulting azo combination gave a marked improvement in the level of wash fastness obtained. The term 'azoic colours' was introduced in the late 1920s [105].

4.104

CI Azoic Coupling
Component 2
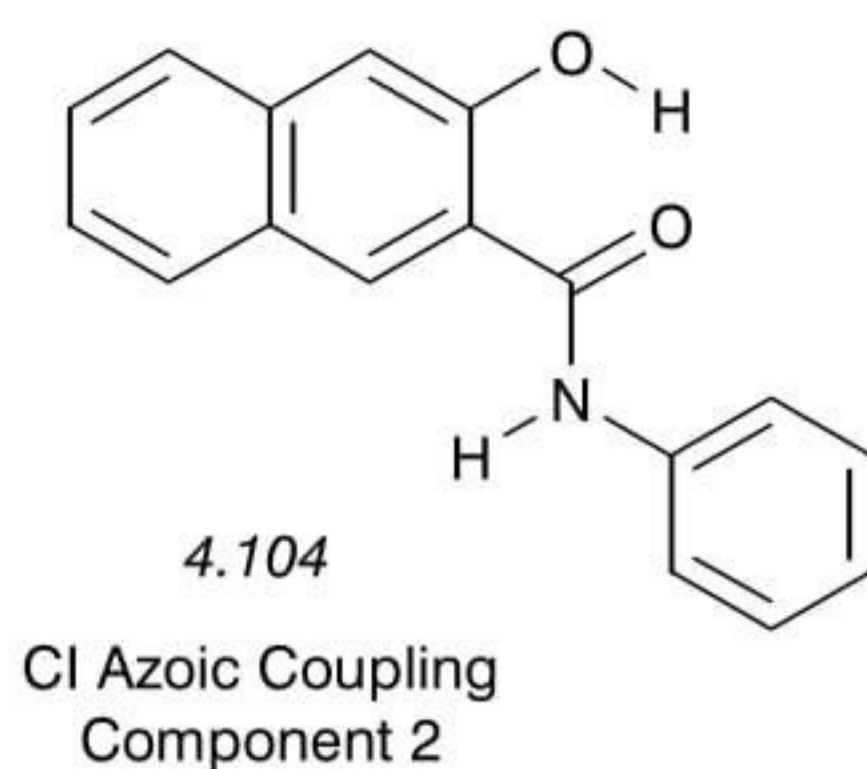
Naphtol AS is best prepared by heating together β-oxynaphthoic (BON) acid, aniline and phosphorus trichloride in an inert solvent, the initially formed intermediate (4.105) reacting further with the naphthoic acid to give the desired anilide. A range of similar products followed, with a variety of arylamines being used in place of aniline. A selection of these compounds is given in Table 4.2. An attempt has been made recently to correlate the chemical structure of azoic coupling components with their substantivity for cotton cellulose. Theoretically computed equations were derived to relate substantivity values to the van der Waals' surface and to molecular volume and hydrophobicity of the sorbed molecule. The results provide support for the hypothesis of microcrystalline multilayered micelles available for sorption of these compounds [106].
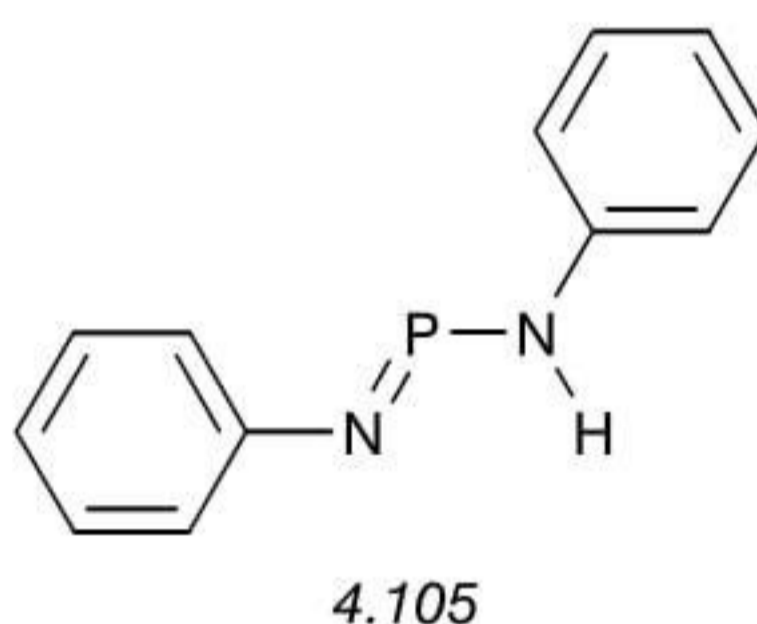

4.105

Table 4.2 Azoic coupling components

Naphtol	A.C.C.	Chemical name
AS–D	18	3-Hydroxy-2-naphthoic 2′-methylanilide
AS–ITR	12	3-Hydroxy-2-naphthoic 5′-chloro-2′,4′-dimethoxyanilide
AS–OL	20	3-Hydroxy-2-naphthoic 2′-methoxyanilide
AS–PH	14	3-Hydroxy-2-naphthoic 2′-ethoxyanilide
AS–TR	8	3-Hydroxy-2-naphthoic 4′-chloro-2′-methylanilide

A.C.C.   CI Azoic Coupling Component

Ranges of diazotisable amines were supplied, designed to go with these coupling components and known as Fast Bases, despite being marketed as the phenylammonium chlorides (hydrochloride salts). Whilst the hues obtainable at first were limited to the orange to red region of the colour gamut, the later introduction of amines heavily substituted with electron-donating groups allowed extension into the violet to blue region. Examples of Fast Bases are given in Table 4.3; the last two entries in this table have been classified by ETAD as toxic compounds [107].

Table 4.3 Fast bases

| Fast base	A.D.C.	Chemical name
Blue BB	20	4-Benzoylamino-2,5-diethoxyaniline hydrochloride
Orange GC	2	3-Chloroaniline hydrochloride
Orange RD	49	2-Chloro-5-trifluoromethylaniline hydrochloride
Red ITR	42	2-Methoxyaniline-5-sulphondiethylamide hydrochloride
Red KB	32	5-Chloro-2-methylaniline hydrochloride
Red RC	10	5-Chloro-2-methoxyaniline hydrochloride
Red RL	34	2-Methyl-4-nitroaniline hydrochloride
Red TR	11	4-Chloro-2-methylaniline hydrochloride
Scarlet GG	3	2,5-Dichloroaniline hydrochloride
Violet B	41	4-Benzoylamino-2-methoxy-5-methylaniline hydrochloride

A.D.C.   CI Azoic Diazo Component

Extension into other hues was not possible using anilides of BON acid, and, to meet this requirement, coupling components of differing structure but similar levels of substantivity were introduced (4.106 to 4.109; the arrows indicate coupling positions). Yellow dyeings were obtained by using the bis-acetoacetarylamide derived from 3,3′-dimethylbenzidine, marketed as Naphtol AS-G (4.106; CI Azoic Coupling Component 5). Browns were supplied by using the 2′-methylanilide, Naphtol AS-BR (4.107; X = CH$_3$, Y = H; CI Azoic Coupling Component 3) and the 4′-chloroanilide, Naphtol AS-LB (4.107; X = H, Y = Cl; CI Azoic Coupling Component 15) of 2-hydroxycarbazole-1-carboxylic acid. Blacks resulted from the 4″-methoxy-2″-methylanilide of 3′-hydroxy-1,2-benzocarbazole-2′-carboxylic acid, Naphtol AS-SR (4.108; CI Azoic Coupling Component 25). Duller greens stemmed from the 2′-methylanilide of 3-hydroxyanthracene-2-carboxylic acid, Naphtol AS-GR (4.109; CI Azoic Coupling Component 36), whilst bright greens were eventually provided by Naphtol AS-FGGR (CI Azoic Coupling Component 108), the reaction product of copper or nickel phthalocyanine with an aminoarylpyrazolone, the constitution of which has not been disclosed [108].

4.106
CI Azoic Coupling Component 5

4.107
CI Azoic Coupling Component 3

4.108
CI Azoic Coupling Component 25

4.109

CI Azoic Coupling Component 36

4.110
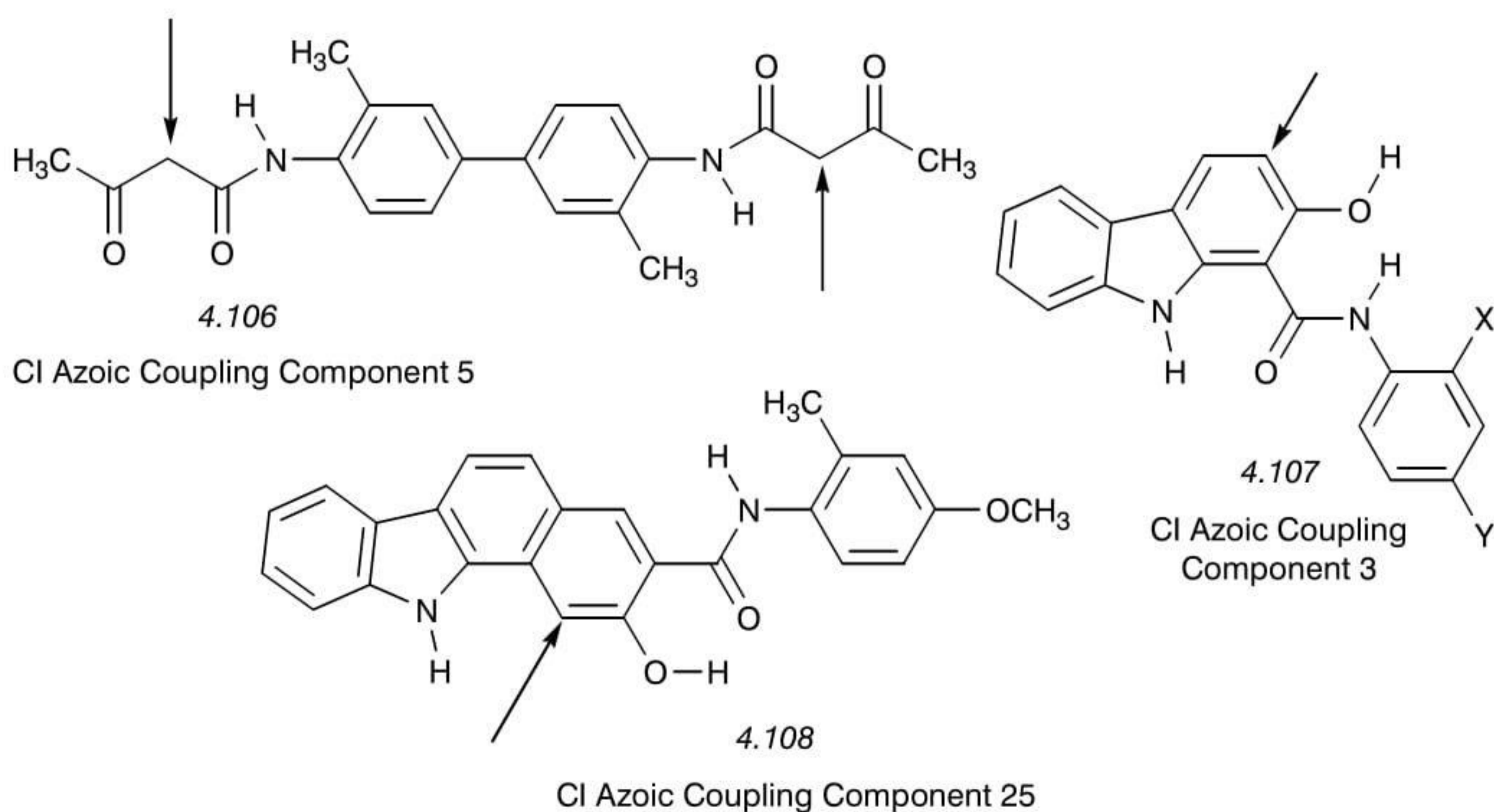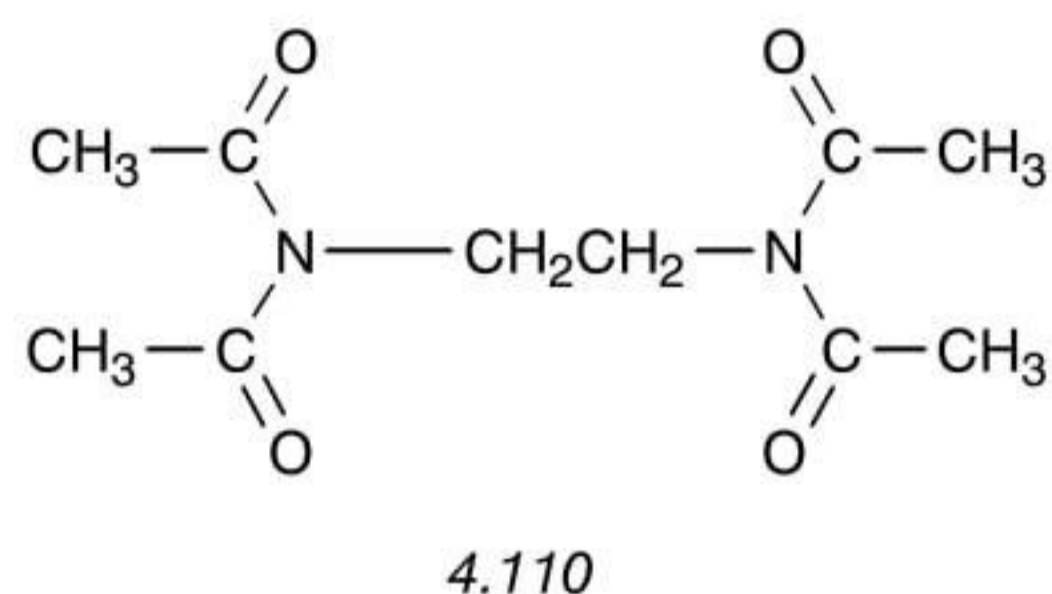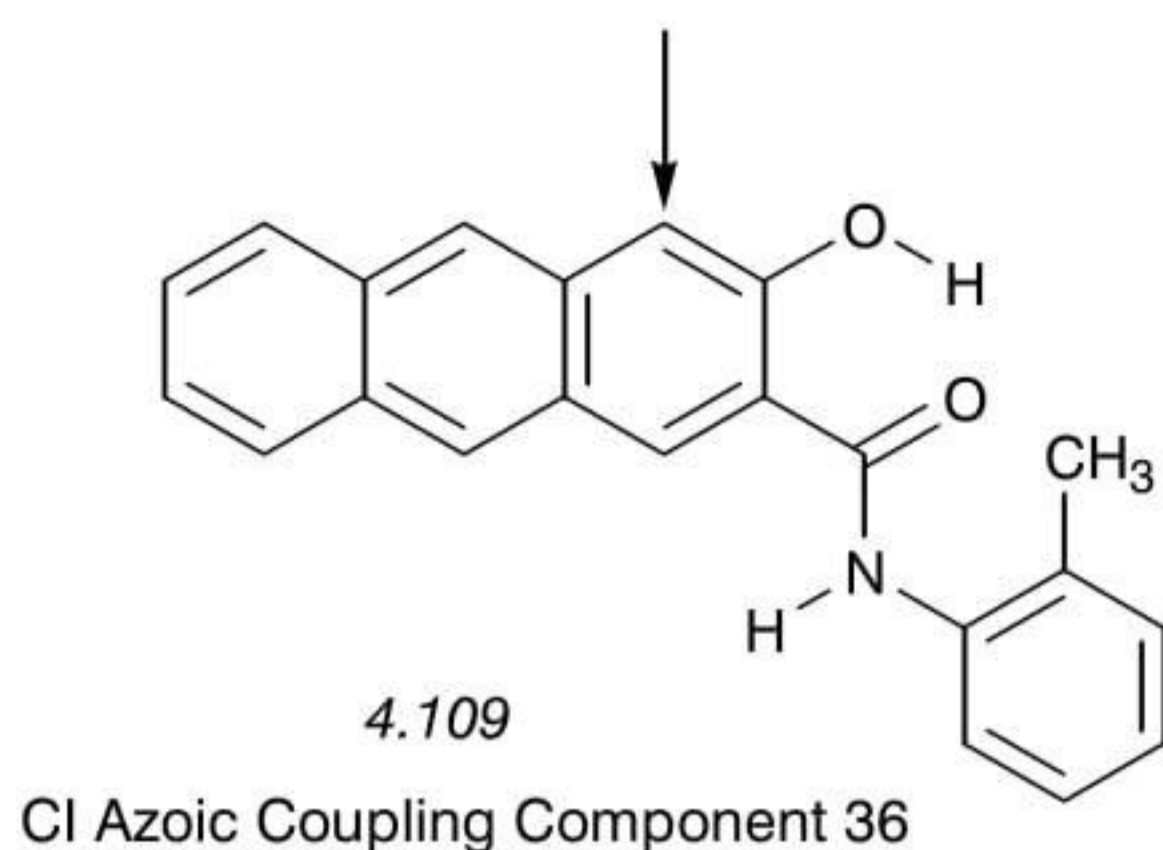
Azoic coupling can be achieved on silk where free amino groups have been introduced into the fibroin structure by condensation with 4-aminobenzaldehyde. The diazotised material can then be treated with an azoic coupling component [109].

As recommended laundering temperatures have tended to fall in recent years, a bleach consisting of sodium perborate activated by addition of tetra-acetylethylenediamine (4.110; TAED) has become an important component of household detergent formulations. This system is effective at temperatures as low as 40–50 °C. A recent study of the effects of TAED-activated peroxy bleaching on the colour fastness of azoic dyeings has demonstrated that the sensitivity of these products can be related to their chemical structure. Electron-donating substituents in the diazo component enhance resistance to oxidative attack under these conditions, as do the size and complexity of substituents present in the coupling component [110].

4.12 STABILISED DIAZONIUM SALTS AND AZOIC COMPOSITIONS

4.12.1 Fast Salts

As the range of components available for use in the azoic dyeing process expanded, research was simultaneously targeted on improvements designed to make the process more attractive to the commercial dyer. The necessity for the dyer to diazotise the Fast Base was removed with the introduction of stabilised diazonium salts [111], known as Fast Salts. Stabilisation was achieved by a judicious selection of the counter-ion to the diazonium cation; various anions have found use in commercial Fast Salts and some examples are listed in Table 4.4. Particularly effective is the diazonium tetrachlorozincate, which can be readily prepared by adding an excess of zinc chloride solution to a solution of the diazonium salt. The precipitated complex diazonium salt is usually admixed with an inert diluent, which enhances its stability, and in use the dyer only needs to dissolve the powder in water to prepare the necessary diazonium salt solution.

4.12.2 Rapid Fast colours

In addition to these 'active' stabilised diazonium salts that give a diazonium salt solution immediately on dissolving in water, there are certain derivatives of diazonium compounds from which the diazonium salt can be readily regenerated. One group of such derivatives is the class of compounds known as *anti*-diazotates [112]. Diazotates are formed when the pH
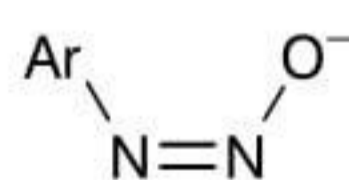
Table 4.4 Stabilised diazonium salts

| Fast salt	A.D.C.	Stabilising anion and parent base
		Tetrachlorozincate
Black K	38	4-Amino-2,5-dimethoxy-4'-nitroazobenzene
Blue B	48	3,3'-dimethoxybenzidine (*o*-dianisidine)
Blue BB	20	4-Benzoylamino-2,5-diethoxyaniline
Bordeaux GP	1	4-Methoxy-2-nitroaniline
Orange GR	6	2-Nitroaniline
Red AL	36	1-Aminoanthraquinone
Red 3GL	9	4-Chloro-2-nitroaniline
Red ITR	42	2-Methoxyaniline-5-sulphondiethylamide
Scarlet GG	3	2,5-Dichloroaniline
Scarlet R	13	2-Methoxy-5-nitroaniline
		Tetrafluoroborate
Orange GC	2	3-Chloroaniline
Red GG	37	4-Nitroaniline
		Naphthalene-1,5-disulphonate
Red B	5	2-Methoxy-4-nitroaniline
Red TR	11	4-Chloro-2-Methylaniline
		Chloride
Variamine Blue B	35	4-Amino-4'-methoxydiphenylamine

A.D.C.   CI Azoic Diazo Component

of a diazonium salt solution is raised to between 9 and 12 with an alkali metal hydroxide. The *syn*-diazotates initially formed are somewhat unstable and isomerise into the stable *anti*-diazotate form. The evidence overwhelmingly points to the two forms being stereoisomers (4.111 and 4.112, respectively).

Stable mixtures of *anti*-diazotates and Naphtols were marketed as Rapid Fast colours for printing onto fabric with development of the azoic dye by steaming. The *anti*-diazosulphonates (4.113) [113], which were prepared by treatment of a diazonium salt with sodium sulphite and which regenerate the diazonium ion on treatment with an oxidising agent, found similar use. Both ranges are now of only historical interest.

| 4.111 | 4.112 | 4.113 |
| *syn*-diazotate | *anti*-diazotate | |
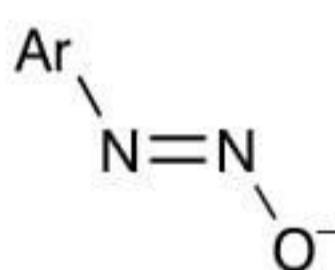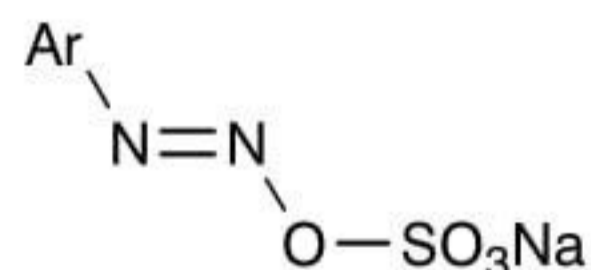
### 4.12.3 Rapidogens and Neutrogenes

Superior 'passive' stabilised diazo compounds are afforded by the diazoamino compounds (triazenes) that arise by reaction of diazonium salts with a variety of secondary amines [114]. Typically, sarcosine (CH_3NHCH_2COOH), which gives products based on structure 4.114, as well as *N*-methyltaurine ($CH_3NHCH_2CH_2SO_3H$) and *N*-methylaniline-4-sulphonic acid,

have been used for this purpose. Again these were marketed in admixture with a coupler for application to cotton and colour development by acid steaming, under the tradename Rapidogen in the 1930s [114]. A disadvantage was the corrosive effect of the acid (usually acetic or formic) on the equipment, but this problem was eventually overcome with the Neutrogene range [115], which used an *N*-substituted anthranilic acid, such as 2-carboxyphenylglycine (4.115), as the secondary amine required for triazene formation.

These products, which have been copied by other manufacturers under various tradenames, are designed specifically for printing applications. Azoic dyeing applications were catered for in 1967 when Hoechst introduced the Azanil salts, a limited range of mixtures of substantive triazenes and Naphtols that can be absorbed onto the fabric and the colour developed by acidification of the dyebath.
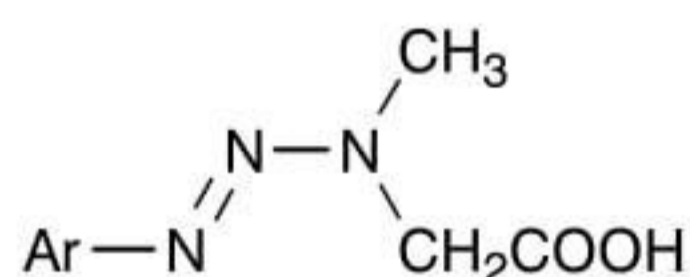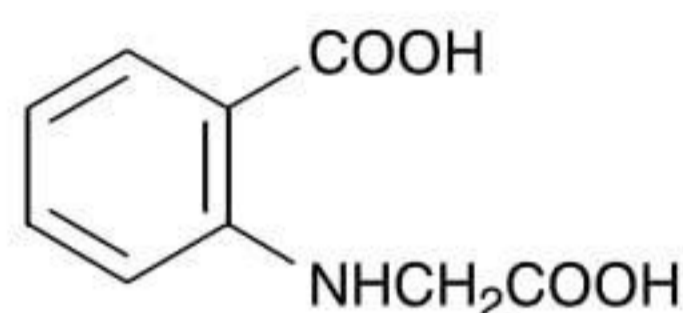

4.114   4.115

4.13 AZO PIGMENTS PRODUCED BY FINAL COUPLING

Insoluble azo pigments produced by a final coupling stage are in the main made from conventional azoic dye intermediates and find wide use as general-purpose pigments where the highest fastness is not essential. For yellow pigments acetoacetarylamide coupling components are the most commonly employed, but the monoazo combinations derived from these, such as CI Pigment Yellow 1 (4.116), are generally of poor fastness to heat and solvents. Superior properties are shown by disazo pigments of the $E_1 \leftarrow D \rightarrow E_2$ type, which are often based on the use of 3,3′-dichlorobenzidine as tetrazo component. A typical disazo pigment is CI Pigment Yellow 170 (4.117). Colour and constitution relationships in azoacetoacetanilide pigments have been examined [116]. Pigments of this type can be identified and analysed by spectroscopic and chemical methods [117].
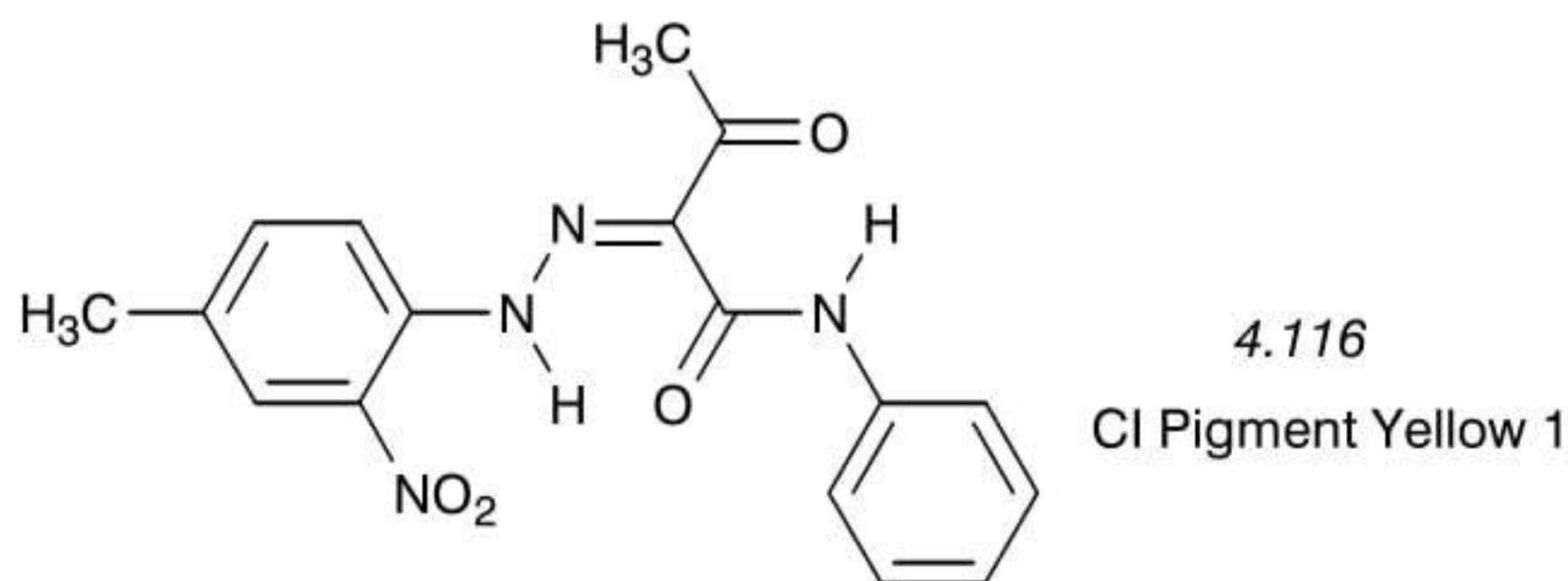

4.116
CI Pigment Yellow 1
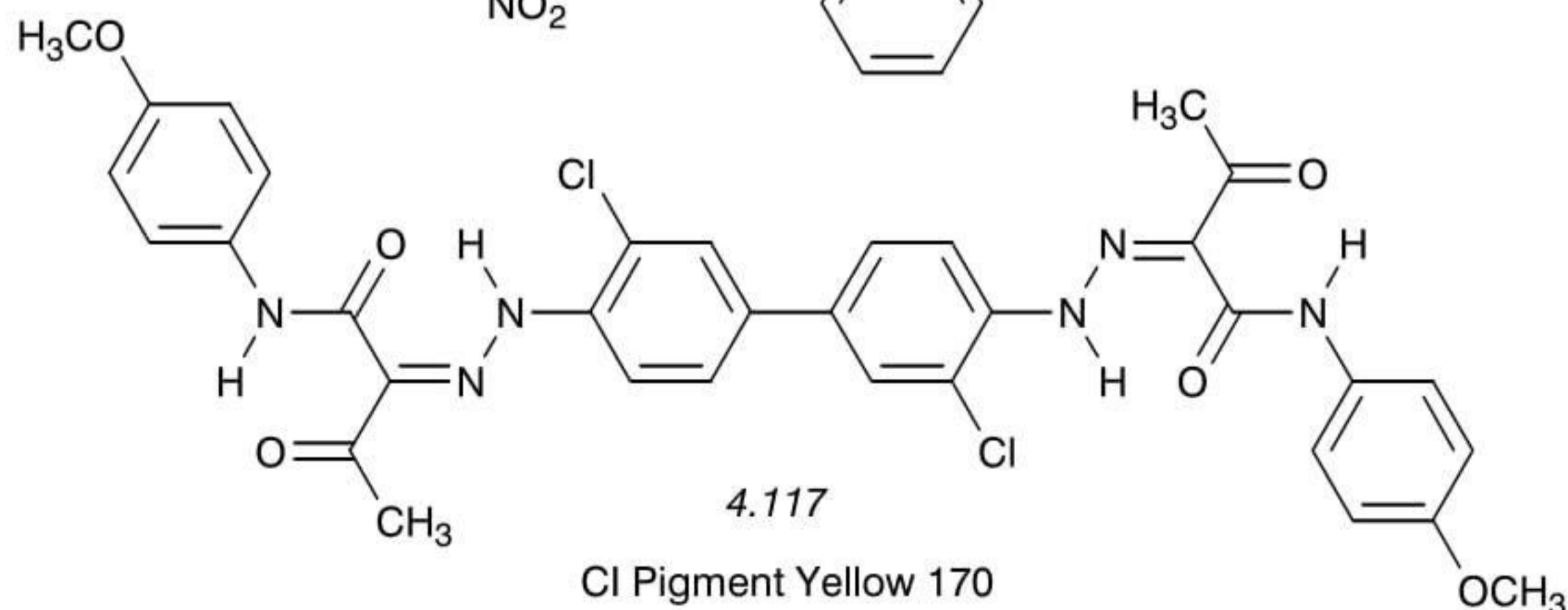
4.117
CI Pigment Yellow 170

For orange colours, simple 2-naphthol derivatives are the most commonly used coupling components as, for instance, in 2,4-dinitroaniline→2-naphthol (4.118; CI Pigment Orange 5). As in the yellow series, superior disazo pigments can be prepared using 3,3′-dichlorobenzidine as tetrazo component with derivatives of 1-phenyl-3-methylpyrazol-5-one as couplers.

4.118
CI Pigment Orange 5
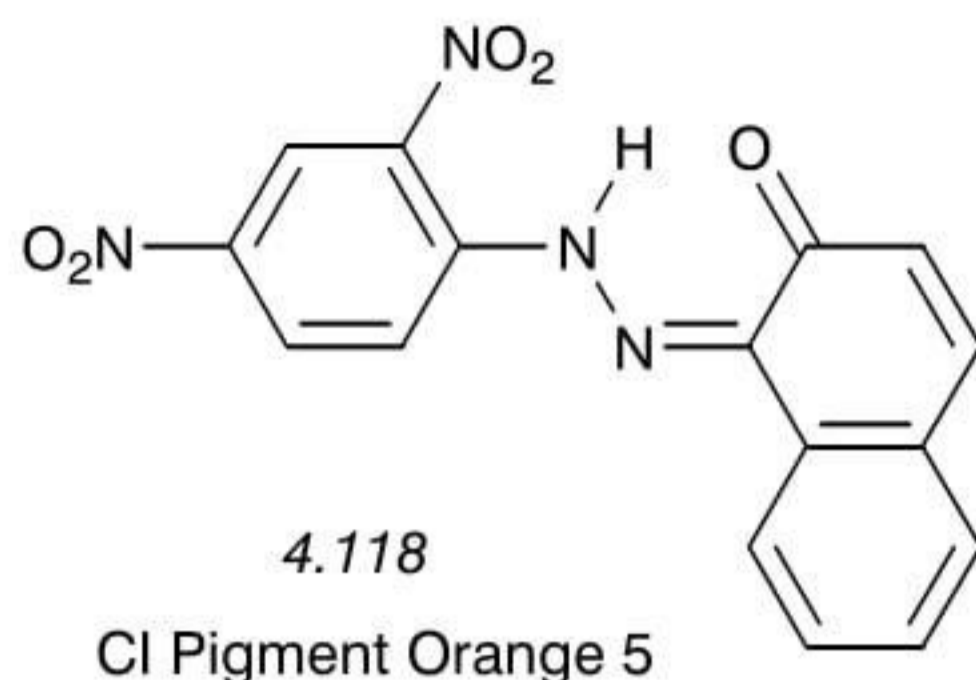
In the red to violet sector Naphtol AS and its derivatives are widely used. Simple monoazo combinations such as 2,5-dichloroaniline and Naphtol AS serve where high heat and solvent fastness are not essential, but for better properties polar features, such as amide linkages, are incorporated. CI Pigment Red 245 (4.119), CI Pigment Red 188 (4.120) and CI Pigment Violet 50 (4.121) are typical of this group.

4.119
CI Pigment Red 245

4.120
CI Pigment Red 188

4.121
CI Pigment Violet 50
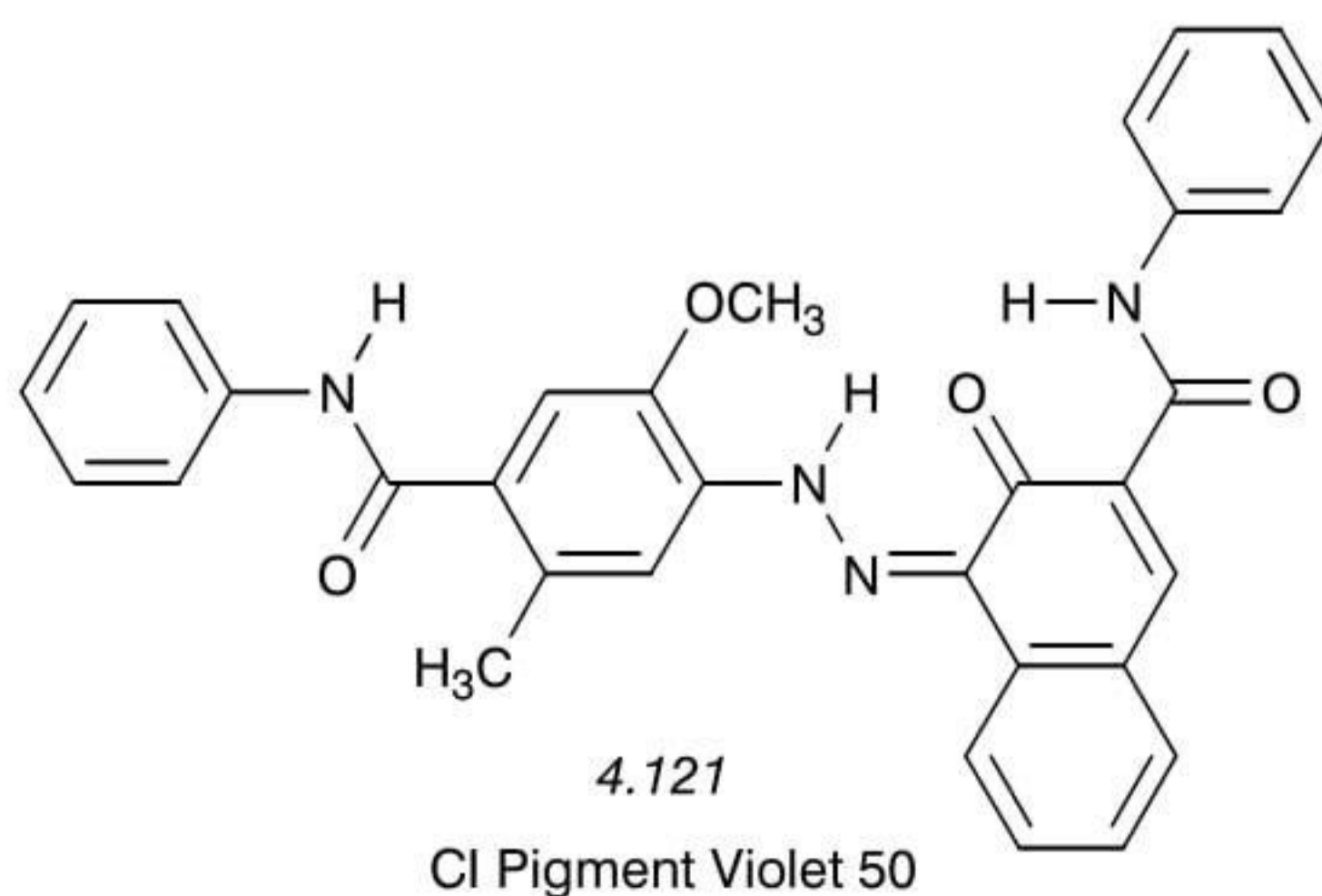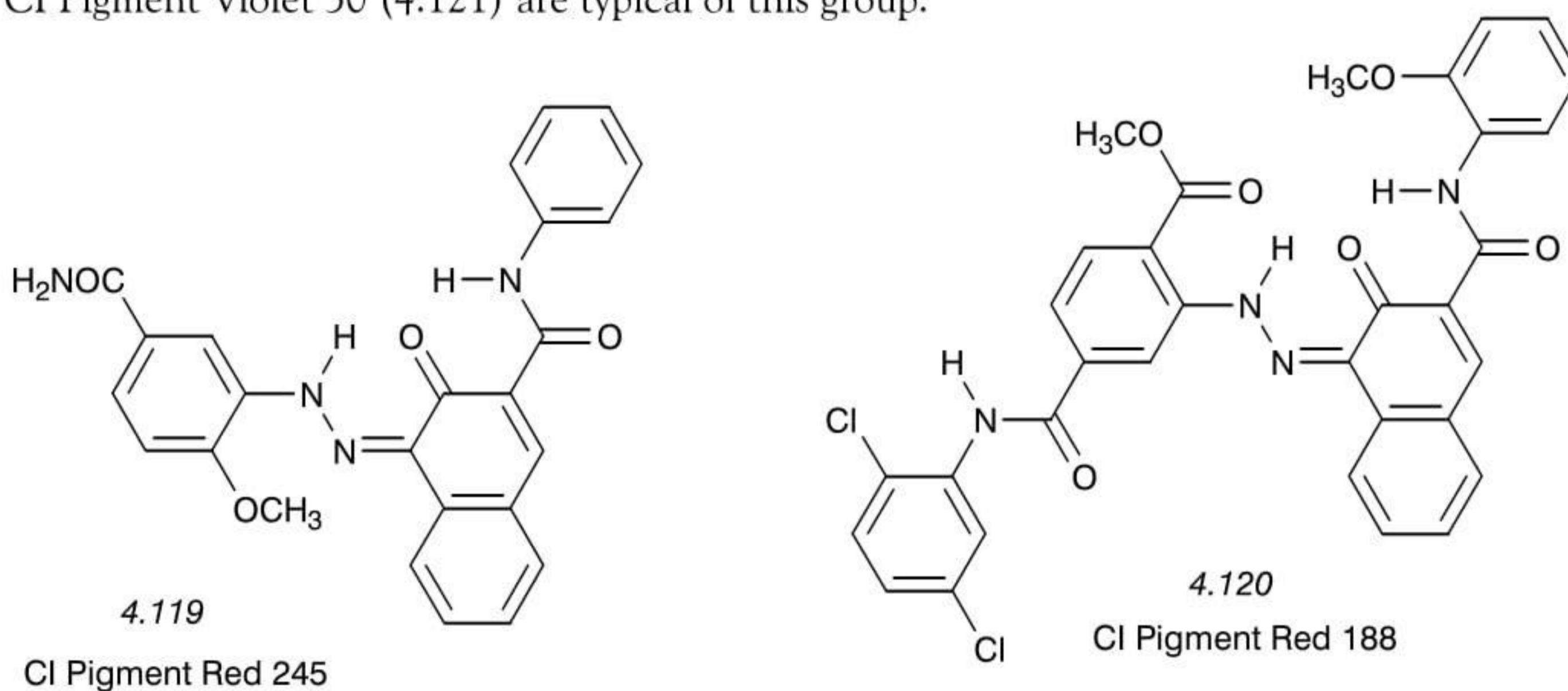
In the blue region, conventional azoic combinations are used as pigments and the adoption of *o*-dianisidine as tetrazo component allows the disazo type to be produced, such as CI Pigment Blue 25 (4.122).

4.122
CI Pigment Blue 25
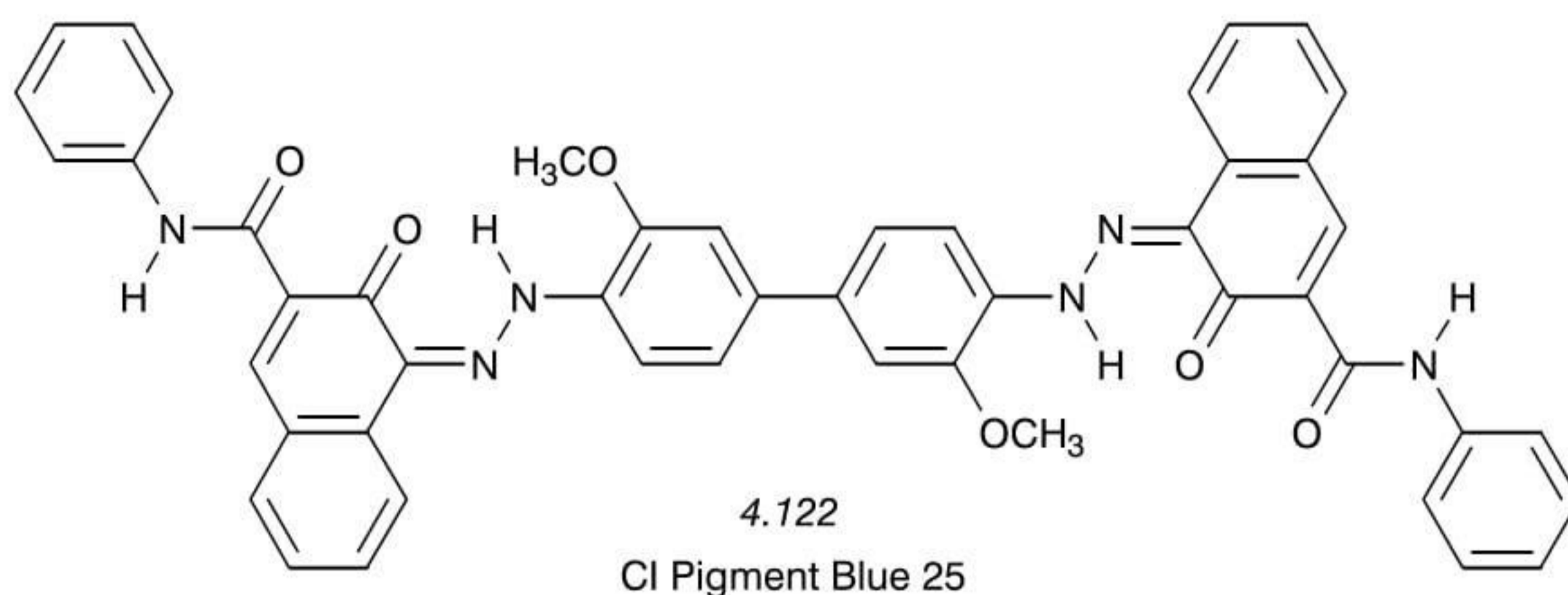
The objective in preparing a pigment is to produce a highly insoluble organic compound and in order to approach this ideal it is necessary to resort to intermediates that themselves have only very limited solubility. These inevitable difficulties in preparation limit the fastness achieved from a final coupling process and have led to the development of alternative procedures for the production of high-grade azo pigments; these alternatives are discussed elsewhere (section 2.3).

The wholly organic azo compounds discussed above have the soft texture and high tinctorial strength that are desired pigmentary properties. Somewhat inferior in these properties are the 'lakes' of sulphonated azo compounds, which are also widely used as pigments. These 'lakes' are insoluble salts, usually calcium or barium salts of sulphonated arylamines linked to cheap coupling components, which rely on the polar character of the ionic bond to provide their low solubility. Examples are CI Pigment Red 57:1, the calcium lake of compound 4.123, and CI Pigment Red 53:1, the barium lake of compound 4.124.

Organic pigments have been reviewed [118]. X-ray powder diffraction data of many organic colorants have been collected and discussed [119].

4.123
CI Pigment Red 57

4.124
CI Pigment Red 53
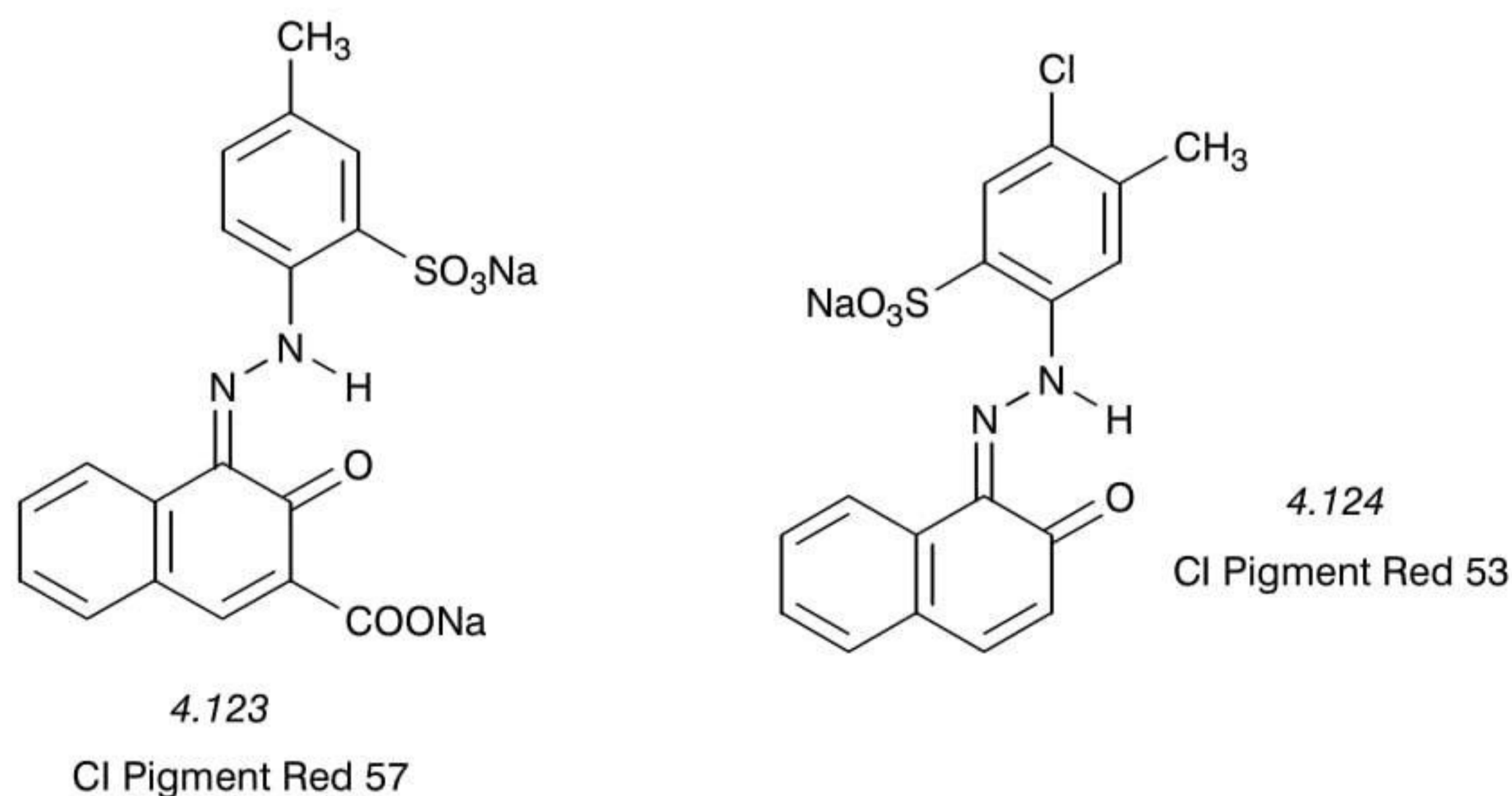
4.14 IMPLICATIONS OF NEW TECHNOLOGY IN DIAZOTISATION AND COUPLING

The manufacture of azo dyestuffs has been for many years a batch operation, individual batches of dye being made in multipurpose plant, isolated by filtration techniques, stove-dried and standardised. The traditional processes [120] are now steadily being replaced [121,122] by more efficient production methods that offer greater cost-effectivenes and

improved working conditions. Although most azo dye production is still carried out by batch operation in vastly improved plants, more dedicated continuous units for the manufacture of high-volume products are being introduced. In these plants the diazotisation and coupling steps are carried out continuously by computer-controlled metering of the intermediates and reactants into a tube, flow rates being chosen to allow the reaction time to be less than the dwell time of the reaction mixture in the tube. The product is still usually isolated by filtration but, even here, automatic discharging has removed much of the heavy physical effort and dirty conditions previously endured. Spray drying of pre-standardised pastes with careful attention to particle form provides much improved products for the user. The supply of dyes as concentrated solutions allows the automatic metering of dyestuffs by the user, making automation easier and allowing greater control over dyeing conditions. These improvements in manufacturing technique, together with the availability of a much wider variety of analytical methods, serve to ensure that the user is supplied with a high-quality product at an acceptable price.

REFERENCES

1. P Griess, *Ann.*, **106** (1858) 123; **113** (1860) 201; *Compt. Rend.*, **49** (1859) 77.
2. P Griess, *Ann.*, **137** (1866) 85; *Ber.*, **9** (1876) 627.
3. H Zollinger, *Color chemistry*, 2nd Edn (Weinheim: VCH, 1991) Chapter 7.2.
4. P Rys in *Physico-chemical principles of color chemistry*, Eds A T Peters and H S Freeman (London: Blackie, 1996) Chapter 1.2.
5. W Bradley, *J.S.D.C.*, **75** (1959) 289.
6. K Bredereck, B Gülec, B Helfrich and S.Karaca, *Dyes and Pigments*, **9** (1988) 153.
7. H Zollinger, *Color chemistry*, 2nd Edn (Weinheim: VCH, 1991) Chapter 7.3.
8. V Chmatal and Z J Allan, *Coll. Czech. Chem. Commun.*, **30** (1965) 1205.
9. ETAD Information Notice No 6 (July 1997).
10. A Geisberger, *J.S.D.C.*, **113** (1997) 197.
11. Y S Szeto and G Taylor, *J.S.D.C.*, **113** (1997) 103.
12. U Sewekov and A Westerkamp, *Melliand Textilber.*, **78** (1997) 56.
13. B Küster and U Wahl, *Textilveredlung*, **32** (1997) 121.
14. K Hübner, E Schmele and V Rossbach, *Melliand Textilber.*, **78** (1997) 720.
15. S W Oh, M N Kang, C W Cho and M W Lee, *Dyes and Pigments*, **33** (1997) 119.
16. O Stein, *Ber.*, **27** (1894) 2806.
17. E Noelting and E Kopp, *Ber.*, **38** (1905) 3506.
18. C Schwalbe, *Z.Farb.Text.Ind.*, **4** (1905) 433.
19. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985) Chapter 1.2.
20. P Rys in *Physico-chemical principles of color chemistry*, Eds A T Peters and H S Freeman (London: Blackie, 1996) Chapter 1.3.
21. E Knoevenagel, *Ber.*, **23** (1890) 2994; **28** (1895) 2048.
22. O N Witt, *Ber.*, **42** (1909) 2953.
23. V V Ershov, G A Nikiforov and C R H I de Jonge, *Quinone diazides*, (Amsterdam: Elsevier, 1981).
24. T S Gore and K Venkataraman, *Proc. Indian Acad. Sci.*, **34A** (1951) 368.
25. H H Hodgson and D E Nicholson, *J.C.S.*, (1943) 379.
26. W R Orndorff and B J Ray, *Ber.*, **40** (1907) 3211.
27. F Muhlert, *Z.Angew.Chem.*, **21** (1908) 2611.
28. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985) Chapter 6.2.
29. H V Kidd, *J. Org. Chem.*, **2** (1937) 206.
30. W Schwarin and O Kaljanov, *Ber.*, **41** (1908) 2056.
31. F Muzik and Z J Allan, *Chem. Listy*, **49** (1955) 212.
32. F Muzik and Z J Allan, *Chem. Listy*, **46** (1952) 774.
33. E R Ward, D B Pearson and P R Wells, *J.S.D.C.*, **75** (1959) 484.
34. C Krohn, *Ber.*, **21** (1888) 3241.
35. V Chmatal and Z J Allan, *Coll. Czech. Chem. Commun.*, **27** (1962) 1835.
36. N Sekar, *J.S.D.C.*, **111** (1995) 390; **112** (1996) 204.

37. N Sekar, *J.S.D.C.*, **112** (1996) 242.
38. G S Hartley, *Nature*, **140** (1937) 281.
39. G S Hartley, *J.C.S.*, (1938) 633.
40. G Zimmerman, L Y Chow and U J Paik, *J. Amer. Chem. Soc.*, **80** (1958) 3528.
41. D Schulte-Frohlinde, *Ann.*, **612** (1957) 131.
42. D J W Bullock, C W N Cumper and A I Vogel, *J.C.S.*, (1965) 5316.
43. D L Beveridge and H H Jaffe, *J. Amer. Chem. Soc.*, **88** (1966) 1948.
44. B Marcandalli, P L Beltrame, E Dubini-Paglia and A Seves, *Dyes and Pigments*, **11** (1989) 179.
45. Y Yagi, *Bull. Soc. Chim. Japan*, **36** (1963) 487.
46. R Jones, A J Ryan, S Sternhill and S E Wright, *Tetrahedron*, **19** (1963) 1497.
47. S Toda, *Nippon Kagaku Zasshi*, **80** (1959) 402.
48. Q Peng, M Li, K Gao and L Cheng, *Dyes and Pigments*, **18** (1992) 271.
49. G Hallas and A H M Renfrew, *J.S.D.C.*, **112** (1996) 207.
50. E Fischer and Y F Frei, *J.C.S.*, (1959) 3159.
51. P F Gordon and P Gregory, *Organic chemistry in colour*, (Berlin: Springer-Verlag, 1983) 100.
52. A Burawoy, A G Salem and A R Thompson, *J.C.S.*, (1952) 4793.
53. L Antonov *et al.*, *Dyes and Pigments*, **38** (1998) 157; **40** (1998) 163.
54. K J Morgan, *J.C.S.*, (1961) 2151.
55. D Hadzi, *J.C.S.*, (1956) 2143.
56. L Antonov and S Stoyanov, *Dyes and Pigments*, **28** (1995) 31.
57. K Yamamoto, K Nakai and T Kawaguchi, *Dyes and Pigments*, **11** (1989) 173.
58. C Szantay, Z Csepregi, P Aranyosi, I Rusznak, L Toke and A Vig, *Magn. Res. Chem.*, **35** (1997) 306.
59. H E Fierz-David, L Blangey and E Merian, *Helv. Chim. Acta*, **34** (1951) 34, 846.
60. J Kelemen, *Dyes and Pigments*, **2** (1981) 73; J Kelemen, G Kormany and G Rihs, *Dyes and Pigments*, **3** (1982) 249; J Kelemen, S Moss, H Sauter and T Winkler, *Dyes and Pigments*, **3** (1982) 27.
61. N Donaldson, *The chemistry and technology of naphthalene compounds*, (London: Edward Arnold, 1958).
62. N N Vorozhtsov, *The chemistry of synthetic dyes*, Vol 3, Ed K Venkataraman (New York: Academic Press, 1970) 93.
63. N N Vorozhtsov, *The chemistry of synthetic dyes*, Vol 3,Ed K Venkataraman (New York: Academic Press, 1970) 110.
64. N N Vorozhtsov, *The chemistry of synthetic dyes*, Vol 3, Ed K Venkataraman (New York: Academic Press, 1970) 146.
65. H T Bucherer, *J.Prakt.Chim.*, (2), **69** (1904) 49.
66. N L Drake, *Organic Reactions*, **1** (1942) 105.
67. H Seeboth, *Angew. Chem. Internat.*, **6** (1967) 307.
68. J Kraska and K Blus, *Dyes and Pigments*, **31** (1996) 97.
69. J Meybeck and P Galafassi, *Appl. Polymer Symp.*, **18** (1971) 463.
70. S Stoyanov, T Iijima, T Stoyanova and L Antonov, *Dyes and Pigments*, **27** (1995) 237.
71. D L Ross and E Reissner, *J. Org. Chem.*, **31** (1966) 2571.
72. C T Helmes, *Amer. Dyestuff Rep.*, **83** (Aug 1994) 40.
73. W Czajkowski, *Dyes and Pigments*, **17** (1991) 297.
74. J Shore, *Rev. Prog. Coloration*, **21** (1991) 23.
75. Y C Chao and S S Yang, *Dyes and Pigments*, **29** (1995) 131.
76. F Calogero, H S Freeman, J F Esaney, W M Whaley and B J Dabney, *Dyes and Pigments*, **8** (1987) 431.
77. J Szadowski, *Dyes and Pigments*, **14** (1990) 217.
78. H S Freeman, D Hinks and J F Esaney in *Physico-chemical principles of color chemistry*, Eds A T Peters and H S Freeman (London: Blackie, 1996) Chapter 7.
79. Chi-Kang Dien, *The chemistry of synthetic dyes*, Vol 8, Ed K Venkataraman (New York: Academic Press, 1978) 81.
80. *Colour Index International, Pigments and Solvent Dyes* (Bradford: SDC, 1997) 198.
81. A G Green and K H Saunders, *J.S.D.C.*, **39** (1923) 10.
82. A G Green and K H Saunders, *J.S.D.C.*, **40** (1924) 138.
83. J F Dawson, *J.S.D.C.*, **107** (1991) 395.
84. S Abeta and K Imada, *Rev. Prog. Coloration*, **20** (1990) 19.
85. K D Wozniak, A Keil and D Müller, *Textil Praxis*, **45** (1990) 965.
86. P Elsner, *Textilveredlung*, **29** (1994) 98.
87. N Sekar, *Colourage*, **45** (Dec 1998) 37.
88. A D Towns, *Dyes and Pigments*, **42** (1999) 3.
89. J Sokolowska-Gajda and H S Freeman, *Dyes and Pigments*, **20** (1992) 137.
90. A T Peters, S S Yang and E Chisowa, *Dyes and Pigments*, **28** (1995) 151.
91. A T Peters and S S Yang, *Dyes and Pigments*, **30** (1996) 291.
92. H G Wippel, *Melliand Textilber.*, **50** (1969) 1090.
93. G Hallas in *Developments in the chemistry and technology of organic dyes*, Ed J Griffiths (Oxford: Blackwell Scientific Publications, 1984) 31.

94. G Hallas and A D Towns, *Dyes and Pigments*, **31** (1996) 273; **32** (1996) 135; **33** (1997) 205; **33** (1997) 215; **33** (1997) 319; **34** (1997) 133; **35** (1997) 45; **35** (1997) 219.
95. H S Freeman, S A McIntosh and P Singh, *Dyes and Pigments*, **35** (1997) 11.
96. M Matsuoka in *Analytical chemistry of synthetic colorants*, Eds A T Peters and H S Freeman (London: Blackie, 1995) Chapter 3.
97. P W Leadbetter and A T Leaver, *Rev. Prog. Coloration*, **19** (1989) 33.
98. P W Leadbetter and S Dervan, *J.S.D.C.*, **108** (1992) 369.
99. J H Choi, S H Hong and A D Towns, *J.S.D.C.*, **115** (1999) 32.
100. J S Koh and J P Kim, *J.S.D.C.*, **114** (1998) 121, *Dyes and Pigments*, **37** (1998) 265.
101. R Raue, *Rev. Prog. Coloration*, **14** (1984) 187.
102. S Hünig, *Angew. Chem. Internat.*, **7** (1968) 335.
103. P F Gordon and P Gregory, *Organic chemistry in colour* (Berlin: Springer-Verlag, 1983) 87.
104. D Brierley, P Gregory and B Parton, *J. Chem. Research*, **5** (1980) 174.
105. E B Higgins, *J.S.D.C.*, **43** (1927) 213.
106. C Daescu and D Hadaruga, *Dyes and Pigments*, **40** (1998) 235.
107. R Anliker, G Dürig, D Steinle and E J Moriconi, *J.S.D.C.*, **104** (1988) 223.
108. F Gund, *J.S.D.C.*, **76** (1970) 151.
109. S Ifrim, *Amer. Dyestuff Rep.*, **84** (Mar 1995) 38.
110. J Wang, *AATCC Internat. Conf. & Exhib.* (Oct 1998) 144.
111. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985) Chapter 3.5.
112. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985) Chapter 5.1.
113. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985) Chapter 5.3.
114. K H Saunders and R L M Allen, *Aromatic diazo compounds*, 3rd Edn (London: Edward Arnold, 1985) Chapter 7.1.
115. B Jomain, *J.S.D.C.*, **69** (1953) 661.
116. R M Christie and P N Standring in *The design and synthesis of organic dyes and pigments*, Eds A T Peters and H S Freeman (London: Elsevier Applied Science, 1991) Chapter 11.
117. C Nicolaou and M Da Rocha in *Analytical chemistry of synthetic colorants*, Eds A T Peters and H S Freeman (London: Blackie, 1995) Chapter 8.
118. W S Czajkowski in *Modern colorants: Synthesis and structure*, Eds A T Peters and H S Freeman (London: Blackie, 1995) Chapter 3.
119. A Whitaker in *Analytical chemistry of synthetic colorants*, Eds A T Peters and H S Freeman (London: Blackie, 1995) Chapter 1.
120. H E Fierz-David and L Blangey, *Fundamental processes of dye chemistry*, (New York: Interscience, 1949).
121. G Booth, *Rev. Prog. Coloration*, **8** (1977) 1; **14** (1984) 114.
122. G Booth, *The manufacture of organic colorants and intermediates*, (Bradford: SDC, 1988).