GENERAL INTRODUCTION TO THE CHEMISTRY OF DYES

1. Principles of Colour Chemistry

1.1 Basis for colour

Unlike most organic compounds, dyes possess colour because they 1) absorb light in the visible spectrum (400–700 nm), 2) have at least one chromophore (colour-bearing group), 3) have a conjugated system, i.e. a structure with alternating double and single bonds, and 4) exhibit resonance of electrons, which is a stabilizing force in organic compounds (Abrahart, 1977). When any one of these features is lacking from the molecular structure the colour is lost. In addition to chromophores, most dyes also contain groups known as *auxochromes* (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility. Figure 1 shows the relationships between wavelength of visible and colour absorbed/observed. Other factors contributing to colour are illustrated in Figures 2–4.

Fig. 1. Wavelength of light absorption versus colour in organic dyes

Wavelength Absorbed (nm)	Colour Absorbed	Colour Observed
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue-Green	Red
500–560	Green	Purple
560–580	Yellow-Green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-Blue
605–700	Red	Blue-Green

Fig. 2. Examples of chromophoric groups present in organic dyes

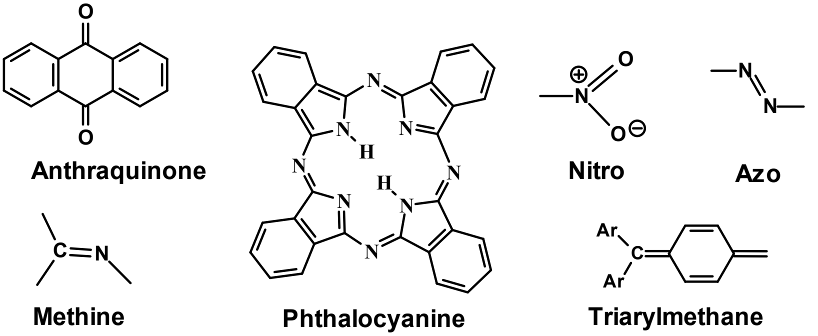


Fig. 3. Conjugated systems in Vitamin A (top) and β-carotene (bottom)

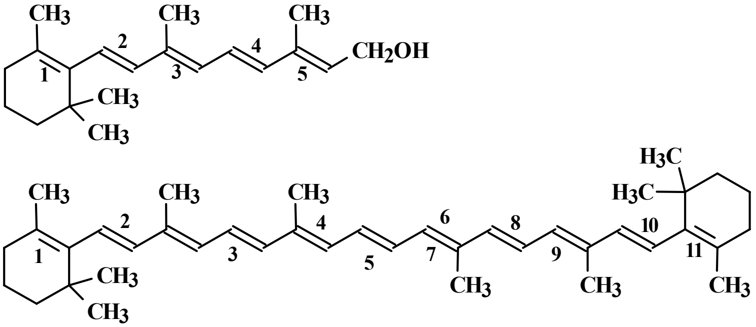
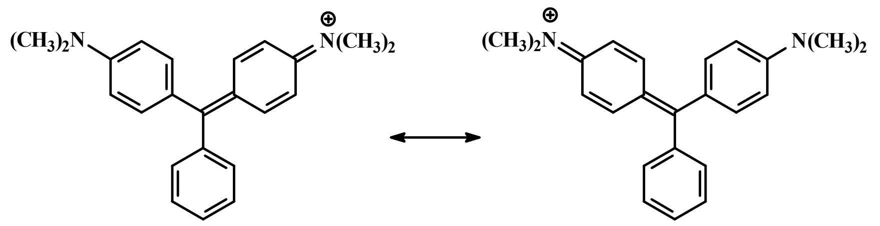
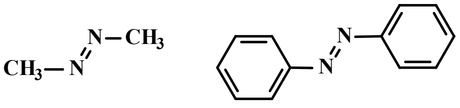


Fig. 4. A pair of resonance structures for Malachite Green (C.I. Basic Green 4)



Regarding the requirement of a chromophore generating colour in organic compounds, it is important to note that the chromophore must be part of a conjugated system. This is illustrated through the examples in Figure 5 where it can be seen that placement of an azo group between methyl groups produces a colourless compound, while a yellow-orange colour is obtained when the azo group is placed between aromatic rings. Similarly, the structures in Figure 3 demonstrate the importance of having an extended conjugated system. It is evident that doubling the length of the conjugated system in Vitamin A to give β-carotene causes a significant bathochromic shift, i.e. to a darker colour.

Fig. 5. Importance of having a chromophore within a conjugated system

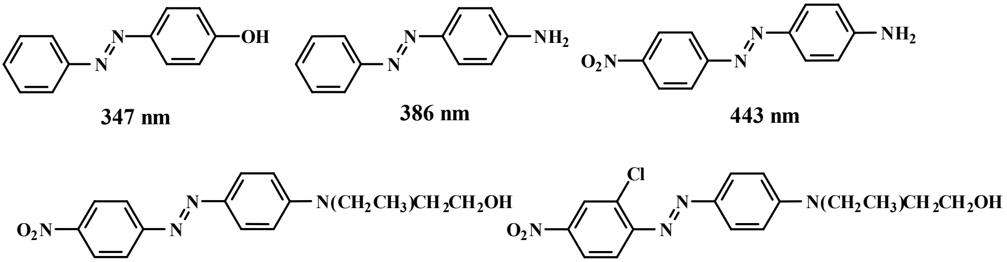


Colourless **Orange**

In addition to influencing solubility, auxochromes are essential ring substituents in providing target colours. This is illustrated in Figure 6, where the following effects of substituents are shown:

- Adding groups of increasing electron-donating ability to the azobenzene structure has a bathochromic effect (*cf.* OH *vs* NH_2).
- Electron-donating (NH_2) and electron-accepting (NO_2) groups placed in conjugation provide a bathochromic effect. In this regard, nitro groups are especially beneficial, contributing to their prevalence in disperse dye structures.
- Increasing the number of electron-attracting groups conjugated with the electron-donor has a bathochromic effect.
- The electron-donating effects of an amino group are enhanced by adding alkyl groups to the N-atom.

Fig. 6. Effects of substituent groups within an azo-dye system



347 nm **386 nm** **443 nm**

502 nm **517 nm**

1.2 Dyes versus Pigments

With regard to their solubility, organic colourants fall into two classes, *viz.* dyes and pigments (Allen 1971). The key distinction is that dyes are soluble in water and/or an organic solvent, while pigments are *insoluble* in both types of liquid media. Dyes are used to colour substrates to which they have affinity. Pigments can be used to colour any polymeric substrate but by a mechanism quite different from that of dyes, in that surface-only colouration is involved unless the pigment is mixed with the polymer before fibre or moulded article formation.

2. Considerations in Dye Design

2.1 Dye-substrate affinity

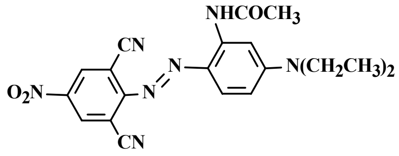
Dyes containing one or more azo groups (i.e. azo dyes) comprise by far the largest family of organic dyes. Prominent types are 1) acid dyes for polyamide and protein substrates such as nylon, wool, and silk; 2) disperse dyes for hydrophobic substrates such as polyester and acetate, and 3) direct and reactive dyes for cellulosic substrates such as cotton, rayon, linen, and paper. Generally, the synthesis of azo dyes involves two steps. Step 1 is the conversion of an aromatic amine to a diazo compound (i.e. Ar-NH2 → Ar-N2+), a process known as diazotization, and step 2 is the reaction of the diazo compound with a phenol, naphthol, aromatic amine, or a compound that has an active methylene group, to produce the corresponding azo dye, a process known as diazo coupling (e.g. Ar-N2+ + Ar'-OH→ Ar-N=N-Ar'-OH). This process is suitable for forming both azo dyes and pigments. Typical structures of colourants that fall into the two groups are shown in Figure 7.

Since the effectiveness of a dyeing or printing process often hinges on the affinity between the dye and substrate, dyes are designed with a specific substrate in mind. In this regard, dyes must be designed that have a) greater affinity for the substrate than the medium (usually water) from which it is applied and b) a high degree of permanence under end-use conditions (e.g. stability to fading upon exposures to water (wet fast) and/or sunlight (light fast)). The following is a summary of the types of considerations associated with the development of dyes for polymeric (especially fibre-based) substrates (Aspland, 1997). The availability of colourants for a specific substrate type is the result of a deliberate molecular design process that takes the target substrate and end-use application into consideration.

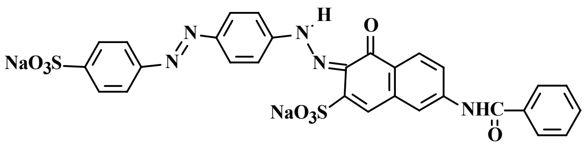
2.1.1 *Dyes for polyesters*

Dyes developed for polyesters are known as disperse dyes. In this case, the mechanism of coloration involves "dissolving" the dye in the polymer matrix to form a solid–solid solution. Taking advantage of the well known principle that "like dissolves like", disperse dyes are designed that are hydrophobic in nature. Such colourants are very sparingly soluble in water and derive their name from the fact that they are dispersed rather than fully dissolved in water to carry out the dyeing process. An example is C.I. Disperse Blue 165 (Figure 7). Disperse dyes have no affinity for hydrophilic polymers such as cellulose, which makes them unsuitable for colouring cotton, cellophane, and paper, but quite suitable for poly(ethylene terephthalate) and cellulose acetate.

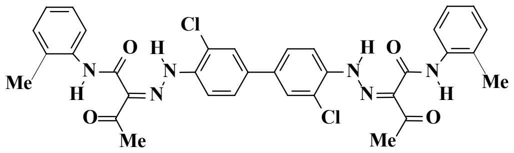
Fig. 7. Structures of some commercial azo dyes and pigments



Disperse Blue 165



Direct Red 81



Pigment Yellow 14

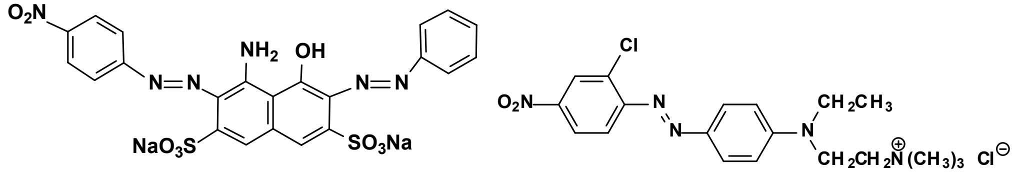
2.1.2 *Dyes for polyamides and proteins*

Dyes for these substrates normally form ionic bonds (Fig. 8) within the polymer matrix. In this case dyes bearing a negative (anionic) charge are used because polyamides such as nylon and proteins such as wool, silk, and leather carry a positive (cationic) charge – especially during the dyeing process. Anionic dyes for polyamide and protein substrates are known as *acid dyes*, an example of which is C.I. Acid Black 1 (Fig. 9). They derive their name from the fact that they are typically applied to suitable substrates from a medium containing acid. These dyes have little to no affinity for polyester, cellulosic, or cationic polymers, since such substrates cannot form an ionic bond with them.

Fig. 8. Schematic representation of dye–polymer binding via ionic bonding on nylon

$$\text{Dye-SO}_3^{\ominus}\text{Na}^{\oplus} + \text{Nylon-NH}_3^{\oplus}\text{Cl}^{\ominus} \longrightarrow \text{Dye-SO}_3^{\ominus}\,{}^{\oplus}\text{H}_3\text{N-Nylon}$$

Fig. 9. Structure of a commercial acid and cationic (basic) dye



Acid Black 1 **Basic Red 18**

2.1.3 *Dyes for cationic polymers*

Dyes for these substrates also form ionic bonds within the polymer matrix. In this case, dyes bearing a positive (cationic) charge are used because polymers such as poly(acrylonitrile) carry a negative (anionic) charge in their backbone, making the ionic character of the interacting substances the reverse of that described above for acid dyes. Cationic dyes for acrylic substrates were initially known as *basic dyes*, an example of which is C.I. Basic Red 18 (Figure 9). Today, they derive their name from the fact that they possess a cationic group. These dyes have no affinity for polyester, cellulosic, or polyamide polymers, since such substrates cannot form an ionic bond with them. However, cationic dyes can be used to dye protein fibres and, in fact, the first synthetic dye Mauveine was a basic dye that was used for dyeing silk. This takes advantage of the presence of carboxylate ($–CO_2^-$) groups in silk and wool.

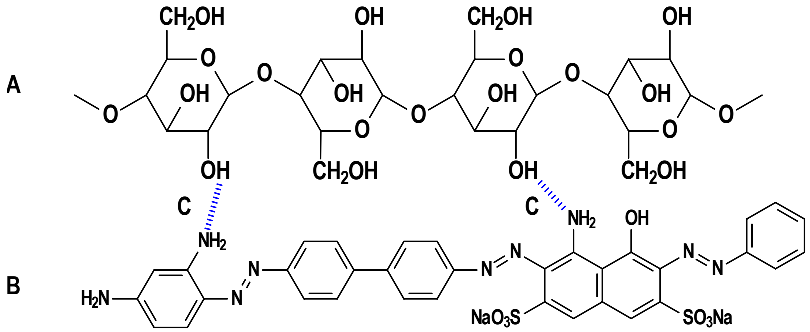
2.1.4 *Dyes for cellulosic polymers*

Cellulosic substrates include cotton, rayon, cellophane, linen, and paper, all of which are very hydrophilic and, therefore, require hydrophilic (water soluble) dyes for their coloration from a dyebath. In addition, dyes must be designed that maintain affinity when the substrate is exposed to water. This allows the colour to remain on the substrate, when, for instance, a cotton fabric is laundered or a cup of coffee is inadvertently spilled on a sheet of paper containing printed information. The ease with which cellulosic substrates such as cotton swell and lose colourants during laundering has led to the design and development of more dye colourant families for cellulosic fibres than any other substrate.

Dyes designed for cellulosic polymers are direct, azoic, vat, sulfur, and reactive dyes. *Direct dyes* are so named because they were the first colourants that had affinity for cotton in the absence of a binding agent known as a mordant. Because these dyes are water-soluble, many have low wet fastness. Figure 10 illustrates two key properties of benzidine-based direct dyes, *viz.* 1) they tend to be linear molecules, and 2) they are able to gain close proximity to the cellulose chain, to maximize the effects of intermolecular interactions such as H-bonding.

To enhance wet fastness on cellulosic fibres, methods were developed to apply water-insoluble dyes to cotton. Such dyes include those that are either water insoluble in their natural form or synthesized inside the polymer matrix as a water-insoluble dye. The idea is that placing a water-insoluble dye within the polymer matrix would prevent colour removal upon exposure of the substrate to water. In turn, this led to the development of *vat dyes* and *sulfur dyes* (Figure 11a,b). Vat dyes owe their name to the vatting process associated with their application, while sulfur dyes are so named because of the essential use of sulfur in their synthesis. The structures of vat dyes are rather well known but sulfur dye structures are less well defined, because their polymeric nature makes them unsuitable for standard methods for structure characterization. In their application, vat and sulfur dyes are converted to a water-soluble form that has affinity for cellulose and are subsequently converted back to their water-insoluble form, giving good permanence under wet conditions. Included in the family of vat dyes is the well known natural dye *indigo*. While indigo is still the most important colourant for denim fabric, its a-typically small size causes this vat dye to be very susceptible to removal in a laundering process, giving jeans a faded appearance even after one wash. This underscores the importance of designing colourants for cellulosic substrates that possess the features required for them to remain within the polymer matrix when water swells the substrate.

Fig. 10. Representation of H-bonding (C) between a cellulose (A) and a direct dye (B)



Azoic colourants (cf. Figure 11c) are also known as naphthol dyes because naphthol compounds are used in their synthesis. These dyes do not exist per se, but they are generated inside the polymer matrix by applying the two necessary components to the substrate separately. Following their application to the substrate, the two components find each other and combine to form a water-insoluble colourant.

The final class of suitable colourants for cellulosic fibres is known as *reactive dyes* (*cf.* Figure 11d). They derive their name from the fact that they undergo a chemical reaction with cellulose to form a covalent bond (Figure 12). Reactive dyes opened the door to bright wet-fast shades on cellulosic fibres that were not previously attainable.

Fig. 11. Characteristic structures of sulfur (a), vat (b), azoic (c) and reactive (d) dyes

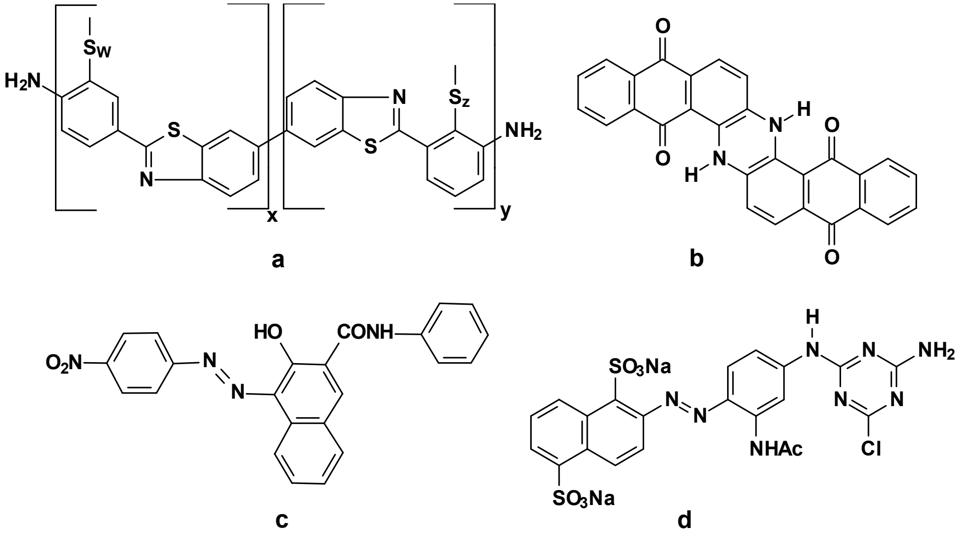
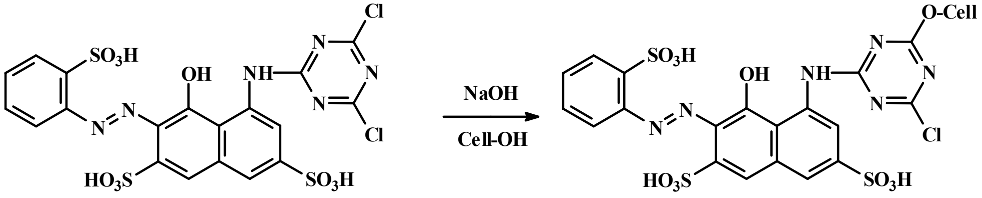


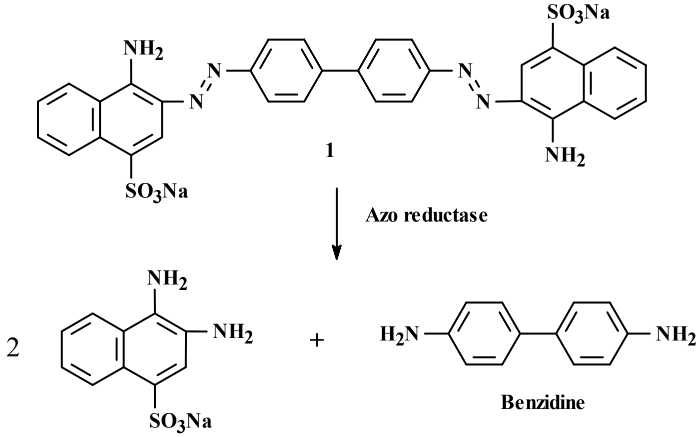
Fig. 12. Dye-fiber fixation via covalent bonding, where Cell-OH represents cellulose



2.2 Toxicological considerations

While dye–substrate affinity is critical, synthetic dyes cannot be commercialized unless they pose little health risk under end-use conditions. Consequently, environmental safety is an essential consideration in molecular design. In this regard, the raw materials employed in the manufacture of synthetic dyes should not involve compounds known to pose health risks. This would include a large group of aromatic amines (Anon, 1996) that are either cancer-suspect agents or established mutagens in the standard *Salmonella* mutagenicity assay (Maron and Ames, 1983). It is clear, therefore, that dye design must take into consideration the likely genotoxicity of the potential metabolites generated in mammalian systems (Prival *et al.*, 1984). In the case of azo dyes, the enzyme-mediated formation of genotoxic aromatic amines as metabolites must be considered, since it is possible that the intact dye is safe but not all of its metabolites. For instance, the use of dye **1** in Figure 13 could lead to the formation of the bladder carcinogen benzidine if this dye were taken up in the body.

Fig. 13. Reductive-cleavage of Direct Red 28 (1) using an azo-reductase enzyme

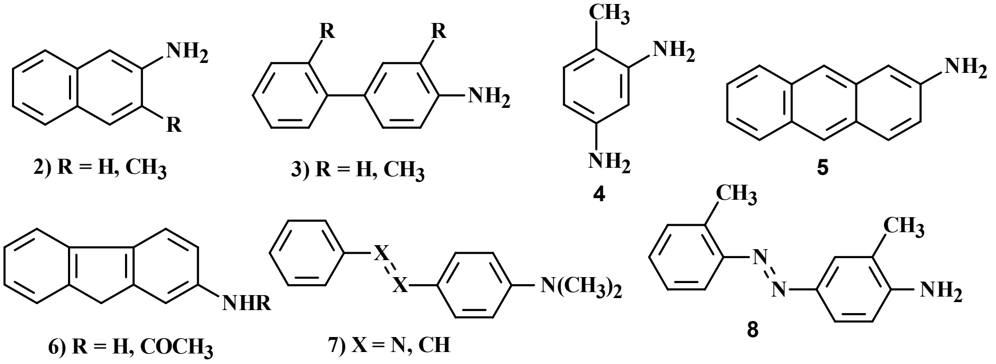


2.2.1 *Structure–Property Relationships*

Following the recognition that certain aromatic amines used in azo-dye synthesis caused bladder cancer, a wide variety of chemicals were evaluated in animal studies, and the results showed that aromatic amines and azo compounds of the type shown in Figure 14 were carcinogenic (Weisburger, 1978). In this regard, it is generally believed that the ultimate carcinogen arises from the metabolic conversion of these compounds to electrophilic species (*cf.* Figure 15) that interact with electron-rich sites in DNA to cause DNA adducts, mutations and subsequent adverse effects on the cell. It is also clear that ring substituents that enhance the hydrophobic character increase carcinogenic potential: this is the case when adding a methyl group to 2-naphthylamine (**2**; R = H) or *meta*-phenylenediamine (*cf.* analogue **4**).

As a follow-up to the study pertaining to carcinogenicity data assessment (Longstaff, 1983), correlations between dye structure and carcinogenicity data were established. In a comparison of hydrophobic azo dyes containing amino groups in the *para*- or *ortho*-position, it was found that the *para*-isomers were carcinogenic while the *ortho*-isomers were not. To account for these results, the chemistry in Figure 16 was proposed (Gregory, 1986). It is believed that the isomeric arylazo amines produce nitrenium ions (**9**) that either interact with DNA (*para*-isomer) or undergo intramolecular cyclization (*ortho*-isomer) to produce adducts (**10**) or benzotriazoles (**11**), respectively.

Fig. 14. Examples of carcinogenic aromatic amines and azo compounds



2) R = H, CH_3

3) R = H, CH_3

4

5

6) R = H, $COCH_3$

7) X = N, CH

8

Fig. 15. Nitrenium ion formation from the metabolism of aromatic amines

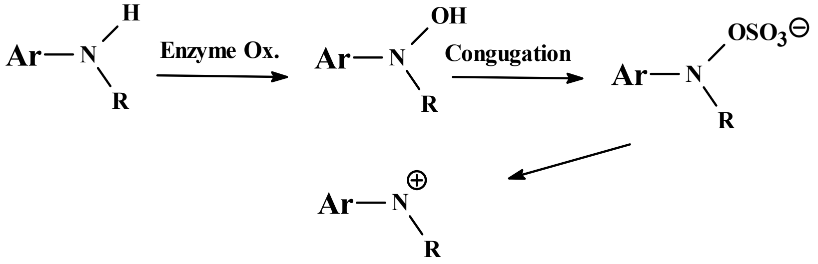
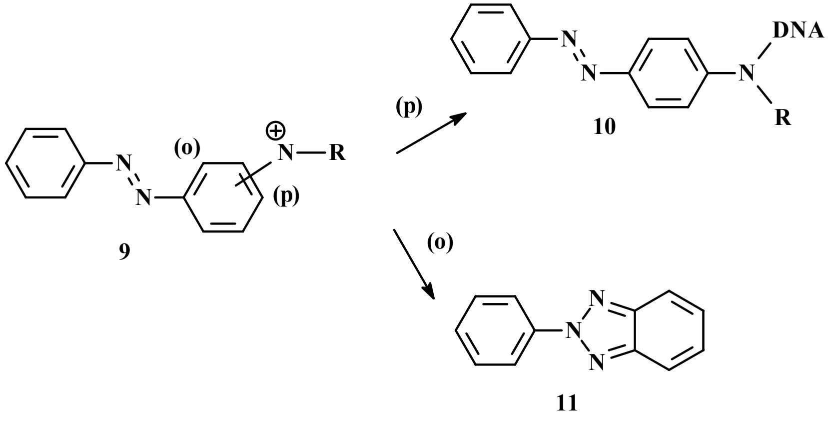
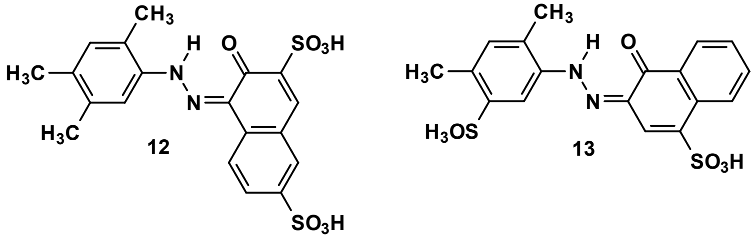


Fig. 16. Reaction pathways for nitrenium-ion (9) metabolites of azobenzene isomers



A correlation of carcinogenicity data with the structures of hydrophilic azo dyes was also presented (Gregory, 1986). Water-soluble dyes of type **12** were carcinogenic, while type **13** dyes (Fig. 17) were not. In this case, the nature of the reductive-cleavage products was the determining factor in the observed carcinogenicity data. Whereas dye **12** produces a lipophilic amine (2,4,5-trimethylaniline), dye **13** produces water-soluble sulfonated amines only, making aromatic amine genotoxicity an important consideration in azo-dye design.

Fig. 17. Carcinogenic (12) and non-carcinogenic (13) water-soluble monoazo dyes



3. Hair Dyes

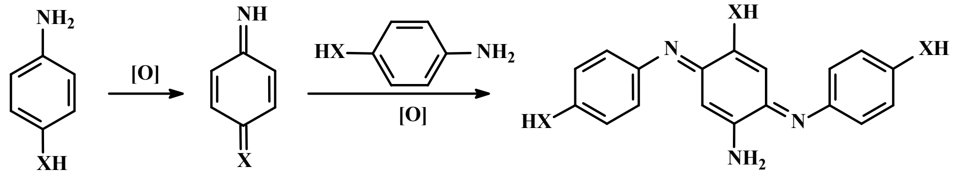
A great majority of the dyes used in hair colouring are known as oxidation hair dyes (Corbett, 1985, 2000). A much smaller number of the commercial hair dyes are synthetic dyes that have affinity for protein substrates such as wool. Oxidation dyes, the more permanent of the two groups, are produced directly on the hair by oxidizing aromatic diamines such as *para*-phenylenediamine or 2,5-diaminotoluene with an oxidizing agent. Suitable diamines have been referred to as "primary intermediates" and the oxidizing agents (e.g. hydrogen peroxide) as "developers." Other useful primary intermediates are aminodiphenylamines, aminomethylphenols, and *para*-aminophenol.

When used alone, the primary intermediates provide a very limited shade-range following their oxidation on hair. To enhance the range of available hair colours, the primary intermediates are oxidized in the presence of suitable "couplers." While most couplers do not produce colours when exposed to developers alone, they give a wide range of shades on hair when applied in combination with primary intermediates. Appropriate couplers include 3-aminophenol, resorcinol, and α-naphthol.

The chemistry associated with the oxidation of primary intermediates is now reasonably well known. For *para*-phenylenediamine and *para*-aminophenol (*cf.* **14**), oxidation-induced self-coupling proceeds via the process outlined in Fig. 18, where it can be seen that permanent hair-dye formation involves oxidation followed by coupling to give type-**15** structures. Fig. 19 provides chemistry representative of combinations arising from joining an α-naphthol-based coupler (**16**) and a sulfonated *N*-phenyl-*para*-phenylenediamine primary intermediate (**17**) to produce experimental dyes **18** and **19**. This chemistry also illustrates the fact that oxidation dyes are often mixtures rather than single products.

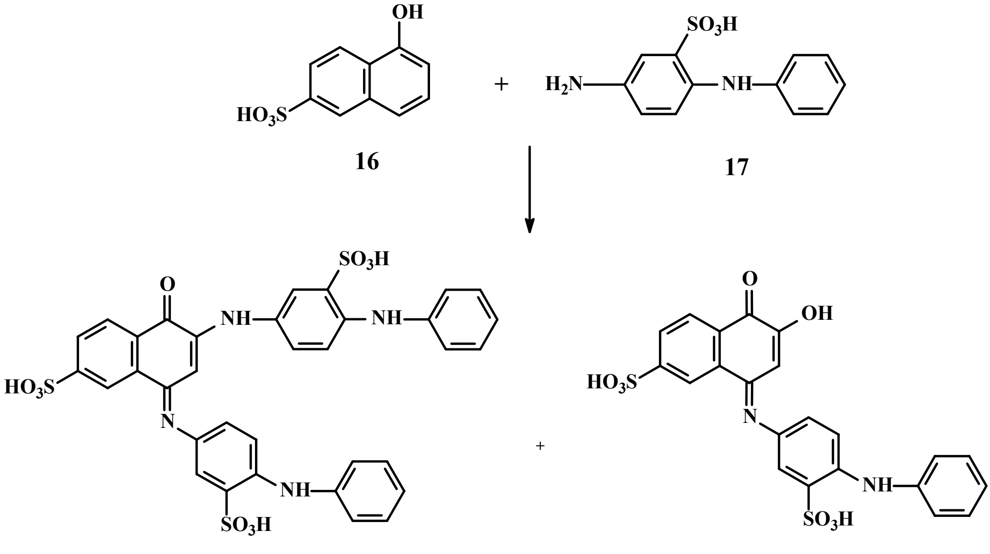
An analytical method has been developed for characterizing the reactants and reaction products of oxidative hair-dye formulations. The results indicated that a significant amount, i.e. ≈20% or more of the initial concentrations of precursor(s) and coupler(s), is always present in the formulation that is not diffused into hairs (see Section 1 of the Monograph on hair dyes in this volume).

Fig. 18. Oxidation hair-dye formation from primary intermediates (X = O, NH)



14 **15**

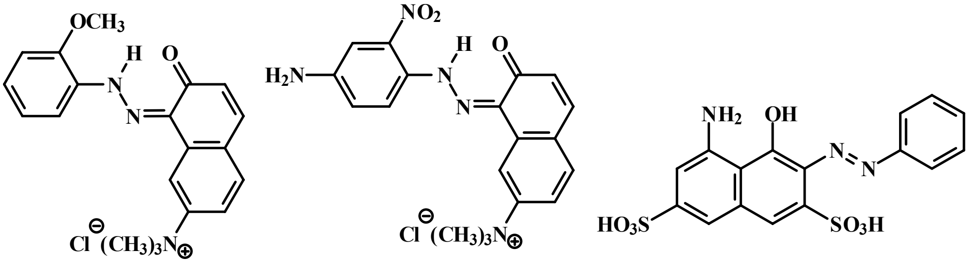
Fig. 19. Oxidation hair-dye formation from a primary intermediate and coupler



16 **17** **18** **19**

C.I. Basic dyes such as Yellow 57, Red 76, Blue 99, Brown 16, and Brown 17 have been used in colour refreshener shampoos and conditioners. Similarly, C.I. Acid dyes such as Yellow 3, Orange 7, Red 33, Violet 43, and Blue 9 have been used in shampoos, in this case to deliver highlighting effects (Corbett, 2000). Example structures of non-permanent hair dyes are provided in Fig. 20, where it can be seen that these dyes are drawn from those known to have affinity for protein-based textile fibres.

Fig. 20. Examples of non-permanent hair dyes



Basic Red 76 **Basic Brown 17** **Acid Red 33**

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