A Series on Dyeing

Chapter 2/Part 2: Direct Dye Structure

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The first synthetic dye was synthesized in 1856 by a young Englishman named William Henry Perkin. His discovery heralded the start of the organic chemical industry and initiated the subsequent discovery of a myriad of synthetic dyes, many of which had unprecedented brightness compared to the natural dyes in use at the time. The 100 to 200 natural dyes available then were products of mainly vegetable origin although there were also derivatives of insects and shellfish. Putting the products of 1856 into the dye application categories of today would show that most natural dyes were mordant dyes, a few were vat dyes, there were a couple of rather poor direct dyes and there was a single basic dye (*1*). Indigo was and is the most important of the vat dyes.

Unfortunately, in most cases, mordant dyeing requires an additional step in which either the mordant has to be applied to the fiber (usually cotton or wool) before dyeing can begin, or more often, the mordant has to be applied to the dyeing as a final processing step. Some of the older dyeing processes required not minutes but days and even weeks to carry out the additional mordanting steps. In previous centuries, producing the water soluble, dyeable, reduced (leuco) form of natural vat dyes was also lengthy and reduction required a long fermentation process before dyeing could begin. The process was known as vatting. Vat dyes will be discussed later in some detail.

It is no wonder that the discovery of the first synthetic dyes for cotton which required neither mordanting nor vatting—C.I. Direct Yellow 11 (Sun Yellow, 1883) and C.I. Direct Red 28 (Congo Red, 1884) resulted in concentrated activity among dye manufacturers to find others. Nor is it surprising that these dyes were given the name *direct* as a tribute to the simplicity of their application (*2*).

ABSTRACT

The details of direct dye molecules include the presence of aromatic rings and sulfonate groups attached to the rings. Direct dye chromophores, the structural groups within a dye molecule mainly responsible for the color of the product, include azo, stilbene, oxazine or phthalocyanine groups. Commercial direct dyes are available primarily in powder form but are also offered as liquids for convenience in such continuous processing operations as paper coloration. Dye standardization, processing aids and drug room practice are also discussed.

KEY TERMS

Aromatic Rings
Chromophores
Direct Dyes
Dye-Metal Complexes
Generic Dyes
Impurities
Liquid Dyes
Processing Aids
Standardization
Sulfonates

Chemical Structure

It is desirable for those without organic chemical training to have at least a good visual idea of the significant features of dye molecules. Those who feel intimidated by dye structures can take comfort in the fact that most organic chemists would be equally intimidated by dye application technology. The following sections walk through only the characteristic structural features of direct dyes, without delving into synthesis.

Aromatic Rings

Dyes owe much of their character to the presence of aromatic ring structures which, in the case of direct dyes, are mainly derivatives of benzene and naphthalene. The aromatic rings are drawn as hexagons, one for benzene, two side by side for naphthalene. Each line represents a carbon-carbon bond, and all the carbon atoms lie in one plane. The hexagons give rise to the idea that dye structural formulae resemble chicken wire.

The hexagons may be decorated or undecorated by internal lines representing the fact that there is additional bonding to keep the rings stable. To include or omit the additional bond lines is a question of convention, but since consistency within a book or article is highly desirable, the lines here will always be included. Surprisingly, they are usually not included in the Colour Index (*2*). The carbon atoms at the corners of the hexagons are attached to a hydrogen atom unless another substituent is indicated, two further bonds are extended or another ring is attached (Figs. 1, 2).

Most direct dyes contain between four and seven aromatic rings.

Sulfonate Groups

Vital substitutents of direct dyes are the sodium sulphonate groups, $-SO_3Na$, attached to the benzene or naphthalene rings. It is the sulfonate group which gives most direct dyes the property of water solubility so imperative to dyeing. When dyes containing these groups are placed in water they ionize into sodium cations and colored sulfonate anions which are positively and negatively charged respectively—i.e., Na^+ and $-SO_3^-$—both of which are extremely attractive to water and become heavily hydrated (surrounded) by water molecules. There are usually from two to four—but can be from one to five—sulfonate groups as an intrinsic part of any direct dye molecule. The number of these groups is a major factor in determining how strongly the dye is attracted to water. This roughly translates into how soluble the dye is, and how much electrolyte is needed to force the dye out of the water and onto the fiber during dyeing. Most direct dye molecules could be described by a general formula:

$$\text{Dye}-(SO_3Na)n$$

where $n = 1$ to 5.

Other substituent chemical groups to be found in direct dyes include the hydroxy group, the amino group and the amido group, –NH–CO–, all of which will be dealt with in other sections. An amino group is necessary for aftertreatment by diazotization and coupling.

Chromophores

Dyes are often subdivided by organic chemists according to the chemical nature of the chromophore, which is the group (or groups) within the molecule largely responsible for the color of the product. These chromophores can be azo, stilbene, oxazine or phthalocyanine.

- Azo: By far the largest number of direct dyes contain the azo chromophore, –N = N–, mentioned in the section on aftertreatment, diazotization and coupling.

About half the azo direct dyes contain two azo groups, a quarter contain three azo groups and they are said to be disazo and trisazo respectively. The rest have either one, four or more, and are known as monoazo or polyazo dyes respectively.

A typical disazo direct dye, C.I. Direct Red 81, is illustrated by the structure in Fig. 3. This dye has two azo groups, three benzene rings, one naphthalene residue (four aromatic rings in all), two sodium sulfonate groups, with one hydroxy and one amido group.

Other important azo direct dyes include C.I. Direct Yellow 28 (monoazo), Blue 78 (trisazo) and Black 22 (polyazo).

- Stilbene: Dyes containing stilbene groups are mostly economical yellows, oranges and dull orange-red and brown shades such as C.I. Direct Yellows 11 and 106, Orange 39 and Red 76. The structure of the stilbene chromophore appears similar to that of the azo chromophore. It is written $-CH{=}CH-$ and this also is sandwiched between aromatic rings.
- Oxazine: Most direct dyes containing this chromophore are dioxazines, with the oxazine—an oxygen and nitrogen-containing ring structure—twice, sandwiched between three benzene rings (Fig. 4). These are mostly bright blue dyes with good lightfastness, such as C.I. Direct Blues 106, 107 and 108.
- Phthalocyanine: This group of direct dyes is small, hard to dye to deep shades, with bulky, plate-shaped molecules. Their dyeings cannot compare in properties with fiber reactive dyes using the same chromophore. But they fill a valuable shade niche, being bright greenish blue or turquoise shades; e.g., C.I. Direct Blues 86 and 189. Phthalocyanine derivatives are usually derived from the corresponding premetallized copper complex, shown in Fig. 5, which will be discussed again in the section dealing with pigments.

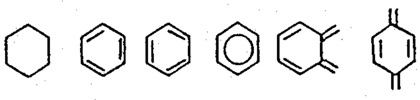

Fig. 1. Representations of benzene rings.

Dye-Metal Complexes

The feature of the copper phthalocyanine structure to be found in the structural formulae of a number of other direct dye molecules is the copper atom, Cu, around which four chemical bond lines radiate. These bonds are indicated by solid or broken lines, with or without arrows. The bonds originate from nitrogen atoms, sometimes in azo groups, and oxygen atoms, sometimes in water molecules. These nitrogen or oxygen groups, or ligands, all have electrons they are prepared to share with the electron-poor copper ion, Cu^{2+}, to form stable, dye-metal, co-ordination complexes. Such complexes will be dealt with in more detail in the section on premetallized acid dyes.

Composite Features

Composite chemical features to be found in many azo direct dye structures are shown in Fig. 6. The chemical groups the figures represent add substantivity to direct dyes. However, major and ethical dye manufacturers no longer make direct dyes which include feature (a) in Fig. 6 because such dyes would require the use of benzidine, which is a known carcinogen. Some of the dyes themselves are also carcinogenic. Similar looking structures, 6b and 6c, do not suffer from the same defect. Such a situation is by no means unique. The potential of all chemical compounds for human carcinogenicity, however similar they may appear structurally, must be tested on an individual basis. Unfortunately, or fortunately, controlled testing in human subjects is unthinkable and animal tests may well give misleading results.

The naphthalene residue shown in Fig. 7 is derived from J-Acid (6-amino-1-naphthol-3-sulphonic acid), which is used more frequently for direct dyes since the demise of benzidine.

Review

Armed with those structural features of direct dyes outlined above, it should be possible to look at a tangle of chemical chicken wire and decide whether it might be a representation of a direct dye molecule. The biggest possibility for confusion is with acid and fiber reactive dye structures for which Dye–$(SO_3Na)n$ is also a useful general formula. However, their molecules are usually only about half the size of direct dye molecules; and fiber reactive dyes will always contain typical, readily-identifiable, reactive species in addition to the colored portion of the molecule (see the section on fiber reactive dyes).

Could the structure in Fig. 8 be a direct dye? What features give it away? What features are particularly interesting? The structure is that of C.I. Direct Blue 98. The structure shown in Fig. 2 of Chapter 2 (TCC, November, p43) was intended to be a generalized structure only, typical of metallized azo direct blue dyes, but it was inadvertently displaced.

What two chromophoric groups are present in the dye structure in Fig. 9? Could the structure represent a direct dye? The structure is that of C.I. Direct Yellow 4. One should notice that some of the structures of direct dye molecules are rather long and linear, as pointed out in the section on the dye-fiber bond, Chapter 1.

Commercial Products

Direct dyes for the textile trade are sold almost entirely in the form of powders, finely ground for homogeneity and ease of dissolving. These powders contain plenty of other chemicals besides the dyes themselves. Some of these chemicals are adventitious, some are deliberately added. There is no such thing as a pure dye for textile dyeing and finishing. Not only would pure dyes be hard to use, but their cost would be prohibitive and comparable with that of pharmaceutical products, many of which are derived from similar basic chemistry, for example, aspirin.

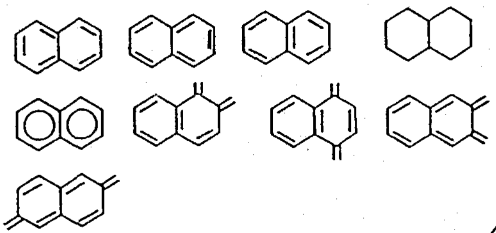

Fig. 2. Representations of naphthalene rings.

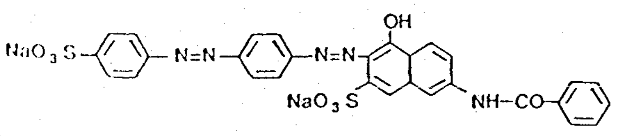

Fig. 3. C.I. Direct Red 81.

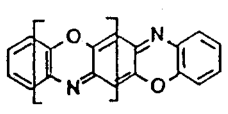

Fig. 4. Dioxazine.

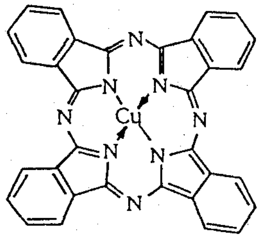

Fig. 5. Copper phthalocyanine C.I. Pigment Blue 15/16.

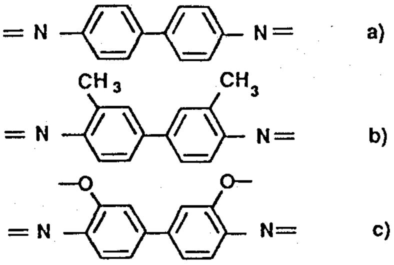

Fig. 6. Composite features of azo direct dyes.

Impurities

Among the impurities commercial dyes may contain are small amounts of intermediates and reaction by-products from the synthesis of the dye, some of which might be colored, and relatively large amounts of electrolytes. This is because most direct dyes are synthesized in aqueous solutions and to precipitate all of the dissolved product out of the solution frequently requires the addition of large amounts of salts. The salts become closely associated with the dye. Impurities also include small amounts of metal ions which may have been introduced during a metallization, or may have had their origin in the plant process water. These may be copper and manganese ions, neither of which is desirable, particularly if the dyed goods are to be brought in contact with rubber.

Processing Aids

Processing aids include ingredients to reduce the tendency of the powder to dust; ingredients to adjust the acidity or alkalinity of the product; ingredients to ensure rapid wetting of the powder during dissolution; ingredients to minimize caking of a product stored improperly in a hot and damp environment; and most importantly, inert ingredients, or diluents.

Standardization

The addition of inert diluents enables the standardization department of the color manufacturer to adjust the strength of batches of product from the plant, so that each successive batch can be shipped out at the same effective strength.

Further standardization ingredients might include shading colors. Sometimes in the course of dye synthesis, colored by-products are formed in sufficient amounts to affect the color of the plant product. Standardization departments must have the leeway to adjust color variations by the addition of small amounts of shading colors. These should be dyes with as closely similar dyeing and fastness properties as possible to the product being standardized.

The actual amount of pure dye within powder products varies widely from manufacturer to manufacturer and product to product. Even within the same company, a product may be sold at several strengths. A standard strength is often designated with either an *S* or 100 after the product name, while numerical designations (200, 300, 50, 67, etc.) all represent percentages relative to the company's own unique, internal, standard strength. Other letters seen following trade names can represent the hue characteristics of redness (R), blueness (B) or yellowness (G, from the German word Gelb, meaning yellow). These may be accompanied by numbers representing the relative importance of the characteristic; e.g., a very blue shade red might be designated Red 4B.

Problems with Generic Dyes

It is a poor idea to treat all dyes with the same C.I. name as if they were equivalent. Not all dyes sold under the same C.I. name dye the same fabric to precisely the same strength or the same hue. So how can a direct comparison be made? For example, when attempting to check incoming dyes of the same C.I. name for relative strength, by making spectrophotometric transmittance measurements on solutions, the results may not agree with those obtained by dyeing. How can this be the case, and what is the appropriate value for their relative strength?

These and other points will be addressed in a later section on color measurement, but in the last analysis, there is no substitute for visual examination of multiple dyeings carried out under carefully controlled conditions.

A more worrisome aspect is that, because of the differing nature of the non-dye chemicals involved, dyes with the same C.I. name may pose different health and environmental hazards.

Drug Room Practice

Direct dyes are not notorious for their dusting properties, but dye powders should always be handled with care and with good ventilation. Protective clothing should be worn. The much abused, obligatory Material Safety Data Sheets (MSDS) should be examined for all products being used. Even if the information is incomplete, it will point out where areas of special care and handling might be required.

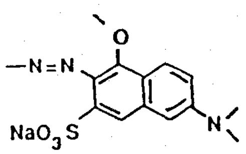

Fig. 7. Composite features of azo derivatives of J-Acid.

Because most direct dyes are adequately soluble at drug room concentrations, it should be no problem to thoroughly stir the required amounts of dyes in cold water to a smooth paste, followed by adding soft, boiling water while still stirring, keeping the temperature of the mix above 180F (85C) for 5 to 10 minutes with good stirring. If in doubt, reputable dye companies have information on the solubilities of their products. There should always be filters or screens on lines between the drug room and the dyeing equipment and they should be checked regularly.

Liquid Dyes

For the paper industry, which uses massive amounts of direct dyes continuously, a selection of the more soluble dyes are available in the form of dye solutions. Here the obvious drawbacks of shipping water are outweighed by the advantages inherent in not having to dissolve large quantities of solid color on a continuous basis. The closest textile parallel is that of the carpet industry where a continuous dye range may be using several pounds of acid dye per minute. Here, metering a liquid product beats batchwise mixing hands down.

Review

Commercial textile dyes are not pure colored products. Finishing and standardization of dyes involves much expertise and hard work. The quality of this endeavor, which is an added cost, could make all the difference between an easy to use product of consistent high quality and a superficially cheaper, inconsistent product which could be nothing but trouble and added expense to a dyeing operation, from drug room to finished goods inspection. A finishing plant should carefully monitor its choice of supplier and products. ∞

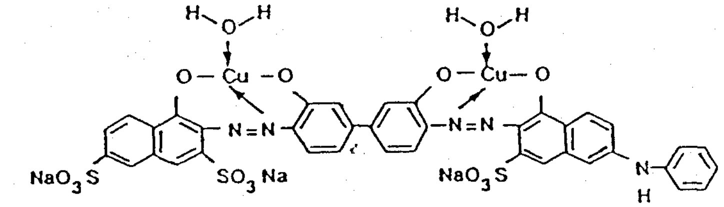

Fig. 8. C.I. Direct Blue 98.

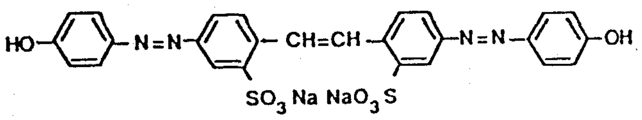

Fig. 9. C.I. Direct Yellow 4.

References

(1) *Colour Index*, Society of Dyers and Colourists and AATCC, Vol. 3, Third Edition, 1971.
(2) Ref. 1, Vol. 4.