FUNDAMENTALS OF THE CHEMISTRY AND APPLICATION OF DYES

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Preface

The evolution of the chemistry of dyes began in 1856 with the discovery and industrial production of Mauvein by W. H. Perkin. The essential basis of modern chemistry evolved at the same time (periodic system, quadrivalence of carbon, the structure of benzene). Thus the chemistry of dyes became that field of technical organic chemistry in which scientific methods were first applied. Other branches did not follow until the end of the 19th century.

It seems to us that this historical background nowadays exerts an inhibiting effect on dyestuff chemistry; it is frequently regarded as closed, conservative and not readily amenable to new discoveries. For this reason teaching institutions pay little attention to it.

However in a number of the more highly developed countries dyestuff chemistry is the basis of an important section of the chemical industry, which is actively engaged on research. Therefore, on the one hand, chemists who enter the dyestuff industry should be specially trained for work in this field but it is essential, on the other hand, that dye chemists always view their work in relation to the present state of general chemistry.

The present introductory work will attempt to meet both of these requirements; we shall provide the beginner who has read little specialized dyestuff chemistry at technical college with a review that covers all classes of dyes, but is confined to essential and characteristic structural features. We have resisted the temptation to enumerate as many commercial dyes as possible; this is the purpose of the Colour Index! We intend to demonstrate how the domain of dyes is connected with the fundamentals of modern inorganic, organic and physical chemistry, and to show that the enlightened dye chemist also requires this knowledge in his sphere of work.

We would also like to show the familiar field in a new light to the experienced, conventionally trained, dyestuff chemist, and induce him to devote his attention to unsolved problems. The more theoretical chapters 2, 3 and 11 are meant as an introduction to the physical and chemical aspects: naturally, they offer little that is new to the true physical chemist.

The only book written after the second World War which considers both the basic principles of dyes in textile chemistry as well as their nontextile applications is the classical work of K. Venkataraman (1952–53, supplementary volumes 1970–71). As we feel that this will be the most productive approach in the future, a large portion of this book will deal also with nontextile aspects of dyestuff chemistry.

The book is based on lectures which both of us have given at the Swiss Federal Institute of Technology (E.T.H.) Experience has taught us that the only way of gaining new friends for dyestuff chemistry is to treat dyes, not as a special section, but as an integrated component of organic and physical chemistry.

Several colleagues have given us valuable hints on planning this book. We are particularly indebted to Dr. H. H. Bosshard (Ciba-Geigy Ltd.), Dr. E. Ganz (Ciba-Geigy Ltd.), Prof. E. Heilbronner (University of Basle, formerly E.T.H.), Prof. W. Jenny (Ciba-Geigy Ltd.), Dr. H. Klessinger (University of Göttingen), Prof. W. Lüttke (University of Göttingen), Dr. H. E. Nursten (University of Leeds), Dr. R. Orwell (University of New South Wales) and Dr. P. B. Weisz (Mobil Oil Corp., Princeton, U.S.A.) for their advice and discussions.

We hope that this small book will help to arouse and increase the interest of industrial chemists, college lecturers and students in dye chemistry.

Zurich, August 1970

Paul Rys
Heinrich Zollinger

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1

Introduction

1.1. HISTORY AND INDUSTRIAL PRODUCTION OF DYES

PREHISTORIC man had already dyed furs, textiles and other objects with natural substances, mainly of vegetable, but also of animal origin. Ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing.

Further developments extending over many thousands of years led to rather complicated dyeing processes and high-quality dyeings. Among these the following deserve special mention: Indigo, which was obtained both from dyer's woad, indigenous in Europe, and from *Indigofera tinctoria*, a native plant of Asia; Ancient purple which was extracted from a gland of the purple snail by a process developed by the Phoenicians; Alizarin, on which Turkey Red is based, which was obtained from madder Campeachi wood extract imported from Africa.

Picric acid, which was obtained by Woulfe in 1771 by treating indigo with nitric acid, was subsequently occasionally used for dyeing silk yellow but did not attain any significance. For this reason—really incorrectly—William H. Perkin, not Woulfe, was given credit for having produced the first synthetic organic dye. In 1856, this young, talented, English chemist, working in a suburb of London, succeeded in obtaining by oxidation of a mixture of aniline bases, not quinine, which he had hoped for, but a violet cationic dye which he called Mauveine; initially, the yield was poor. If Perkin is to be regarded as the founder of the synthetic dye industry this is correct in the sense that, on the one hand, with the primitive means then at his disposal he was able to prepare a relatively pure and technically interesting product and, on the other hand, was able to develop its synthesis so that it could be used in large-scale production.

The brilliant violet hue on silk immediately attracted much attention and stimulated other chemists to carry out similar experiments. In this way, in 1859, E. Verguin in Lyon discovered fuchsine, whilst the discovery of diazo compounds by P. Griess in England laid the foundation for the development of the currently largest class of synthetic dyes, namely the azo compounds. The first true azo dye, Bismarck Brown, was developed by Martius in 1863.

After the decisive work by August von Kekulé on the quadrivalence of carbon (1858) and on the constitution of benzene (1865), the way was opened for the planned preparation of purely synthetic dyes, as well as for the artificial production of natural dyes. The first success to be mentioned is the elucidation of the constitution (1868), and the synthesis immediately afterwards, of alizarin (1,2-dihydroxyanthraquinone) by Graebe and Liebermann. The elucidation of the constitution, and the synthesis, of indigo (Adolf von Baeyer, 1870; K. Heumann, 1890) involved research work extending over several decades. The development of indigoid dyes reached a climax at the beginning of the 20th century as a result of the work of G. Engi and of P. Friedländer who synthesized Ciba Blue 4B and thioindigo, respectively. Shortly before the turn of the century, Vidal opened up the field of sulphur dyes, whilst the year 1901 was characterized by the discovery of indanthrone, the first anthraquinonoid vat dye, by R. Bohn.

The natural dyes already included metal complexes (Turkey Red). In this domain, the 20th century yielded important contributions with Neolan dyes (1915), phthalocyanine (1936) and the 1:2-metal complex dyes (Irgalan dyes, 1949). R. Clavel and H. Dreyfuss, in the 1920's, solved the problem of dyeing hydrophobic fibres by means of disperse dyes. The post-war era is characterized by the development of pigments which achieved importance for colouring plastics (e.g. quinacridone, 1958), Cromophtalic dyes (1957), reactive dyes for wool (1951/52: Remalan and Cibalan Brilliant dyes) and especially reactive dyes for cellulose fibres (Procion dyes, 1956). New developments in this field have been reviewed by H. Pfitzner[1] and K. Venkataraman.[2]

Reactive dyes, for example, clearly show the general tendency of dyestuff research to move away from purely empirical syntheses of coloured molecules to the study of the mechanisms of interaction of substrates and dyes with already known chromogens (e.g. azo, anthraquinone and cyclic aza compounds).

The fact that nowadays thousands of dyes of different constitution are commercially available clearly shows that a thorough knowledge of synthetic organic

Table 1.1 A review of dyestuff production 1966/67[3]

	Production			Export	
	10^3 t	10^6 \$	\$/kg	10^3 t	10^6 \$
Western Europe					
German Federal Republic	77·3	278	3·60	46·9	170
Great Britain	38·5	128	3·33	21·4	62
Switzerland	30·9	158	5·35	26·4	141
France	20·7	60	2·93	8·0	23
Italy	13·0	23	1·79	2·1	5
Remainder	17·5	23	—	—	—
U.S.A.	112·1	436	3·89	10·0	35
Japan	48·8	101	2·08	4·6	9
Eastern Europe and China	180	—	—	—	—
Remainder (India, Brazil, Canada, etc.)	30	—	—	—	—
Total	560	—	—	—	—

chemistry (leading to the preparation of new dyes, the discovery of new reactive groups, etc.), of the reaction mechanisms (leading to the optimization of manufacturing processes) and of the techniques of applying the results of dye research can ultimately bring success.

The manufacture of dyestuffs is characterized by its concentration, in a few large concerns, in a few countries. Whilst before the first World War almost the whole of the world's requirements of synthetic dyes was manufactured in Germany (apart from Germany, only Switzerland contributed a significant proportion of world production), nowadays manufacture is spread over a larger number of countries. Table 1.1 indicates that Germany is still the largest exporter of dyestuffs, that Switzerland produces particularly high-grade dyes, and that the production of markedly cheap dyes is concentrated in countries like Italy and Japan. Unfortunately, there are no recent reliable statistical data available for Eastern Europe and for China.[3]

1.2. THE CLASSIFICATION OF DYES

Dyes can be grouped in accordance with two different principles:

(a) chemical structure (chemical classification),
(b) dyeing methods and areas of application (colouristic classification).

Chapters 4–10 of this book discuss the most important classes of dyes primarily according to their chemical grouping. Chapter 11 discusses the physical and chemical basis of the colouristic classification, but the more practical aspects of dyeing technology are included at the appropriate places in Chapters 4–10.

A review of the whole field of technical dyes shows that the two classifications overlap, i.e. there is hardly a chemical class of dye which occurs solely in *one* colouristic group, and vice versa. In the same way, some colouristic groups can be applied to two or more substrates, whilst others are specific to a single substrate. Reactive dyes, for example, are classified chemically as coloured compounds having a group capable of forming a covalent bond with a substrate. The coloured parent substance can, in principle, be derived from all classes of Chapters 4–10 but the compounds mainly involved are of the azo, anthraquinone and aza annulene types (sections 4.2.6, 10.5.4 and 7.2, respectively).

When classified according to the dyeing method, they may be anionic, direct or disperse dyes, depending on whether they are intended for use on protein, cellulose or polyamide fibres. Moreover, certain reactive dyes having a particular type of chemical structure can be used for several substrates, whilst others (having the same type of structure) are suitable for only a single substrate.

It is possible to devise a logical method of chemical classification,[4] and the present book is based upon it. However, owing to space limitation, we are unable to discuss it in detail. With some classes of dyes, however, we have abandoned the conventional nomenclature, since it is either wrong (for instance, 'basic' instead of 'cationic'

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dyes) or insufficiently comprehensive (e.g. phthalocyanine as a sub group of aza annulene structures).

The third edition of the Colour Index (1971)[5] (5 volumes in all) describes all dyes that were being manufactured at the time of going to press. In Part 1, dyes are grouped, according to colour, in the following classes: acid, mordant, basic, disperse, natural dyes and pigments, food, leather, direct, sulphur, vat, reactive, an ingrain section including ingrain dyes, azoic diazo components, azoic coupling components, azoic compositions, oxidation bases, pigment and solvent dyes, optical brighteners, intermediate products, developers and reducing agents. The various classes of dyes are subdivided according to colour, viz. yellow, orange, red, violet, blue, green, brown and black and (for pigments) white.

Part 1 also gives methods of application, usage, the more important fastness properties and other basic data.

Part 2 gives the structural formulae (where known) of the dyes, methods of manufacture and literature references, including patents.

Part 3 includes abbreviations of manufacturers' names, details of fastness tests, a patents index and a commercial names index.

Each dye is given two reference numbers, one relating to its class with respect to dyeing method (e.g. C.I. Vat Blue 4 for indanthrone) and the other to its chemical description in Part 2 (e.g. C.I. 69800 for indanthrone). All the commercial names under which each dye is sold (over 37 for indanthrone e.g. Indanthrene Blue RS, Cibanone Blue RSN, Caledon Blue XRN, Ponsol Blue GZ etc.) are also listed in Part 1.

1.3. LITERATURE

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2

The Basis of Colour in Organic Compounds

2.1. RELATION BETWEEN CHEMICAL CONSTITUTION AND LIGHT ABSORPTION

DYES are characterized in accordance with their capacity to absorb the energy of that part of electromagnetic radiation to which the human eye is sensitive. Of the whole spectrum of electromagnetic vibrations, the microwave (wavelength above 500 μm, wave numbers below 20 cm^{-1}), infrared (0·7–500 μm, 15,000–20 cm^{-1}), visible (400–700 nm, 25,000–15,000 cm^{-1}) and ultraviolet (10–400 nm, 10^6–25,000 cm^{-1}) regions are important in chemistry because the molecules, by absorbing energy, are raised to (higher energy) excited states. Absorption of the relatively low-energy microwave and infrared radiations is associated with changes in the rotational and vibrational energy of molecules and atomic groups. However, the higher energy of visible and ultraviolet light (40–70 and 70–3,000 kcal/mol) raises the electrons into excited states (electronic spectra). There is, therefore, no fundamental difference between visible and ultraviolet spectra.†

Naturally, chemists have been occupied with the relation between chemical *constitution* and *colour of organic compounds* since the origin of structural chemistry. Several 'chemical' theories have been based on the first, purely empirical, system, which was developed by O. N. Witt[1] in 1876; the authors will briefly deal with these towards the end of this chapter.‡

A full understanding of electronic spectra requires a knowledge of the energy values of the ground and the excited states of the absorbing molecules and ions. According to the Einstein–Bohr frequency condition ($\Delta E = h\nu$), the energy differences ΔE of these states are directly proportional to the frequency (or wave number respectively), i.e. inversely proportional to the wavelength, of the absorbed light. With the aid of W. Heisenberg's quantum mechanics (1925) and E. Schrödinger's wave mechanics (1926) it was possible to obtain information about the energy levels of electrons in atoms and molecules.

In the wave mechanical model for the three-dimensional states of an electron, the electron 'paths' in the original Bohr atom model are replaced by *orbitals*, i.e. the partition functions of single electrons. The Schrödinger equation (2.1) describes the motion of an electron of mass m and potential energy U as a function of the three space coordinates x, y, and z, the total energy E and the eigenfunction ψ. ψ^2 here is a measurable quantity related to the electron density.

---

† Electron transitions are also responsible for bands in the near infrared (up to about 1,000 nm and in isolated cases 1,500 nm).

‡ A. Maccoll[2] has compiled an up-to-date summary.

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2m}{h^2}[E-U(xyz)]\psi=0 \qquad (2.1)$$

A solution of the Schrödinger equation is possible with atoms which are similar to hydrogen (H, Li^+, etc.); however, difficulties are encountered with atoms with more complex electron structure, since the interaction of several electrons has not been precisely elucidated. Although these problems are being intensively studied at the present time, it is still necessary to reduce these poly-electron systems, by means of approximate solutions, to single electron problems.

Of the methods which are used for this purpose, the molecular-orbital method (MO) (Mulliken 1928, Hund and Lennard-Jones) will first be described. Here a linear combination of wave functions (LCAO-MO, linear combination of atomic orbitals) is formed from the atomic orbitals of the valency electrons. With a diatomic molecule, e.g. HD, combination may occur in phase ($\psi' = N'(\psi_H + \psi_D)$), and out of phase ($\psi'' = N''(\psi_H - \psi_D)$) ($N'$ and N'' are normalizing factors). ψ' has a lower energy and ψ'' a higher energy than the electrons of the isolated hydrogen and deuterium atoms. For this reason HD is more stable than H + D; in accordance with the Pauli principle the two electrons of HD have opposite spin and occupy the molecular orbital ψ'; this is termed bonding and ψ'' anti-bonding.

The energy level of ψ' decreases as the extent of the atomic orbital 'overlap' increases. The so-called overlap integral is $S = \int \psi_H\psi_D\, dV$, taken over all space.

The molecule HD can absorb the light energy when one of the two electrons is raised from the bonding (ψ') ground state into the anti-bonding excited state (ψ''). The energy difference between ψ' and ψ'' therefore determines the absorption frequency (or wavelength)—see above. These two states are denoted by σ and σ^* because σ-electrons participate.

Since both electrons in the excited state no longer occupy the same molecular orbital, the restriction imposed by the Pauli principle no longer applies; there are, therefore, two excited states, the singlet and the triplet state, with anti-parallel (↓↑) or parallel (↑↑) spins of the two electrons, respectively. The triplet state, which is important in respect of phosphorescence, has a lower energy level than the singlet of the same electron configuration.

It is well known, from classical chemical investigations, that benzene is a uniform compound, the properties of which do not correspond to the hypothetical cyclohexatriene. The electron distribution of benzene may be deduced from a molecular-orbital consideration: thus, as with ethylene the two π-orbitals overlap, with the hexagonally-symmetrical benzene there is paired overlapping not only of 3 × 2 adjacent, but of all six, orbitals.

Calculation of the energy levels of the π-electrons, according to the MO method, by E. Hückel[8] has shown that pairs of the second and the third bonding molecular

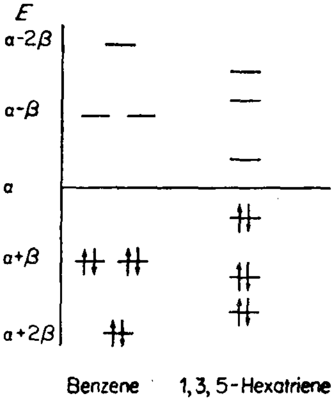

Figure 2.1 Orbitals of benzene and 1,3,5-hexatriene

orbitals as well as the two lower anti-bonding orbitals possess the same energy ('degenerate' MO). The scheme shown in Figure 2.1 illustrates the energy levels of these orbitals calculated by the simplest MO approximation method ('Hückel–MO' or HMO).

Here the so-called Coulomb integral α serves as reference energy level, corresponding approximately to the ionization potential of an electron in a $2p$ atomic orbital. The resonance integral β is a measure of the interaction between two orbitals; it is approximately proportional to the overlap integral S and with aromatic hydrocarbons amounts to about 18–20 kcal/mol. The energy 2β is termed the mesomeric energy, or better the '*delocalization energy*', of benzene.

E. Hückel demonstrated that this particularly strong stabilization occurs only in homo- and heterocyclic compounds which have a total number of $(4n + 2)\pi$-electrons in the perimetric ring system (Hückel rule). As the investigation of annulene systems (Chap. 7) showed, it is of no fundamental importance whether they are mono- or polycyclic systems when $n = 1, 2, 3$, (etc.). The cycloheptatrienylium cation, which E. Hückel in 1931 predicted to be stable (tropylium ion, $C_7H_7^{\oplus}$), was first prepared by W. E. von Doering in 1956 and it represents one of the neatest proofs of the usefulness of quantum theoretical work in organic chemistry!

Where an aromatic compound carries a group with π-orbitals in a position adjacent to aromatic carbon (e.g. NO_2 or COOH), overlapping of both π-electron systems normally occurs, leading to new bonding and anti-bonding electron states. The same thing occurs on substitution with atoms that have lone pairs of electrons (e.g. OH, NR_2, etc.). These electrons occupy p-orbitals and, for geometrical reasons, they can also overlap with the aromatic π-electrons. Because of the possibility of an interaction of the p-electrons with protic solvents (H-bond), the absorption bands which are responsible for the *p*-electron transitions exhibit, with increasing polarity of the solvent, a displacement of the absorption bands to shorter wavelengths ('negative solvatochromy'), whilst this change of medium generally has the opposite effect with different types of bands.

When hyperconjugation, inductive and steric effects are neglected, substituents without *p*- or π-electrons (e.g. CH_3, $NH_3^{\oplus}$) exert a negligible influence on π-orbitals of conjugated systems.

The simple MO treatment has been developed in different ways; with the free electron model[4] the energy states of π-electrons are, in principle, treated as if they vibrate freely in a 'box' determined by the molecular dimensions. H. Kuhn[5] and J. R. Platt[5] showed quite early (1948 and onwards) that this model, using relatively simple means, leads to striking agreement between calculated and experimentally measured spectra, particularly for polymethine dyes and aromatic compounds. The 'self-consistent field' method (SCF)[6] embodies, semi-empirically, the interelectronic interactions, and the Pariser–Parr–Pople method[7] embodies the configuration interactions. In the MIM method (molecules in molecules),[8] with complicated molecules, only those changes (which relate to the known spectra of sub systems) that occur when these systems are coupled to the whole of the molecule are calculated. Here coupling is attributed to the electrostatic interaction between the transition moments occurring in the individual excitation of the subsystems and to an electron transition from one subsystem to another.

The *valence bond method* (VB) uses a starting point different from that of the MO method for the approximate solution of the Schrödinger equation; this is a polyelectron theory which, in contrast to the above-mentioned methods, results in a linear combination of polyelectron functions and not atomic orbitals. These functions can be assigned to different mesomeric structures of the particular molecules. Instead of orbital diagrams (e.g. Figure 2.1), (overall) state diagrams for the different mesomeric structures are obtained. These states are coupled.

A coupling of mesomeric structures which do not exist as such is also termed resonance.

The *qualitative* application of the valence bond method (the so-called resonance theory) has led to many misunderstandings within the last three decades. On the one hand, mesomeric structures were repeatedly assumed to be different structures of the same compound—in the same way as tautomers are discrete isomers ('oscillation between two mesomeric structures')—and on the other hand the mesomeric structures were connected with excited states. Since the term 'resonance' refers to the coupling of two (true) oscillatory systems, it is not as good as the term 'mesomerism', coined by Ingold, which indicates in a better way that the true low energy state lies *between* two (hypothetical) mesomeric structures.

The electron spectrum of a molecule exhibits a multiplicity of absorption bands of widely differing intensity which are partly superimposed. In principle, *one* particular electron transition is assigned to one band. However, these bands are not clearly

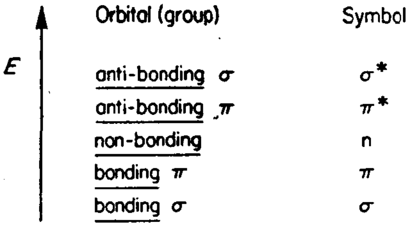

Figure 2.2 Scheme showing molecular orbitals

defined since simultaneous changes in the vibrational and rotational states are superimposed on the electron transitions. Figure 2.2 shows, in the simplest form, the essential types of energy levels. From the previous discussion it is clear that with polyatomic molecules more than one of each of these levels is present. As demonstrated in Figure 2.2, a transition of a p-electron from a non-bonding orbital (n) into the anti-bonding π^*-orbital ($n \rightarrow \pi^*$-transition) requires light of lowest energy; therefore a $n \rightarrow \pi^*$-transition usually occurs at longer wavelengths than a $\pi \rightarrow \pi^*$-transition.† In some cases however (e.g. with α,β-unsaturated ketones) a $\pi \rightarrow \pi^*$-transition corresponds to the absorption band with the longest wavelength. $\sigma \rightarrow \pi^*$- and $\sigma \rightarrow \sigma^*$- transitions mainly result in absorption in the far ultraviolet. Not all transitions lead to anti-bonding states; with triphenylmethane dyes, for example, transitions to non-bonding excited states are of importance.

The *intensity* of absorption bands, as well as their wavelength, is of outstanding importance in technical dye chemistry. The molar extinction coefficient ε of the Lambert–Beer law is a measure of the former (2.2).

$$\log \frac{I_0}{I} = E = \varepsilon\, d\, c \qquad (2.2)$$

I_0, I: Intensity of the incident or transmitted light
E: Extinction (or optical density)
d: Layer thickness (cm)
c: Concentration (mol/l)
ε: Molar extinction coefficient (l/mol cm)

For commercial dyes ε has values of from 10^4 (better 2×10^4) to over 10^5 l mol^{-1} cm^{-1}. The area ($\int \varepsilon\, d\tilde{\nu}$) of the absorption bands is important in determining a quantity, the oscillator strength f ($f = 4{\cdot}3 \times 10^{-9} \int \varepsilon\, d\tilde{\nu} = \varepsilon_{max}\, \Delta\tilde{\nu}_{1/2}$ where $\Delta\tilde{\nu}_{1/2}$ is the width of the band at half height) which is related to the nature of the electronic transition. Strong absorption bands ($f \simeq 1$; $\varepsilon_{max} = 10^4$–10^5) correspond to 'permitted', and weak ones to 'forbidden' electron transitions. When an electron is

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† Here we denote excited states with the sign * (some authors also use this sign for anti-bonding orbitals); the form $\pi^* \leftarrow \pi$ (instead of $\pi \rightarrow \pi^*$) is also used.

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