

Chapter 2

Dyes and Pigments: Their Structure and Properties

Abstract Dyes and pigments are the most important colorants used to add a color or to change the color of something. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. Dyes are colored substances which are soluble or go into solution during the application process and impart color by selective absorption of light. Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble in, and essentially chemically unaffected by, the vehicle or medium in which they are incorporated. On the other hand, the color, which is highly dependent on the chemical and physical properties of a matter, is a result of the interaction between light and substance. This chapter is focused on the chemical and structural properties of dyes and pigments, as well as the relationship between light and color.

Keywords Dye • Pigment • Colorant • Chromophore • Auxochrome • Color

2.1 Introduction

A color additive is a substance capable of imparting its color to a given substrate, such as paint, paper or cotton, in which it is present. Dyes and pigments are the most important colorants used to add a color or to change the color of something. A dye must be soluble in the application medium, usually water, at some points during the coloration process. It will also usually exhibit some substantivity for the material being dyed and be absorbed from the aqueous solution. On the other hand, pigments are the colorants composed of particles that are insoluble in the application medium (Broadbent 2001). Dyes and pigments as colorants are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. It is estimated that over 10,000 different dyes and pigments are used industrially and over 7×10^5 tons of synthetic dyes are annually produced worldwide (Zollinger 1999; Chequer et al. 2013). The terms, *dye*, *dyestuff*, *pigment*,

color, *colorant*, and *paint* are often wrongly used interchangeably. This chapter focused on the properties of dyes and pigments, chemical and structural considerations, the relationship between light and color.

2.2 Dyes and Pigments

Paint is defined as any liquid, liquefiable, or mastic composition designed for application to a substrate in a thin layer which is converted to an opaque solid film after application. Paint is used for protection, decoration, or identification, or to serve some functional purpose such as the filling or concealing of surface irregularities, the modification of light and heat, etc (Kirk-Othmer 1998a).

Both pigments and dyes are used to provide color to all sorts of substances and have been important to humans since the dawn of history. The difference between the two is that dyes are soluble in the substrate and thus disperse at a molecular level, while pigments are insoluble and are dispersed as particles. Dyes provide brighter color than conventional pigments, but they are less light stable and less permanent (Rothon 2012).

Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble in, and essentially chemically unaffected by, the vehicle or medium in which they are incorporated. They alter appearance either by selective absorption and/or scattering of light. Organic and inorganic pigment powders are finely divided crystalline solids that are essentially insoluble in application media such as ink or paint (Kirk-Othmer 1998b).

Dyes, on the other hand, are colored substances which are soluble or go into solution during the application process and impart color by selective absorption of light. In contrast to dyes, whose coloristic properties are almost exclusively defined by their chemical structure, the properties of pigments also depend on the physical characteristics of its particles (Kirk-Othmer 1998b).

Ever since pre-historic time, man has been fascinated to color the objects of daily use employing inorganic salts or natural pigments of vegetable, animal, and mineral origins. These coloring substances, known as dyes, are the chemical compounds used for coloring fabrics, leather, plastic, paper, food items, cosmetics, etc., and to produce inks and artistic colors. Dyes are of two types, i.e. synthetic and natural. Synthetic dyes are based on petroleum compound, whereas natural dyes are obtained from plant, animal, and mineral matters (Singh and Bharati 2014).

Colorants are normally understood to include both pigments and dyestuff. Pigments refer mainly to inorganic salts and oxides, such as iron and chromium oxides, which are usually dispersed in crystal or powder form in an application medium. The color properties of the dispersion depend on the particle size and form of the pigment. Pigment colorants tend to be the highly durable, heat stable, solvent resistant, lightfast, and migration fast. On the other hand, they also tend to be hard to process and have poor color brilliance and strength. Dyes (also called dyestuff) are conventionally understood to refer to organic molecules dissolved, as molecular

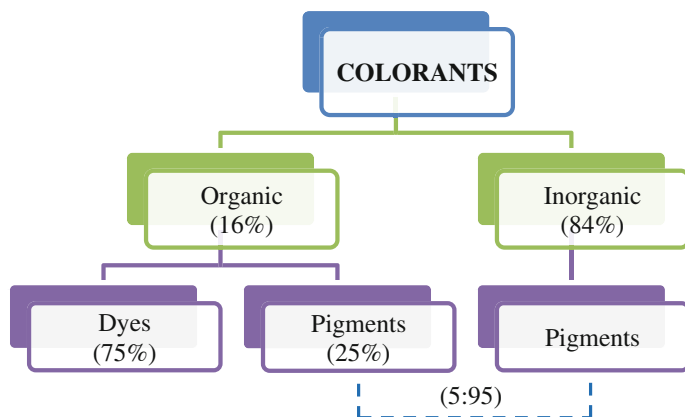


Fig. 2.1 Share of colorants from organic and inorganic classes. Reproduced from Zollinger, Copyright 2003, with permission from Wiley

chromophores, in the application medium. Examples are azo dyes, coumarin dyes, and perylene dyes (Zhang 2010).

Figure 2.1 presents total production amount (weight %) of different classes of colorants (Zollinger 2003; Chakraborty 2010). The global market production of organic colorants in 2010 is forecast to be 2.1 million metric tons valued at 14.4 billion dollars and projected to grow at an annual rate of 3–4 %. The market for inorganic colorants is roughly 5 times larger (Barden 2010).

The color imparted by dyestuff to the resulting solution depends on the electronic properties of the chromophore molecule. Dyestuff colorants tend to have excellent brilliance and color strength, and are typically easy to process, but also have poor durability, poor heat and solvent stability, and high migration. Because of the contrasting properties of both types of colorants, much work has been done trying to improve the attributes of each class of colorant. Nanocolorants were regarded as a new class of colorants that could get out of dilemma between dyestuffs and organic pigments. In nature, nanocolorants are a class of nanocomposites that recombine dye acted as an essential ingredient and suitable polymeric matrix, and its performance target is to integrate excellent chromatic properties and good processibility of dyestuffs and good durability of organic pigments. Nanocolorants are new kind of colorants that can combine the advantages of both pigments and dyes, and will be promisingly applied to photoelectric high-tech fields (Zhang 2010).

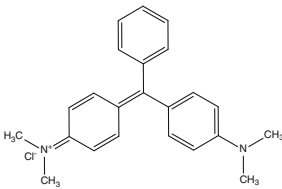
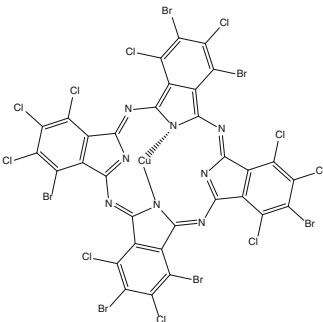
Dyes can generally be described as colored substances that have affinity to the substrates to which they are being applied (Pereira and Alves 2012). Dyes are soluble and/or go through an application process which, at least temporarily, destroys any crystal structure by absorption, solution, and mechanical retention, or by ionic or covalent chemical bonds (Nwokonkwo 2013). Color Pigment Manufacturers Association (CPMA) has defined pigments as colored, black, white

or fluorescent particulate organic or inorganic solids which usually are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light (Merchak 2012).

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 color substrates to which they have affinity. Pigments can be used to color any polymeric substrate but by a mechanism quite different from that of dyes, in that surface only coloration is involved unless the pigment is mixed with the polymer before fiber or molded article formation (IARC 2010).

The most important differentiation of colorant is that colorant is either dyes or pigment. These terms are often used indiscriminately, in particular, pigments are quite often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied. Pigment particles have to be attached to substrates by additional compounds, for example by a polymer in paint, in a plastic or in a melt. Dyes, on the other hand, are applied to various substrates (textile materials, leather, paper and hair) from a liquid in which they are completely, or at least partly, soluble. In contrast to pigments, dyes must possess a specific affinity to the substrate for which they are used (Zollinger 2003). Some properties of malachite green and pigment green which are important colorants and they are used as coloring agents for different materials were presented in Table 2.1.

Table 2.1 Some properties of malachite green and pigment green 36

	Malachite green (basic green 4)	Pigment green 36 (phthalocyanine green YS)
CAS No	569-64-2	14302-13-7
Chemical structure		
Class	Triarylmethanes	Phthalocyanines
Chemical Formula	$C_{23}H_{25}N_2Cl$	$C_{32}Br_6Cl_{10}CuN_8$
Solubility	Very soluble in water	Insoluble in water
Physical form	Green crystals	Yellowish green powder

2.3 Color and Constitution

The absorption of electromagnetic radiations in the UV and visible regions by a molecule causes to the electronic excitation and an electron moves to higher electronic energy level from a lower. A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, $C=C$, $C\equiv C$, $C=O$, $C\equiv N$, $N=N$, NO_2 etc. If a compound absorbs light in the visible region (400–800 nm), only then it appears colored. Thus, a chromophore may or may not impart color to a compound depending on whether the chromophore absorbs radiation in the visible or UV region. Table 2.2 shows the some organic dyes and their chromophoric groups (Gangani 2006).

Chromophores like $C=C$ or $C\equiv C$ having π electrons undergo $\pi \rightarrow \pi^*$ transitions and those having both π and non-bonding electrons, e.g., $C=O$, $C\equiv N$ or $N=N$, undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. Since the wavelength and intensity of absorption depend on a number of factors, there are no set rules for the identification of a chromophore. Characteristics of some common unconjugated chromophores are given in Table 2.3.

A covalently saturated group which, when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as auxochrome, e.g., NH_2 , OH , SH , halogens etc. Auxochromes generally increase the value of λ_{max} as well as ϵ_{max} by extending the conjugation through resonance. These are also called colour enhancing groups. An auxochrome itself does not show absorption above 200 nm. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different values of λ_{max} and ϵ_{max} . For example, benzene shows λ_{max} 256 nm, ϵ_{max} 200, whereas phenol shows λ_{max} 270 nm, ϵ_{max} 1450 (both increased). Hence, OH group is an auxochrome which extends the conjugation involving the lone pair of electrons on the oxygen atom resulting in the increased values of λ_{max} and as ϵ_{max} .

When two or more chromophoric groups are conjugated, the absorption maximum is shifted to a longer wavelength (lower energy) and usually to a greater intensity compared to the simple unconjugated chromophore, e.g., ethylene shows λ_{max} 171 nm, ϵ_{max} 15,530 and 1,3-butadiene λ_{max} 217 nm, ϵ_{max} 21,000. In conjugated dienes, the π molecular orbitals of the separate alkene groups combine to give two new bonding molecular orbitals designated π_1 and π_2 , and two antibonding molecular orbitals designated π_3^* and π_4^* . Schema 2.1 shows the $\pi_2 \rightarrow \pi_3^*$ transition, i.e. the promotion of an electron from a highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of a conjugated diene, is of very low energy, 1,3-butadiene shows λ_{max} 217 nm which is lower than the $\pi \rightarrow \pi^*$ transition of an unconjugated alkene, ethylene shows λ_{max} 171 nm.

Similarly, in case of other conjugated chromophores, the energy difference between HOMO and LUMO is lowered resulting in the bathochromic shift. Thus, α,β -unsaturated carbonyl compounds show both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions at longer wavelengths (e.g., acrolein, λ_{max} 210 and 315 nm) compared to unconjugated carbonyl compounds (acetaldehyde, λ_{max} 180 and 290 nm) (Schema 2.1).

Table 2.2 Some of chromophoric groups present in organic dyes

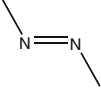
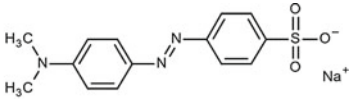

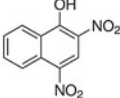
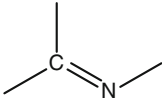
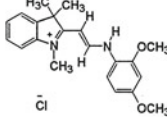
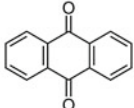
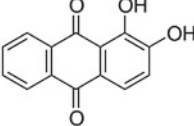
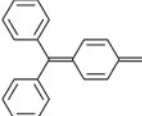
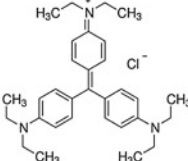
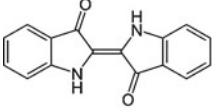
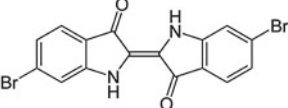
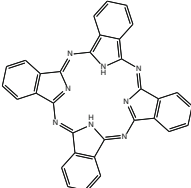
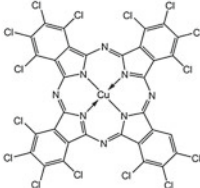
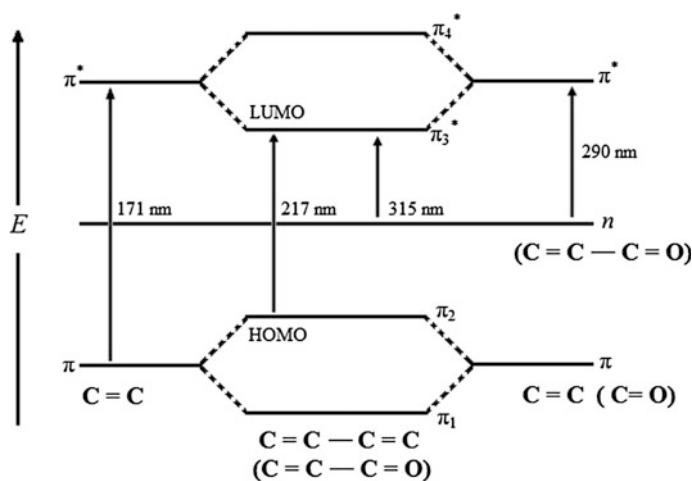
Chromophoric Groups	Sample Dye
 <p>Azo</p>	 <p>Methyl orange</p>
 <p>Nitro</p>	 <p>Martius Yellow</p>
 <p>Methine</p>	 <p>Basic Yellow 11</p>
 <p>Anthraquinone</p>	 <p>Alizarin (Turkey Red)</p>
 <p>Triarylmethane</p>	 <p>Ethyl Violet</p>
 <p>Indigo</p>	 <p>Tyrian purple</p>
 <p>Phthalocyanine</p>	 <p>Pigment green 7</p>

Table 2.3 Characteristics of some common unconjugated chromophores

Chromophore	Example	λ_{\max}	ϵ_{\max}	Transition	Solvent
	Ethylene	171	15,530	$\pi \rightarrow \pi^*$	Vapor
$\text{—C}\equiv\text{C—}$	Acetylene	150 173	$\sim 10,000$ 6000	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Hexane Vapor
	Acetaldehyde	160 180 290	20,000 10,000 17	$n \rightarrow \sigma^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Vapor Vapor Hexane
	Acetone	166 188 279	16,000 900 15	$n \rightarrow \sigma^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Vapor Hexane Hexane
—COOH	Acetic acid	204	60	$n \rightarrow \pi^*$	Water
—CONH_2	Acetamide	178 220	9500 63	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Hexane Water
—COOR	Ethyl acetate	211	57	$n \rightarrow \pi^*$	Ethanol
—NO_2	Nitromethane	201 274	5000 17	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Methanol Methanol
	Acetoxime	190	5000	$n \rightarrow \pi^*$	Water
$\text{—C}\equiv\text{N}$	Acetonitrile	167	Weak	$\pi \rightarrow \pi^*$	Vapor
—N=N—	Azomethane	338	4	$n \rightarrow \pi^*$	Ethanol

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Schema 2.1 Relative energies of electronic transitions in conjugated systems. Reproduced from Yadav, Copyright 2005, with permission from Springer

Table 2.4 Characteristics of some simple conjugated chromophores

Chromophore	Example	λ_{\max}	ϵ_{\max}	Transition	Solvent	Band
$\begin{array}{c} >C=C-C=C \\ \quad \end{array}$	1,3-Butadiene	217	21,000	$\pi \rightarrow \pi^*$	Hexane	K
	1,3,5-Hexatriene	258	35,000	$\pi \rightarrow \pi^*$	Hexane	K
$\begin{array}{c} >C=C-C\equiv C- \\ \end{array}$	Vinyl acetylene	219	7600	$\pi \rightarrow \pi^*$	Hexane	K
		228	7800	$\pi \rightarrow \pi^*$	Hexane	K
$\begin{array}{c} >C=C-C=O \\ \quad \end{array}$	Acrolein	210	11,500	$\pi \rightarrow \pi^*$	Ethanol	K
		315	14	$n \rightarrow \pi^*$	Ethanol	R
	Crotonaldehyde	218	18,000	$\pi \rightarrow \pi^*$	Ethanol	K
		320	30	$n \rightarrow \pi^*$	Ethanol	R
	3-Pentene-2-one	224	9750	$\pi \rightarrow \pi^*$	Ethanol	K
		314	38	$n \rightarrow \pi^*$	Ethanol	R
$\begin{array}{c} -C\equiv C-C=O \\ \end{array}$	1-Hexyn-3-one	214	4500	$\pi \rightarrow \pi^*$	Ethanol	K
		308	20	$n \rightarrow \pi^*$	Ethanol	R
$\begin{array}{c} O=C-C=O \\ \quad \end{array}$	Glyoxal	195	35	$\pi \rightarrow \pi^*$	Hexane	K
		280	3	$n \rightarrow \pi^*$	Hexane	R
HOOC—COOH	Oxalic acid	~185	4000	$\pi \rightarrow \pi^*$	Water	K
		250	63	$n \rightarrow \pi^*$	Water	R

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It is known that as the energy of electronic transitions decreases, their probability usually increases and so ϵ_{\max} also increases. Since conjugation lowers the energy required for electronic transitions, it increases the value of λ_{\max} and usually that of ϵ_{\max} also. Thus, ethylene shows λ_{\max} 171 nm, ϵ_{\max} 15,530 and 1,3-butadiene λ_{\max} 217 nm, ϵ_{\max} 21,000. For more examples of various conjugated chromophores, see Table 2.4.

In general, the longer the conjugated system, the higher are the values of λ_{\max} and ϵ_{\max} . Thus, a compound with sufficient conjugation absorbs in the visible region (400–800 nm) and becomes colored. For example β -carotene, an orange pigment present in carrots, has eleven carbon-carbon double bonds and absorbs in the visible region (λ_{\max} 450 nm, ϵ_{\max} 14×10^4) and is colored (Yadav 2005).

The historical development of theories with respect to the relationship between the color of a dye and its chemical constitution has been thoroughly investigated. As previously stated, during the mid-nineteenth century, since organic chemistry was only at its embryonic stage of development, chemists utilized mostly empirical methods to synthesize dye. Nonetheless in 1867, Graebe and Liebermann proposed that the color of dye molecules was related to unsaturation within the molecules, having observed that reduction destroyed the color of dyes. An early theory of dyes first formulated by O. Witt provided a basis for understanding the relation between color and the structure of molecule. According to this theory, a dye consists of three components: one or more the fused benzene rings attached to the unsaturated groups called as chromophores (e.g., $-N=N-$, $-NO_2$, $-C=O$) and basic groups called as auxochromes (e.g., NH_2 , OH groups). Both of them are responsible for the color (Iqbal 2008). Witt's theory was expanded by Dilthey and Wizinger in 1927.

They realized that a chromophore is usually an electron-withdrawing group, while an auxochrome is commonly an electron-donating group and the two are linked through a conjugated system. This particular approach can be considered as the starting point of the donor–acceptor chromogen concept. Although Witt's theory applied to anthraquinoid and azo dyes, it was less successful in comparison with the theory proposed by Armstrong and Nietzki regarding triphenylmethane dyes and an alternative quinonoid theory since color was attributable to the presence of quinonoid ring structure. While the following approaches were investigated to link tautomerism with visible and UV light absorption by dyes together the progress in quantum mechanics during the mid-1920s contributed to the development of qualitative approaches to associate color to chemical constitution (Burkinshaw 2016).

In simple terms, it can be considered that the organic dye molecules contained three main components such as chromogen, chromophore and auxochrome.

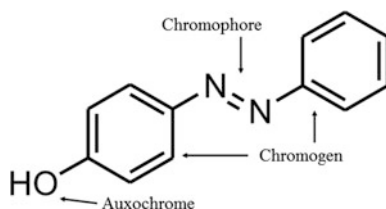
- The chromogen is a chemical compound that is either colored or could be made colored by the attachment of suitable substituent. The chromophore and the auxochrome(s) are also part of the chromogen (Carmen and Daniela 2012).
- The chromophore is a chemical group that is responsible for the appearance of color in compounds (the chromogen) where it is located. The colorants are sometimes also classified according to their main chromophore (e.g., azo dyes contain the chromophore $-N=N-$) (Iqbal 2008).
- The auxochrome is a substituent group found in a chromogen that influences its color. Whereas, the chromophore or chromophoric group is responsible for chromogen which will be colored. The chromophore itself is not capable of determine a particular color and hue (Marsden 1982). Also, Gurr differentiates two types of auxochrome namely colligators, which are responsible for dye–substrate interactions and which are either ionic (e.g., acidic: $-SO_3^-$, $-COOH$, etc., or basic: $-N^+$, $-NH_2$) or non-ionic and non-colligators which modify color (Burkinshaw 2016).

The components responsible for color are presented in Schema 2.2 for 4-Hydroxyazobenzene (Solvent Yellow 7).

Unlike most organic compounds, colorants possess color because they:

- absorb light in the visible spectrum (400–700 nm),
- have at least one chromophore (color-bearing group),

Schema 2.2 The components of 4-Hydroxyazobenzene



- have a conjugated system, i.e. a structure with alternating double and single bonds, and
- exhibit resonance of electrons, which is a stabilizing force in organic compounds (Hossain 2014).

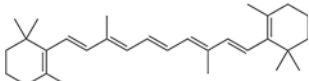
When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (color helpers), examples of which are carboxylic acids, sulfonic acid, amino, and hydroxyl groups (Kumar 2013). While these are not responsible for color, their presence can shift the color of a colorant and they are most often used to influence dye solubility (IARC 2010). Table 2.5 shows the relationships between wavelength of visible and color absorbed/observed. The wavelength spectrum of absorbed light, which determines the color of the matter, is affected by its chemical structure consisting of components such as the chromophores and auxochromes.

Other factors contributing to color are illustrated in Table 2.6 and Schema 2.2. The structures in Table 2.6 demonstrate the importance of having an extended conjugated system. It is evident that doubling the length of the conjugated system in β -carotene and its synthetic homologues causes a significant bathochromic shift, i.e. to a darker color. In addition, resonance also exists across molecules with delocalization of electrical charge among the conjugated atoms and affects the color (Baser and Inanici 1990; Pauling 1939). Consequently there is always more than

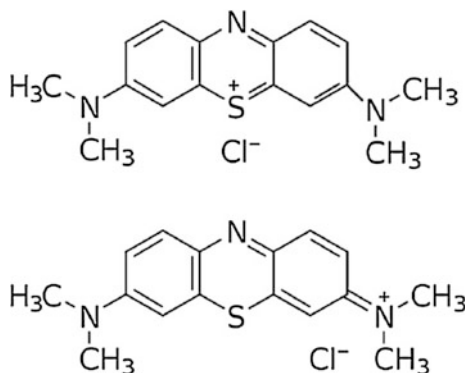
Table 2.5 The relationship between color and wavelength of absorbed light

Wavelength absorbed (nm)	Color absorbed	Color 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

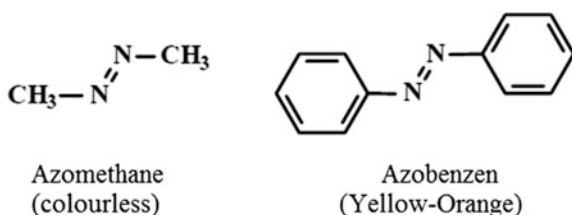
Table 2.6 Conjugation in β -carotene and its synthetic homologues

Carotenes	Double Bond (C=C) Number	Color
 $C_{30}H_{44}$	7	Yellow
$C_{40}H_{56}$ (β -carotene)	11	Red-Orange
$C_{50}H_{68}$	15	Dark blue
$C_{60}H_{80}$	19	Black

Schema 2.3 Different resonance structures of Methylene blue



Schema 2.4 The relation of chromophore group, conjugation and color. Reproduced from IARC, Copyright 2010, with permission from WHO

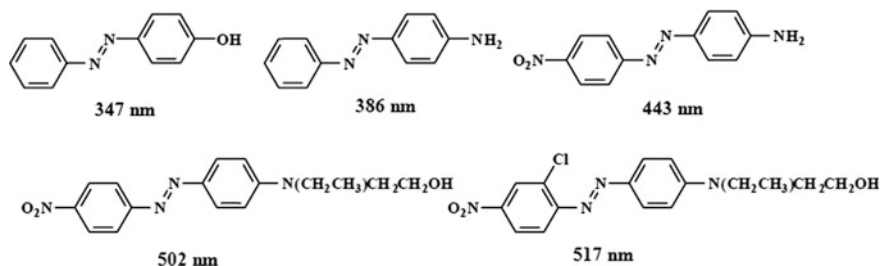


one way to draw the structure of a dye. For example, Methylene blue, commonly used in textile and paper industry is represented by Schema 2.3. The alternating double bonds are all equivalent. The positive charge is shared by the nitrogen and sulfur atoms; in fact it is distributed across the whole cation and not localized at any particular atom (Kiernan 2001).

Regarding the requirement of a chromophore generating color 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 Schema 2.4 where it can be seen that placement of an azo group between methyl groups produces a colorless compound, while a yellow-orange color is obtained when the azo group is placed between aromatic rings (IARC 2010).

In addition to influencing solubility, auxochromes are essential ring substituents in providing target colors. This is illustrated in Schema 2.5, 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. NH₂).
- Electron-donating (NH₂) and electron-accepting (NO₂) 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 (Asiri 2001).
- The electron-donating effects of an amino group are enhanced by adding alkyl groups to the N-atom.



Schema 2.5 Effects of substituent groups within an azo-dye system. Reproduced from IARC, Copyright 2010, with permission from WHO

2.4 Light and Color

Visible light is that part of the electromagnetic spectrum, shown in Fig. 2.2, with wavelengths between the red limit at about 700 nm and the violet limit of 400 nm. Depending on the observer, light intensity, etc, typical values for the spectral colors are red, 650 nm; orange, 600; yellow, 580; green, 550 and 500; and blue, 450 (Chittka and Waser 1997).

Color is the part of perception that is carried to the eye from our surroundings by differences in the wavelengths of light (Edge 2003). First, this involves the nature and spectral power distribution in the light from the illuminating light sources. Next, there are several often interrelated processes derived from the interaction of the illumination with matter including absorption, reflection, refraction, diffraction, scattering, and fluorescence. Finally, there is the perception system, involving the eye and the transmission system from eye to brain, leading to the final interpretation reached in the brain (Kirk-Othmer 1998c).

Dye chemistry has evolved together with the organic chemistry during the nineteenth century. Initially, the developments about dye have been faster and such developments provided significant contributions also to the development of structural organic chemistry. The structural theory is developed to understand not only the

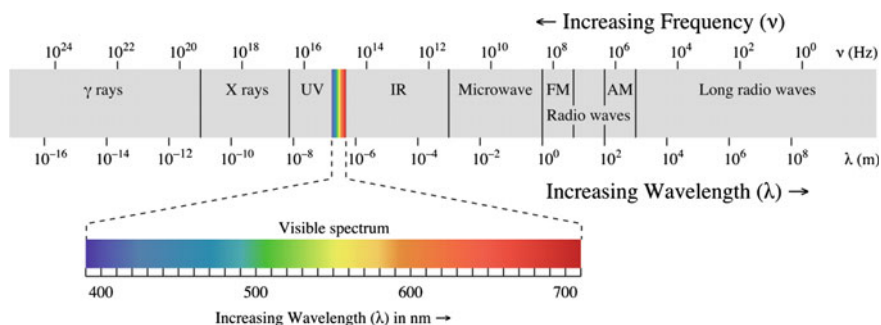


Fig. 2.2 The electromagnetic spectrum

chemistry of dye but also the origins of colors in dyes. This was particularly true for the late nineteenth-early twentieth century period, as the electronic theory of molecular structure began to be developed. Thus it is of interest to review briefly the development of color and constitution theory from the time of the first synthetic dyes, and to see how this has led to a situation where modern computers can now be used to predict the color of a dye before it has even been synthesized. At the time of Perkin's discovery, organic chemistry as a science was still in its infancy. Therefore, the structure of benzenoid compounds could not be properly understood until Kekule's theory in 1865. It should also be considered that the electron was not discovered until 1897 and the concept of the electron-pair bond was formulated by Lewis in 1916 (Shaik 2007). Until 1868, the sufficient data that are associated with the unsaturation in the dye molecules and color about synthetic dyes have accumulated (Akaoui 1976). The first real attempt to interpret the color of dyes in terms of their molecular composition was made by Witt in 1876. By this time, structural chemistry had progressed to a stage where functional groups were well understood, and Witt had imagined a dye molecule formed from three components. Thus, he defined benzene, or fused benzene, rings, and simple unsaturated groups attached to these rings, e.g., $-\text{NO}_2$, $-\text{N}=\text{N}-$, $-\text{C}=\text{O}$ as chromophores. He also defined basic groups, e.g., $-\text{NH}_2$, $-\text{OH}$, as auxochromes and remarked that the presence of all three units produced intense color. Witt's theory was readily applicable to the azo and anthraquinone dyes, but it could not easily be reconciled with the triphenylmethane cationic dyes. Thus, a complementally alternative interpretation associated with the origin of color was proposed quite independently by the theory proposed by Armstrong and Nietzki. Eventually, it was suggested that color is associated with the presence of quinonoid structures (i.e., benzenoid rings modified to a cyclohexadiene residue with two exocyclic double bonds). For example, these units had to be present in the formulated structures of the cationic dyes. Generally more than one quinonoid structure could be drawn, and it was a logical step to assume that some kind of oscillation of the structure between these possibilities was responsible for light absorption. In fact, the electromagnetic wave theory of light had been accepted for a long time, and the interaction of a vibrating wave with an oscillating bond system provided an attractive mechanism for the absorption process. However, simple theoretical considerations showed that the frequency of atomic vibrations were far too low to be matched with the frequency of light. After the discovery of the electron, it was pointed out that vibrations of such a particle would involve the correct sort of frequency for light absorption, but this suggestion was not treated seriously by chemists at the turn of the century. By Lewis's electronic theory related with the bonding in molecules after significant progresses in theoretical chemistry in the early 1900s, light absorption over electronic excitation was widely accepted.

One important theoretical concept associated with color was mesomerism. In 1899, conjugation and partial valence hypothesis in order to explain the anomalous chemical properties of conjugated polyene systems had been published. Therefore it was suggested that chain termini possess partially unsatisfied valencies in such system. In subsequent years, the concept of "limiting structures" for depicting of the true structure of a molecule had been developed. Such ideas that laid the

foundations for mesomerism exposed the concept of “average structure” as the chromostate in recognition of its apparent direct relevance to color. For example, a triphenylmethane dye can be regarded as an average of three limiting structures, and the consequent chromostate is highly colored.

The most important advance in theoretical chemistry was the quantum mechanics whose mathematical formulation was first developed in 1925 with the independent contributions of Schrodinger and Heisenberg. By the early 1930s, quantum mechanics has been applied to the subject of bonding in molecules (for example the π -bond was mathematically formulated in 1930). At this stage, the concept of mesomerism used by the organic chemist, and a new concept called as resonance began to be used as equivalent on the basis of quantum mechanical calculations. The approximation related with this concept is based on the valence bond theory, and it was subsequently used also to calculate the absorption spectra of dyes. Also in the early 1930s, an alternative mathematical approximation that utilizes quantum mechanics to calculate the properties of molecules was developed, namely, molecular orbital theory (Jones 2015). Many of the properties of complex conjugated organic molecules were quantified by using this method referred to as Hückel molecular orbital (HMO) theory.

With the introduction of the valence bond and HMO methods, the applications of these theories in subsequent years contribute a great deal to dyes and the attempts to predict color. For example, in 1939 the application of the HMO method to the absorption spectra of polyenes and cyanine dyes was made with considerable success, and by the same year, valence bond theory was also used in relation with the colors of cationic and anionic dyes. In 1940 the spectroscopic shifts in polyene dyes caused by increasing chain length were calculated, and then the well-known convergent and non convergent vinylene shifts in unsymmetrical and symmetrical cyanine dyes were also determined by using valence bond theory. Thus, it may be said that satisfactory physical interpretations about the structure of organic molecules with the means for calculating the light absorption properties of dyes were established sufficiently until 1940. In 1942, a new quantum mechanical approach to calculate the properties of conjugated organic molecules was introduced. This approach known as the “electron gas” or “free electron” method has been quite successful for calculating the spectroscopic properties of simple dyes, and has been exposed to the many changes in later years. In 1950s, a different form of HMO theory was used to determine the color for many cyanine-type dyes with notable success.

In 1953, the theoretical approaches based on HMO theory that could include electronic interactions were emerged. The new computational procedure as referred to as the Pariser-Parr-Pople (PPP) method has been very successful for calculating the electronic spectra of π -electron systems. Then, by the development of suitable molecular parameters it has been proved to be one of the most successful color prediction techniques for routine use at the present time. One disadvantage of the PPP method is that it ignores σ -electrons and considers the π -electrons only.

Until the 1970s, Various MO procedures were developed and these methods have become as easily applicable to complex dye structures as the PPP method. Although enormous strides in the area of mathematical color prediction have been made, qualitative color and constitution theory still occupy an important place in terms of dye chemistry. As all these approaches have an important place in the context of the modern dye chemistry, they may give an insight about the origins of color in dyes and also general electronic structural theory of organic compounds (Griffiths 1990).

A completely new approach which would not only provide a new insight into color structure relationships but would also allow quantitative assessments to be made was required. The Einstein-Planck quantum theory, which states that energy is not continuous but can only have certain discrete (quantized) values, constituted such a breakthrough. From this new fundamental theory, two modern theories of color and constitution have emerged: Valence Bond (VB) theory and Molecular Orbital (MO) theory. The major difference between the two theories is that the former is based on the concept of bonding valence electron pairs being localized between specific atoms in a molecule, whereas the latter is depend on the pictures of electrons showing distribution among a set of molecular orbitals of discrete energies. On the other hand, Huckel made the major breakthrough using these theories to calculate the various properties of unsaturated molecules. Huckel had made perhaps the most drastic assumption considering σ and π electrons separately. Use of MO (HMO) theory by Huckel provided the calculation of properties of unsaturated molecules (ethylene, butadiene and benzene). In 1948, Kuhn developed the Free Electron MO (FEMO) model, which is the simplest of the MO models. It is suitable only for conjugated systems in which all the bonds have similar n-bond order such as the cyanine dyes. The first general MO theory for dyes was proposed by Dewar in 1950. A set of rules for predicting qualitatively the effect of substituent on the color of a dye was formulated by using MO (PMO) theory. In 1951, the many equations based on LCAO-MO theory was developed by Roothaan to describe the behavior of molecules. If these equations could be solved for dye molecules, it would enable to calculate precisely both the color and the tinctorial strength. However, they are theoretical in nature and unsuitable for tackling the complex molecules of organic chemistry. Consequently, Pariser, Parr and Pople designed a semi-empirical theory to predict the wavelengths and intensities of the main visible and ultra-violet bands of unsaturated organic molecules by using Roothaan equations in 1953. The Pariser-Parr-Pople (PPP) model incorporated the n-electron by considering only the assumption of Huckel plus a self-consistent-field (SCF) treatment to take account of electron-electron interactions. It also considers the configuration interaction (CI) treatment to include the effect of other transitions on the main highest occupied to lowest unoccupied MO (HOMO \rightarrow LUMO) transition. Both these treatments provide to obtain a better (more real) solution. In addition, more complex integrals in the equations were neglected whilst values for others were obtained from experimental data.

PPP model was used widely and successfully for predicting the color and tinctorial strength of dyestuffs especially for azo dyes (Gordon and Gregory 1987).

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