CHAPTER

ONE

INTRODUCTION
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A.I Beauce du diable of the fascinating variety of things that fulfil our universe may be largely attributed to the most captivating aesthesiogen: the colour. The man, since the advent of civilization, has always enjoyed colour. Captivated most by its fascination, he has ever since tried to duplicate the colours of nature and has exploited them in a number of ways. Ancients used coloured substances of natural origin to decorate their skin, fabrics and other materials. However, the choice was limited. It was only in the nineteenth century that man succeeded in synthesizing the coloring substance in the Chemist's laboratory. Today, the colourants having every colour of the rainbow and their various hues and shades have been synthesized. In many cases, the man has improved over nature and given mankind not only many new substances with colours and shades but also those that are far more superior.

A. I DEVELOPMENTS IN THE HISTORY OF COLOURANTS:

Even though its appeal has only been aesthetic, colour has increasingly been called upon to sell products and so vast industries are now dependent upon the availability of artificial colourants. Clothing's, carpets, well paints, plastic veneers, colour photographs, medicine, food and what not, all contain colouring substances. Throughout the history of man, dyes and pigments, both natural and artificial, have been important articles of commerce. Consequently, considerable interest has been shown in the theoretical and empirical evaluation of relationship between their colour and molecular structure. The widening areas into which the colours now intrude have accentuated this interest. In fact, colour - structure relationships are now of value to the scientists working in many seemingly unrelated disciplines. Save apart business and industry, dyes and pigments enjoy their applications in science, biology, medicine, engineering, architecture and technology, art.

Philosophy and psychology and above all, modern living as we see every dry day. Liquid crystal systems, high energy radiation sensors and organic dye lasers are recent examples of varied uses of synthetic colouring matters. But the burden to meet the ever-increasing demand of artificial colourants consequent upon a bewildering range of their applications rests with the humble organic chemist.
In the ancient times the materials used to produce colours were few in numbers and were obtained from vegetable sources. The three most prized colours were the blue indigo, the red madder and the yellow of the saffron. Other colouring matters were those of animal origin. ‘Tyrian Purple’ obtained from a small snail ‘Murex Bandaris’ found near Tyre was so costly that it was available only to those of high status. Hence its name ‘Royal Purple’. Then there was ‘Cochineal’ obtained from the dried body of female insects cacti. These along with some other natural products constituted the dyeing material of those times.

1.3 SYNTHETIC COLOURANTS:

The properties of natural colourants were far from ideal, and together with their limited availability from sources of supply, encouraged the early search of synthetic dyes with superior properties and availability in plenty. However, only a few additions couldn’t made to the existing natural colourants until the rise of the modern synthetic dye industry 41 during the closing years of the nineteenth century.

The modern multi billion dollar synthetic dye-stuff industry owes its initiation to the academic research due to Perkin 42 and the vigorous efforts by such leading organic chemists as Haffmann, Baeyer, Caro, Griess, Graebe, Liebermann, Otto fischer, Emil fischer, Nietzsche 43 and a host of others. Later however, research chemists more closely concerned with industry largely carried out the development of new organic dyes some of them are Sandmeyer, Heumann, Schmidt, Green 44 etc.

PICRIC ACID was born to Woulfe in 1771 as the first synthetic dye by the action of nitric acid on natural Indigo. Not until 1885 was a technical method introduced to prepare it from coal tar AURIN, the ROSOLIC ACID, became in 1834 the first coal tar dye reported by Ferdinand Runge. It along with usual mordants produced the red colours and lakes that rivaled those produced from natural dye cochineal and Alizarin. Yet neither of these compounds were being manufactured on a commercial scale. The unreliability of supply and the heavy cost was the cause. That, for the little knowledge about the components of coal tar and that for Kekule’s theory of structure of benzene was not proposed until 1865, Ringe’s experiments couldn’t be extended. As early as 1843, Hoffman had observed that aniline prepared at the time gave red colours under certain conditions. In 1856, Perkin 45 oxidized aniline sulphate with
potassium dichromate and obtained a purple dye called MAUVE. Mauvine or aniline purple was the first dye to be manufactured commercially. It was the sensation of 1862 World Exhibition in London. The first coal tar dye caught on and the race for new dyes and colours began in right earnest. From a waste product the coal tar was transformed into a commodity of immense use. Synthesis of martius yellow, caro’s induline blue and Hoffman’s violet followed quickly and was accepted widely. The discovery that the colouring matter could be prepared by the oxidation of aniline led to the study of behaviour of this base towards various oxidizing agents. Soon, thereafter, the bright red dye FUCHSIN was prepared in 1859 by Verguin in Lyons, France by the oxidation of aniline by tin chloride, which made an even greater impact than the MAUVE. After Hoffman showed that FUCHSIN is a derivative of tri phenylmethane, this class of dyes was investigated extensively and came into widespread use.

The discovery of early synthetic aniline dyes was necessarily the result of intuitive following of clues derived from fortuitous experiments since the constitution of even benzene was unknown. In the year 1865 Kukule published his theory of the structure of benzene and thus paved the way for elucidation of the structure of organic compounds aromatic in nature and for the development of dye industry on a rational basis. The artificial dyes although more brilliant, were less permanent than the natural dye chemists set out to work analyzing the structure of the natural products.

The structure of Alizarin, the popular red dye from the route of madder, was quickly determined in 1868 by Carl Graebe and Carl Liebermann, to be a derivative of anthracene. Benzene, naphthalene and anthracene are colourless products of coal tar distillation. By simple chemical addition of chromophoric groups beautiful dyes can be created. This finding in the 19th century excited the fashion world to colourfull fantasies. Graebe and Liebermann in 1868 afforded the synthesis of alizarin. In 1869, Graebe, Liebermann and Perkin were able to achieve its commercial production. This followed the manufacture of a family of alizarin like dyes with different colours. In 1871, Baeyer prepared FLUORESCINE and in the same year caro prepared Eosine after the start of commercial production of resorcinol. While the attention of the chemists were directed towards the synthesis of alizarin, another class of dyestuffs, the azo dyestuffs, appeared in the market in 1876. Griess had already synthesized azo compounds in 1862 and one member of group BISMARK BROWN had already been prepared on the commercial scale since 1863. In 1875 Caro discovered CHRYSOIDINE and indicated the technical value of the Griess method of preparing the azo compounds.
When azo dyestuffs were first introduced, it was considered that only orange and yellow colours could be obtained in this series. This idea was dispelled by the discovery of FAST RED A by Caro in 1878. Thus we see that Heinrich Caro\textsuperscript{54} contributed much to the synthetic dye industry.

By the turn of the century, in 1879 the oldest known colouring matter indigo was synthesized by Baeyer and was put to commerce in 1880. However, Karl Heumann\textsuperscript{55} achieved successful industrial production of synthetic indigo 1890. Baeyers Indigo synthesis marked the begging of the chemical industry and led to the development of organic chemistry whose economic strength was then recognized. Thus was born the chemical industry\textsuperscript{56}.

Since then the progress in the field of dyes has been very rapid\textsuperscript{57-85}. Here is a list of new milestones: Direct dyes from azo compounds for cotton were introduced in 1880; sulphur colour from coal tar derivative in 1893; anthraquinone dyes, vat dyes in 1901; azoic dyes or ice colours in 1911; acetoanilides in 1923; phthalocyanines in 1934; fluorescent brightening agents in 1940 and fiber reactive procion dyes in 1956. Thus natural dyestuffs were almost completely displaced by synthetic colourants. Fundamental research on new dyes is constantly in progress\textsuperscript{86-100} and thus synthetic dyes are dominating the field now. Today the industry occupies an important place among the major chemical industries.

\textbf{A.4 DYESTUFFS AND PIGMENTS: DEFINITION}

A dye-stuff is mostly an organic compound, which may be used to impart colour to a substance. It may be used as for the colouring of animal, vegetables or synthetic fibres and similar products such as wool, cotton, silk, linen, rayon, fur, leather, paper, nylon, or other materials such as oils, waxes, rubber and plastic. In these cases, the dyes may form a chemical union with the substance being dyed or it may become associated with it in an intimate physical union. Dyes, which are more or less soluble in water or may be made so simply, by a simple chemical reaction such as reduction, generally are used for dyeing and printing of fibers and related materials. Dyes of solvents, oil, waxes or plastic are either soluble in these media or else so finely divided that may be effectively dispersed throughout to give high colour strength. These insoluble colouring substances are called pigments\textsuperscript{101}.  

\textsuperscript{101}
Fundamentally all the organic dyestuffs are classified in the following two ways:

1. Based on method of application of the dyes.

1. Based on the chemical constitution of the dyes.

The first classification of dyes is very useful to the dyers who are mainly concerned with the process of dyeing. Moreover, this classification gives the various method of dyeing various fibers with different dyes. Thus, the dyes are classified into the following categories:


The second classification is mainly useful for those chemists who are mainly interested in chemical constitution of the dyes. O.N. Witt was the first who suggested a classification of the dyes according to chromophore or the essential colour producing group present in the dyes. But a number of dyes contain the same chromophoric group and so it became necessary to adopt a classification on the basis of the characteristic structural groups present in the dye molecule. This chemical classification divided all the dyes into the following principal groups put under two main classes: Homocyclic hetro ring absent and Heterocyclic- atleast one ring present.

(A) *Homocyclic dyes:*

(a) Anthraquinone dyes, (b) Azo dyes, (c) Azomethine dyes or benzilidene dyes, (d) Diphenylmethane dyes (e) Ethylenic dyes, (f) Ketimine dyes, (g) Nitro dyes, (h) Nitroso dyes, (i) Pyrazolone dyes (j) Quinonimine dyes and (k) Triphenylmethane dyes.

(B) *Heterocyclic Dyes:*

There is no uniformity in naming of the synthetic dyes. In most cases they bear the name given to them by their manufacturers. Furthermore, each dyestuff may have a number of names or different dyes may be known by the same names. In the colour index of the society of Dyers and colourists \(^{103}\), however each dye is given an individual number called the colour index Number abridged as C.I.No.

A.7. PHTHALEINS:

These dyes are the subject of the present work, which were first discovered by Baeyer\(^{104}\) in 1872 as a new class of dye. He prepared GALIEN, FLUORESCEN and PHENOLPHTHALEIN by condensing phthalic anhydride with pyrogallol; resorcinol and phenol respectively in the presence of a dehydrating agent like sulphuric acid or zinc chloride. Baeyer established that the parent member of the group phenolphthalein was dihydroxy derivative of phthalophenone which in turn could be degraded to triphenylmethane. Thus, he illustrated that phenolphthalein was a derivative of triphenylmethane. Following analogous arguments\(^{105}\) for fluorescein and for similar dyes called rhodamines; Baeyer classed them under triphenylmethane dyes which some authors\(^{106}\) still follow. Elsewhere\(^{107}\) only phenolphthalein, its tetralodo derivative and sulphophthaleins constitute the group, phthaleins and fluorescein its derivative uranine, eosine, mercurochrome, and rhodamines constitute another group called xanthenes. Both phthaleins and xanthenes, in turn, form a subclass of triphenylmethane dyes.

In Baeyer’s accord, all the dyes prepared by the condensation of phthalic anhydride with different phenols, aromatic hydroxyl compounds are grouped as phthaleins. Pyronines, rhodamines, and other similar dyes, which could be prepared in a similar manner that used for the preparation of phthaleins, phthaleins included, contain a Characteristic dibenzo-1,4 pyran nucleus dibenzo-1,4-pyran is called xathen\(^{108}\) which is an inner anhydride of o-o’ dihydroxydiphenylmethane. From xanthenes these dyes can be derived by introducing auxochromes\(^{109}\) into position-3 and-6, i.e. in para position with respect to carbon atom linking the two benzene rings. Therefore, in the classification used herein these dyes are grouped as xanthen dyes or xanthenes\(^{110}\).

In facts phenolphthaleins, although a phthalein, is not a xanthene derivative\(^{111}\) yet generally, xanthenes are prepared\(^{112}\) like phenolphthaleins by the method mentioned earlier.
Succineins were prepared by the condensation of aromatic hydroxyl compounds with succinic anhydride in presence of concentrated sulphuric acid as the dehydrating agent and are represented as follows:

\[
\begin{align*}
\text{Ar} & \quad \ast \quad R \\
H_2C & \quad C \quad O \\
H_2C & \quad \quad \quad \quad CO
\end{align*}
\]

Succineins
The most common manner in which the colour is generated is by the absorption of certain wavelengths of the visible light. Organic compounds with extensive conjuction absorb certain wavelengths of light because of \( \pi - \pi^* \) and \( n-\pi^* \) transitions. We do not observe the colour absorbed but we see its complement that is reflected. A complementary colour sometimes called a subtraction colour is thus the result of the subtraction of some of the visible wavelengths from the entire visual spectrum.

Before the theories of electronic transition were developed, it was observed that some types of organic structures gives rise to colour while other don’t the partial structures that are necessary for colour, the unsaturated groups\(^{115}\) can undergo \( \pi - \pi^* \) transition, were called chromophores, a term Witt\(^{114}\) coined in 1876 (Greek chroma-colour and phorous-bearing). These he specified as nitro, nitroso, azo and carbonyl groups that he suggested fall in this category. Molecules containing such groups e.g. nitrobenzene and azobenzene were referred to as chromogens since they had potentiality for developing colours even if they were not in themselves intensely of colours. Witt observed that presence of some other groups caused an intensification coloured. These groups were called auxochromes (Greek auxanein-to increase). These groups which were called the typically polar such as hydroxyl – or amino - did not in themselves produce colours, as we knonow that they can not under go \( \pi - \pi^* \) transitions, but could produce hypsochromic effect i.e. a shift in the absorption bands to shorter wave lengths, or a bathochromic effect where the shift is in the opposite direction, i.e. to longer wave lengths, as they can under go transition of n electrons. However, in practice, intense colour can be obtained without the presence of auxochromic groups and it has since been shown that this concept has nothing of scientific significance. The theories of Graebe, Leibermann, Witt, Neitzki\(^{115}\) Armstrong\(^{116}\) etc, were the results of successful attempts to determine the molecular structure of organic compounds and interpretation of colours in terms of chemical structure without regard to its physical causation. During the early years chemists were intrigued by the elusive relationship between the absorption spectra and the molecular structure and therefore the progress was severely hampered for want of suitable theory for the light absorption process itself. Today, thanks to the advent of quantum theory, we are in a more fortunate position, and mathematical treatments of varying levels of sophistication are available for the prediction of absorption spectra. Equally important are the qualitative treatments of light absorption, which have stemmed from the valence bond the molecular orbital theories and which can be used to predict qualitatively the effects of structural changes on the absorption spectra of a molecule.
B. 1 THE MECHANISM OF ABSORPTION OF LIGHT BY MOLECULES

A complete and satisfactory explanation of the colour of the organic compounds was found to be associated with absorption and transmission of light in general with the spectra of the molecule. The absorption of light was recognized to be associated with certain process of molecule energy changes and the process could also take place with many other substances besides those as appeared coloured to the human eyes. The colour as it appears to the human eyes is only a special case of the general feature of general phenomenon of absorption of electromagnetic waves and the colour of the substance for which the human eye is sensitive is determined by the selected absorption of light consisting of those waves. The phenomenon of light absorption is not limited to the visible part of the spectrum only but takes place in the ultra and infra red regions as well, as said before. Since white light imparts different colours to different chemical compounds, it is obvious that colour is a function of the chemical constitution of the molecules.

The wave particle duality of matter when applied to the electromagnetic radiation and to atomic particle forms the basis of quantum theory that uses the famous de Broglie relation

\[ P = \frac{h}{\lambda} \] .............. Eq. 1

Where \( P \) is the momentum of the particle, \( \lambda \) is its associated wavelength and \( h \) is the Planck's constant.

The absorption and emission of light by matter\(^{117}\) is explained by the wave properties of light. An electromagnetic wave is characterized by an electric vector \( E \) and a magnetic vector \( H \) which form a mutually perpendicular set of axes with the propagation of the vector \( C \). The absorption of light arises mainly through an interaction of electric vector of light with the electrons and nuclei in the molecule. The magnetic vector is only important for an understanding of phenomenon of optical rotation. A molecule initially in a state of \( E_a \) can absorb light of frequency \( \nu \), provided there is existing a state \( E_b \) by an amount \( E \) that satisfies the relation.

\[ E = E_b - E_a = h\nu = \frac{hc}{\lambda} \] ......................... Eq. 2

And it is said that the molecule has absorbed a photon of energy \( h\nu \) and is in the excited state \( E_b \). The stability in the excited state is limited and after a very short time e.g. less than \( 10^8 \) second the excited molecule dissipates its excitation energy and comes back to the ground state \( E_a \).
A molecule can exist in many excited states corresponding to the changes in its rotational, vibrational and electronic energy levels. And all these energies are quantized. Therefore, the absorption spectra can be further classified\textsuperscript{118} into three types:

1. Pure rotation spectrum which is associated with the changes in the rotational states of the molecule without the simultaneous changes in the vibrational and the electronic states. Since the separation between the various rotational levels are relatively small, it follows from Equation 2 that the corresponding occur in the far infra red and the microwave regions.

2. Rotational – vibrational spectrum is associated with transitions in which the rotational and the vibrational states of the molecule are altered, but the electronic state remains unchanged. The energy differences are relatively greater than in pure rotational spectrum and, accordingly, the absorption occurs at shorter wavelengths i.e. in the near infra red region.

3. Electronic spectrum that arises from the transitions between the electronic states, changes both the vibrational and the rotational levels. Therefore, a broad-spectrum band instead of a sharp line is observed. Relatively large differences are involved in the electronic spectra, which occur at still shorter wavelengths, i.e. in the ultra violet and the visible region.

Since the electrons can only be raised up to certain levels. $\Delta E$ must have some definite value; i.e. absorption of light by a molecule is not indiscriminate and discontinuous, but selective and gives rise to colour. A part from the frequency of the absorption band, colour also depends upon the intensity of the absorption that in turn depends upon probability of transition between the two energy levels concerned. The probability of the photon being absorbed depends upon the magnitude of the transition dipole moment between the two concerned energy states. The light absorption by a molecule\textsuperscript{119} can only occur when dipole moment changes in a molecule. The more symmetrical the molecule, smaller is the probability of the transition dipole and, therefore, the less likelihood of absorption of light by the molecule. Calculations have shown that greater is the transition dipole, greater is the intensity of absorption. The introduction of a group in a molecule that decreases the symmetry will thus increase the transition dipole and consequently increase the intensity of absorption. At same time, however, new ‘resonance paths’ may be introduced, and hence, not only a change in the intensity of absorption occurs, but also there is shift of the band to longer wave lengths.
B.2 THEORETICAL MODELS FOR CALCULATING LIGHT ABSORPTIONS:

The process of absorption of ultra violet and visible light by a molecule, as already mentioned, causes an electronic from a lower to a higher energy level; or more exactly causes an excitation from the highest energy level in the ground state to the lowest permitted energy level in the excited state as shown in figure to follow.

Compounds where the valence electrons are involved in sigma bond formation such as saturated hydrocarbons, only show absorption due to excitation of an electron a $\sigma^*$ antibonding or a higher orbital. The energy requirement are high, above 150 kcal mole$^{-1}$ and absorption occurs below 2000Å or 200 nm. This type of excitation process is referred to $\sigma--------\sigma^*$ transition, where the asterisk denotes an excited state. In compounds containing lone pair electrons; $O$, $N$, $S$ which are not utilized in bonding, the energy requirements for excitations are less since these electrons are generally less strongly held. The $n....\pi^*$ transitions (following the nomenclature of Kasha$^{120}$) in simple molecule thus gives rise to spectral bands at the longer wavelengths than those associated with $\sigma--------\sigma^*$ or $\pi--------\pi^*$ transitions. Proton addition to the non-bonding electron pair in $O$, $N$, or $S$ atoms causes the disappearance of the band at long wavelengths confirming that these non-bonding electrons take part in the excitation process. $\pi--------\pi^*$ transitions occur in the molecules containing double bonds in which there is an overlap of $p$-orbital causing formation of $\pi$-bonds. Because the overlap of $p$-orbital is not as great as in $\sigma$-bonding $\pi--------\pi^*$ transitions generally occur at the wavelength intermediate between those $\sigma--------\sigma^*$ and $n--------\pi^*$ transitions, i.e. in the near ultra violet and the visible region of the spectrum.

Thus, form the foregoing discussion, it becomes clear that to understand the colour of a compound, it is necessary to have a knowledge of the electronic structure of the molecule and its effect on the absorption of light in the visible and the near ultra violet region of the spectrum. For this purpose, three main theoretical approaches to the problem have been made.

B.3 MOLECULAR ORBITAL THEORY (MO) THEORY:

It is necessary to explain the term antibonding, which arises from the concept of the molecular orbital theory. It is best illustrated in the case of hydrogen molecule. When the constituent atom A and B are at equilibrium distance characteristic of the stable molecule, the two atomic orbitals $\phi_A$
and $\phi_B$, each of which accommodates one electron, will combine to form two molecular orbitals. The first of the lowest energy, is represented by the wave function $\psi_B$ and is called the bonding orbital. This orbital has characteristics separately possessed by $\phi_A$ and $\phi_B$ and may be written in a simplified treatment as a linear combination of the two,

$$\psi_B = \phi_A + \phi_B$$

Since molecular orbits arise from the atomic orbitals without the consideration of the electrons they have to accommodate. This treatment is referred to as Linear combination of Atomic Orbitals. The second molecular orbital $\psi_A$ is formed in hydrogen with the condition that,

$$\psi_A = \phi_A - \phi_B$$

This $\psi_A$ is the antibonding molecular orbital. The electron density or probability of finding an electron at a given point in this system is given by $\psi^2$.

The charge distribution in both molecular orbitals is cylindrically symmetrical. In the bonding orbital, the electron density is greatest between the two nuclei. In the antibonding orbital it is low between the two nuclei and the more stable configuration of the molecule is when the two nuclei are farther apart. It is this energy difference between the two molecular orbitals, which determines wavelength of the absorbed or the emitted light.

The energies of $\psi_A$ and $\psi_B$ molecular orbitals may be represented by the combined energy level diagram drawn on a following page wherein the electrons, $x$, contributing to separate functions $\phi_A$ and $\phi_B$ are shown combined in the case is zero. The two molecular orbitals $\psi_A$ and $\psi_B$ lie at equal difference in energy above and below the individual atomic orbitals. When the degree of interaction or overlap is positive, it can be shown that the antibonding orbital is displaced to higher energy above initial energy and the bonding orbital is displaced to a lower energy to the same extent. Dewar\textsuperscript{121} has extended this method of energy demonstration to hybrids of classical structures i.e. where the wave functions $\phi_A$ and $\phi_B$ differ in energy, using as an example two classical structures of Michler’s Hydrol Blue. The interaction of the two classical structures will give rise to two hybrid states, one of higher energy and the other of lower energy. The energy difference will be smaller when the energies of classical structures
are comparable i.e. mesomeric; and the absorptions occurs at longer wavelengths than when the classical structures have greater divergence in energy.

In the ground state of hydrogen, according to Pauli's Exclusion Principle, the electrons have opposing spins and the state is known as singlet state. Both electrons occupy $\psi_B$ bonding molecular orbital. In the first excited state, one electron is transported to an antibonding orbital. Since the electrons are now in different orbitals, the exclusion principle is no longer applicable and the electrons may now either be paired to give an excited singlet state, or unpaired to give a triplet state. In the latter case, there are three possible states all having the same energy since the $z$-components of the spin quantum numbers of the two electrons may be both $+1/2$ or both $-1/2$ or one may be $+1/2$ while the other is $-1/2$. The $z$-component of the resultant angular momentum may thus be 1, 0, or -1 and the three possible states are known jointly as the triplet state. A further excited state is possible when both the electrons occupy the antibonding orbital. Since the exclusion principle is now applicable, this must be, of necessity, a singlet state, the excited singlet state.

This elementary MO treatment can be extended to molecules which are electronically more complex, such as nitrogen and carbon monoxide, but which, as molecules, are relatively simple, provided due account is taken of hybridization in the simplifications and assumptions have to be made. In applying the theory it is necessary to neglect all overlap integrals between non-adjacent to average electron repulsions and to assume they are unchanged by the excitation process.

Further according to the theory of molecular orbitals \(^{123-124}\) the absorption of the u.v. and the visible light corresponding to the electron cloud of a molecule, resulting in the formation of electronically excited state. According to quantum theory, a molecule can exist only in a limited number of discrete energy states. The electronic structure of a molecule can be built up by the feeding of electrons one after another in the lowest available quantum state in accordance with the Aufbau Principle. A concept of united atom i.e. an atom whose atomic number is equal to the sum of the two separated atoms is helpful to understand the filling of electrons in the MO. The electrons, which in the united atom occupy in the excited state, are the antibonding electrons and those that do not are bonding electrons. The electrons in the atoms that remain unaffected by the process of molecule formation are said to be nonbonding electrons.
It is possible to consider the phenomenon of light absorption from the point of view of the molecular orbital theory. A molecule is excited when one electron is transferred from an orbital of lower energy to one of higher energy. Such transitions can occur only between permitted orbitals. In a molecule a g state go to a u state, or vice versa; transitions \( u \rightarrow u^* \) and \( g \rightarrow g^* \) are forbidden. Here \( u \) and \( g \) bear their usual meaning.

The ethylene molecule in its ground state has, in addition to \( \sigma \)-bond, at \( \pi \)-bond i.e a \( \pi_g \) orbital (bonding molecular orbital) in which there is the first excited state \( \pi_u \) orbital (antibonding molecular orbital). If one electron is excited from \( \pi_g \) to \( \pi_u \) a large amount of energy is required and the molecule therefore absorbs in the u.v region in compounds containing more than one double bond and that too in conjugation, delocalization of bond takes place and the molecular orbital formed covers all the carbon atoms of the conjugated system. The electron, therefore, has greater freedom of movement than in localized bonds and the total energy of the system is lowered which decreases the energy difference, \( \Delta E \) between the highest occupied and the unoccupied orbitals. Thus, as the conjugated extends, the absorption of light takes place at yet longer wavelengths.

Benzene molecule is symmetrical with all the carbon atoms have equal charges of unity and hence there is no transition dipole in the benzene molecule. It is not expected to absorb the light hence it is colourless. However, a weak absorption in the u.v region is expected and so exhibited. Nitrobenzene is not symmetrical and has unequally charged carbon atoms. Unequal charge produces a definite dipole moment in the molecule of nitrobenzene. The result is high transition dipole and absorption at longer wavelengths.

Furthermore, since nitrobenzene has an extended conjugation, the energy difference between the highest occupied orbitals is decreased, and therefore, it absorbs at longer wavelengths than benzene.

Nitroaniline (orange red) having more extended conjugation and greater separation of charge absorbs light at still longer wavelengths than nitrobenzene. Thus, in general, any such group, which exists in conjugation with benzene ring, happens to practically cause the shifts in the frequencies of the absorbed light towards the lower region or the wavelengths towards the longer regions. This effect of shifting of absorbed light towards the longer region in the electromagnetic spectrum, is that
which we understand and name as the Red Shift or the Bathochromic shift, or the Bathochromic effect. These shifts, if effects in the directions exactly opposite to those mentioned before, are said to be the Blue shift, or the Hypsochromic shift or the Hypsochromic effect.

Despite the fact that the molecular orbital method appears to be more promising from a quantitative point of view, and it has been possible to calculate the light absorption of many molecules by the ingenious applications of the great Molecular Orbital Method resulting in good agreement that has been obtained between the calculated and the observed values\textsuperscript{125} the Valence bond method as applied to absorption of light and prediction of colour stands satisfactory for qualitative purposes; and, therefore, one can not do well in keeping away from it. Thus, the valence bond approach is being discussed in the following section.
Electronic Energy Levels in Ground and Excited State

Molecular Orbitals
Combined Energy Level Diagram

Classical Structures of Michlers Hydrol Blue
structures lowers the energies of both the ground and the excited states and since charged structures contribute more to the excited state than the ground state, the lowering of the energy will be more prominent in the former than the latter. Thus, a greater resonance among the various charged forms results in the deepening of colour.

It can be safely inferred from the foregoing discussion that a given chromophore will not necessarily give absorption bands in the same position of the spectrum; the rest of the molecule also affects it. Benzene has a definite u.v absorption, 255 nm, ethylene has 185 nm and allylbenzene 249 nm, which is equivalent to the superimposition of spectra of benzene and ethylene. However, styrene has a quite different spectrum, 282 nm where the fine structure of benzene is absent.

Therefore, it can be observed that in styrene, the benzene nucleus is not in the same state, as it was in allylbenzene itself. This observation can be explained by assuming styrene to be a resonance hybrid of the structure II, III and IV.

The cyanine dyes, studied by Brooker and coworkers\textsuperscript{133} are intensely coloured substances exhibiting a high degree of resonance. These dyes can be represented by the general structures V and VI.

If aromatic ring systems are made part of conjugated chain of a cyanine, the characteristic properties of the chromophore are not altered. Thus, they will still be isoconjugate with an alternate add hydrocarbon anion, and will absorb at long wavelength by virtue of the presence of a nonbonding molecular orbital. The di- and tri-aryl methane dyes are example of this type.

Michler’s hydrol Blue. A diaryl methane dye, which is a resonance hybrid of two equivalent structures VII and VIII, absorbs at 607.5 nm in 98% acetic acid. The auramine IX, an important commercial dye of diaryl methane series, which is formed by the attachment of an amino group to the central carbon atom of Michler’s Hydrol Blue, shows large hypsochromic shift that result from the strongly electron donating amino group and absorbs at 434 nm in ethanol. Substituents other than amino group exert a hypsochromic shift related to electron donating capacity e.g. the attachment of a weaker ethoxy group to the central atom of Michler’s Hydrol Blue gives a smaller shift, and the dye is purple, $\lambda_{\text{max}}$ 525 nm.

The triaryl methane dyes, on the other hand, can be divided into two distinct types; those with two terminal amino groups, e.g Malachite Green,
X, and those with three terminal amino groups e.g. Crystal Violet, XI. From the foregoing discussion it is expected that increased number of resonance forms would deepen the colour. But the case of Malachite Green and Crystal Violet proves contrary to the expectations as the colour of the former is deeper than the latter. Malachite Green has two resonating forms where as crystal violet has three. The former shows two absorption bands; one at longer wavelength $\lambda_{\text{max}}$ 621 nm in 98% acetic acid, as expected for the attachment of the neutral conjugating group at any position in the chromophore; and a second band at a shorter wavelength, $\lambda_{\text{max}}$ 427 nm, as this provides a yellow component to the colour, the dye is green rather than blue. Polarization studies have shown that the two transitions are polarized along mutually perpendicular axes\textsuperscript{134}. The longer wavelength band is due to polarization along X-axis and the shorter along Y-axis.

Now consider hypsochromic shift shown by Crystal Violet when a dimethyl amino group is substituted in Malachite green. As per resonance theory, Crystal violet ion has a high symmetry and consequently a number of levels will have the same energy although the total number of levels has actually increased and are responsible for the remarkable hypsochromic effect. The average separation of the oscillating charges is, however, increased. Thus, the band is displaced to the shorter region, while intensity has increased due to increased transition probability proportionate to increased number of corresponding levels. Lewis and Calvin proposed that the oscillation of a charge along one direction only is responsible for colour. In Malachite Green all charge is linear oscillations while in crystal violet positive charge can oscillate linearly, horizontally as well as perpendicularly, vertically. Thus 2/3 positive charge is effectively oscillating horizontally in crystal violet. Hence, Malachite Green has a deeper colour than crystal Violet.

**B.5 FREE ELECTRON MOLECULAR ORBITAL (FEMO) THEORY:**

The applications of MO and VB to theories to dyes practical importance and interest which have complicated structures and their colour is strongly affected by even a slight structural change, requires unless simplification to obtain even the most general agreement with the observed facts. A third theoretical treatment which on the one hand is highly simplified, and still based on highly valued quantum mechanical treatment on the other, and also avoids rigorous mathematical dilemma; which has been applied to such complex chromophores with a great degree of success is the one known as Free Electron Gas Method, Free method\textsuperscript{137}. This was first proposed by sommerfield\textsuperscript{138}, to describe the metallic state and later
extended to organic molecules by Baylyiss\textsuperscript{139}, Simpson\textsuperscript{140}, and notably developed by Kuhn\textsuperscript{141-142} and Platt\textsuperscript{143}. In its application, this model is limited to consideration of conjugated \( \pi \)-electron systems; but then dyes are considered to owe their colour to these electrons, this theory will be treated in greater detail.

Simplest of all the molecular orbitals methods for conjugated organic molecules, as this theory is, remarkably successful too in calculating transition energies in certain cases. Quite like valence bond and the molecular orbital treatments, in this model too, all the carbon atoms and all the hydrogen atoms are supposed to lie in one plane so that all atomic orbitals are of either \( \sigma \) or \( \pi \) type. The fundamental assumption, rather approximation, in this treatment is the sigma-pi-separation principle\textsuperscript{144}, i.e. the sigma and pi electrons can be treated separately and independently. Consequent upon this specifically characteristic assumed feature of this treatment, and that the pi electrons are comparatively free to move within the conjugated system and, provided that this movement is only in the direction of the conjugated chain, their behaviour can be represented by that of an electron in a box or a potential well. Figure XII represents the potential energy of such an electron, where the minus occurs at the positions of the individual carbon atoms along the chain. The energy shown in the lower part of the said figure represents an assumed constant potential along the chain length. The terminal potential barriers are situated at an arbitrary distance beyond the extreme carbon atoms. The quantum mechanical solution of a wave equation for a particle moving under these conditions is,

\[
\psi_n = \left( \frac{2}{L} \right)^{1/2} \sin \left\{ \frac{\pi n}{L}x \right\}^{1/2}
\]

where \( 0 < x < L \), \( L \) is the wavelength, \( x \) is the distance along the well and \( n \) is a quantum number (1, 2, 3, 4 \ldots \) etc) for each value of \( \psi_n \) there is a corresponding energy,

\[
E_n = \frac{n^2 \hbar^2}{8\pi m^2} \quad \text{Equation 1}
\]

Where \( \hbar \) is planck's constant and \( m \) is the mass of an electron. In a system consisting of alternate double and single bonded carbon atoms, each carbon atom contributes one pi electron. If the total number of pi electrons is \( N \), then in the ground state are the \( N/2 \) levels of the lowest energy since each level is doubly occupied by the electrons having opposing spins =1/2, -1/2 according to Pauli's exclusion principle. As no limitation is placed on the number of the possible levels, all others except filled \( N/2 \) levels will be
\[
\begin{array}{c}
\text{CH} = \text{CH} \quad \text{CH} \quad \text{CH} = \text{CH}_2 \\
\text{O} \quad \text{O} \quad \text{C}^+ \\
\end{array}
\]

\[\begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
N & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
\lambda_{\text{max}} & 2515 & 3190 & 3520 & 3770 & 4040 & 4240 & 4450 & 4650 \\
\hline
\end{array}\]

\[\begin{array}{c}
\text{CH} - \text{CH}_3 \quad \text{R}_2\text{N}-(\text{CH} = \text{CH})_n\text{CH} = \text{NR}_2 \quad \text{R}_2\text{N}+ \quad \rightarrow \quad \text{R}_2\text{N} = \text{CH}-(\text{CH} = \text{CH})_n\text{NR}_2 \\
\text{V} \quad \text{VI} \\
\text{IV} \quad \text{VII} \quad \text{VIII} \\
\end{array}\]

\[\begin{array}{c}
\text{Me}_2\text{N} = \text{CH} - \text{CH} - \text{CH} - \text{CH} = \text{NMe}_2 \\
\text{IX} \\
\text{Malchite Green} \\
\lambda_{\text{max}} 621 \text{ nm in acetic acid} \\
\text{X} \\
\text{Cryst Violet} \\
\lambda_{\text{max}} 589 \text{ nm (in acetic acid}} \\
\text{XI} \\
\text{NH}_3 \\
\text{Atoms} \\
\text{Potential Energy} \\
\text{Distance, x} \\
\text{Potential Well Diagram XII} \\
\end{array}\]
empty. When the molecule or the ion absorbs light, this corresponds to one electron jump from the highest filled level with quantum number $n_1 = N/2$ to the next higher energy level, i.e. the lowest empty level with quantum number $n_2 = N/2 + 1$. The energy change or the excitation energy for this transition is therefore,

$$E = E_{N/2+1} - E_{N/2} = (N+1)\frac{\hbar^2}{8mL^2}$$  \hspace{1cm} E.2

Since $\Delta E = h\nu = hc/\lambda$, where $c$ is the velocity of light and $\lambda$ is the wavelength in centimeters,

$$\lambda = \frac{8mcl^2}{h(N+1)}$$  \hspace{1cm} E.....3

This equation can therefore be applied to any linear conjugated system provided that the number of the double bonds is known and assignment of $\lambda$ is made. Since $\lambda$ is proportional to $L^2$, correct values for $L$ are impotent. If need be the above treatment may be extended to three dimensions by supposing the electron to be residing in a three dimensional box.

**B.6 APPLICATION OF THE FREE ELECTRON MODEL TO BUTADIENE:**

The pi electron structure of 1, 3- butadiene is obtained by assigning two electrons of opposing spins to the lowest orbital and two similarly spin paired electrons to the second lowest. The absorption of light is then assumed to involve the promotion of one of these four electrons to any of the higher orbitals. Equation 3 can then be used to calculate transition energies. The only uncertain parameter is $L$, the length of the conjugated chain, say that of the potential well. It is usual to regard $L$ as equal to the length of the conjugated chain molecule assuming that the molecule is distorted into a straight line plus one additional bond length at each end of the molecule. For example, 1,3- butadiene has an average bond length of 1.4 Å, which gives a value of 7 Å, for $L$. Using aforesaid equation for 1,3- butadiene a first transition energy of about $3.0 \times 10^4$ cm$^{-1}$, or a wavelength of 325 nm is found. The experimental value, 220 nm, may seem indicative of poor agreement but in view of the many gross approximations inherent in the FEM treatment, and its greater simplicity of approach, the agreement is supposed to be remarkably good.
The series of compounds known as cyanines typified by figure XIIIa and XIIIb are ideally suited for this method, since they show appreciable bond uniformity that arises from resonance.

\[
\text{Me}_2\text{N} \rightarrow (\text{CH} = \text{CH})_m - \text{CH} = \text{N}^+ \text{Me}_2 \quad \leftrightarrow \quad \text{Me}_2\text{N}^\equiv\text{CH-} (\text{CH} = \text{CH})_m^- \text{NMe}_2
\]

XIII(a) \hspace{5cm} XIII(b)

A symmetrical cyanine dye molecule such as Figure XIVa and b may be considered here in order to find a plausible explanation for its electronic absorption band in the visible region, here the C, N, and hydrogen atoms are linked by sigma bonds and are located in a common plane,

XIV (a) Cyanine molecule

XIV (b) Cyanine sigma skeleton in common plane
Each carbon atom and each nitrogen atom uses its three valence electrons to form the sigma bonds; pi electronic system in each molecule is formed by the contribution of the fourth valence shell electron of each carbon atom and the remaining electrons of the two terminal of nitrogen. These electrons are placed in the electrostatic field of the molecular skeleton. They will be attracted to positive charges of C and N atoms, but their wave function must not have a node at all points of the plane of the molecule. They form an electron gas, which in the shape of a charge cloud stretches along the cyanine chain, both above and below the plane of the molecule. N has five electrons and in the said cyanine dye, three are used form sigma bonds, thus N atom with no charge sign contributes two electrons to the pi electron gas and that we find a total of six pi electrons or three pi electron pairs in this case. Now a single pi electron is considered in the electrostatic filed of the rest of the molecule and it should be assumed for a moment that it could only move in the direction of the zigzag line connecting C and N atoms in the chain. The potential energy of the electron is then roughly constant along the chain. Since the electron is practically in the coulomb field of the nearest C and N atom only, while the field of more distant C and N is neutralized by other pi electrons. And, consequently, this electron can move almost freely along the zigzag line, but not beyond the ends of the chain except when the chain itself stretches. Thus, this electron is in the same condition as a free electron considered earlier in a one-dimensional box and the length L of the chain corresponds to the length of the box. It must be noted, however, that the component of the motion of the pi electron in the direction perpendicular to the zigzag line connecting C and N atoms in the chain has been neglected here (XIIb).

In the normal state of the molecule, the three electron pairs present in the resonating chain occupy the three lowest levels. The light absorption is caused by transition of an electron from the highest occupied molecular orbital (HOMO) with n = 3 to the lowest unoccupied molecular orbital (LUMO) with n = 4. Accordingly, the energy difference $\Delta E$ between these states is,

$$\Delta E = E_4 - E_3 = (4h)^2 / 8mL^2 - (3h)^2 / 8mL^2 = \frac{7h^2}{8mL^2} = 6.1 \times 10^{-12} \text{ ergs}$$

And, \(\lambda_{max} = \frac{hc}{\Delta E} = (6.624 \times 10^{-27}) (2.998 \times 10^{10}) / 6.1 \times 10^{-12}\)

$$= 3.3 \times 10^{-5} = 330 \text{ nm}$$

This value is in good agreement with the experimental value of 313nm. As another case, let us discuss a specific dye, 1,1'-diethylcyanineiodide (cryptocyanine): figure XV. The cation can resonate between two limiting
structures, which really means that the wave function for the ion has equal contribution from both states. Thus, all the bonds along this chain can be considered as equivalent, with bond order of 1.5 similar to C-C bond in benzene. Each carbon atom in the chain and each nitrogen atom in the ends are here involved in bonding with three atoms by three localized bonds, so the called sigma-bonds. The extra valence electrons on the carbon atoms in the chain and the remaining three electrons on the two nitrogen atoms form a mobile cloud of pi electrons along the chain and extend above and below the plane of the chain. We then, assume that the potential energy is constant along the chain and that rises sharply to infinity at the ends; that is the pi electron system is replaceable by free electrons moving in a one dimensional box of length L, for example, if it is supposed that total number of pi electrons in this system be N, then as said before, for electron transition and consequent light absorption, the transition energy and the wavelength of maximum absorption can be arrived at as in equation E.2 and E.3 respectively. To reproduce the latter,

\[ \lambda = 8mcL^2/h(N+1) \]  

The number of carbon atoms in polymethylene chain, if supposed, are p, then \( N = p+3 \). Kuhn assumed that \( L \) was the length of the chain between nitrogen atoms plus one bond distance on each side; thus, \( L = (p+3) \) \( I \) where \( I \) is the bond length between atoms along the chain. Therefore,

\[ \lambda = 8mcL^2(p+3)^2/h(p+4) \]  

Putting \( L = 1.39 \times 10^{-8} \) cm (the bond length of benzene, a molecule with similar bonding) and converting from centimeters to nanometers \( (1 \text{ nm} = 10^{-9} \text{ m}) \), we find,

\[ \lambda \text{ (in nm)} = 63.7(p+3)^2/(p+4) \]  

If there are easily polarizable groups at the ends of the chain, such as benzene rings, the benzene, the potential energy of the pi electrons in the chain doesn’t rise so sharply at the ends. In effect, this lengthens the path \( L \), and we can write,

\[ \lambda \text{ (in nm)} = 63.7 \ (p+3+\alpha)^2/(p+4) \]  

Where \( \alpha \) should be constant for a series of the dyes of a given type. If such a series is studied experimentally, this empirical \( \alpha \), may be adjusted to achieve the best fit the data; in any event, should lie between 0 and 1 \(^{145}\).
In order to compare the result of this method with the more sophisticated Valence bond (VB) or the molecular orbital (MO) calculations, let us use equation 5 which assumes that $\alpha = 0$, to calculate the wavelength of maximum absorption of cryptocyanine, in which $p = 9$ and compare that value with those given by others in literature

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Free electron</td>
<td></td>
<td>707 nm</td>
</tr>
<tr>
<td>Bond orbital (case 1)</td>
<td></td>
<td>3900 nm</td>
</tr>
<tr>
<td>Bond orbital (case 2)</td>
<td></td>
<td>2900 nm</td>
</tr>
<tr>
<td>Molecular orbital</td>
<td></td>
<td>2700 nm</td>
</tr>
</tbody>
</table>

It may be noted that only FEM predicts an absorption band in the visible region of the spectrum in agreement with the actual observation. Kuhn has applied this method to the determination of the wavelength of maximum absorption of a number of cyanine dyes with varying values of $\alpha$, whose classical structures are depicted in figure XVI. Both structures are equivalent. The potential energy of the well of the model is not, however, constant due to the presence of two nitrogen atoms. The number of atoms in the conjugated chain is $2a + 9$ and since the potential energy barrier extends beyond the terminal nuclei by about one bond length, the number of pi electrons $N$ is $2a + 10$, each carbon atom contributes one electron and two terminal atoms together contribute three electrons. Since the C-C bond distance is known, the total length, $L$, of the well can be calculated. The individual bond distance is taken as $1.39 \times 10^{-8}$ cm, i.e. the C-C bond distance in the benzene molecule. Table 2 summarizes the calculated values of $\lambda_{\text{max}}$ which are in good agreement with the experimental values by Brooker$^{147}$ over the range where $a$, the number of vinyl groups, increases from zero to three.

**TABLE 2**

<table>
<thead>
<tr>
<th>Positions of Absorption Bands in the Spectra of Cyanine Dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
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<tr>
<td>-----</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
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<td>2</td>
</tr>
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<td>3</td>
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The agreement is good considering that the terminal benzene rings are not included in the calculations. By using linear compound similar to cyanine dyes in structure but not containing benzene ring, i.e. those of the general structure,

\[(\text{CH}_3)_2 \text{N}^+ = \text{CH-(CH =CH)}_a - \text{N(CH}_3)_2\]

Where the value of \(a\) is 1, 2, or 3, Simpon\textsuperscript{149} has found excellent agreement between observed and the calculated values of \(\lambda_{\text{max}}\). The total number of pi electrons is \((2a + 4)\) including again a contribution of three electrons from the nitrogen atoms. With a reasonable estimate of the length of the potential well, values of \(\lambda_{\text{max}}\) shown in table 3 were obtained.

### Table 3

<table>
<thead>
<tr>
<th>(a)</th>
<th>Calculated (\lambda_{\text{max}}) nm</th>
<th>Observed (\lambda_{\text{max}}) nm</th>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>409</td>
<td>409</td>
</tr>
<tr>
<td>3</td>
<td>509</td>
<td>511</td>
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</tbody>
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A symmetrical cyanine dye with \(m\) conjugated double bonds in the resonating chain connecting the two nitrogen atoms. The number of pi electrons in the chain amounts to \(2m+2\), and the absorption band corresponds to a jump of electron from the HUMO level \(m+1\) to the LUMO level \(m+2\). as before the energy for this transition:

\[
\Delta E = h^2(m+2)^2/8m_eL^2 - h^2(m+1)^2/8m_eL^2 = h^2(2m+3)m_eL^2\quad \text{and} \quad \lambda_{\text{max}} = \frac{hc}{\Delta E} = \frac{m_e^2}{hL^2}/(2m+3) \quad \text{equation...7}
\]

This remarkable result in this approximation indicates that the position of the absorption band is determined by the chain length and by the number of pi electrons \(2m+2\), since \(m_e\), the mass, \(h\), the Planck's constants and \(c\), the velocity of light are universal constants. Further \(\lambda_{\text{max}}\) does not depend upon any specific property of the atoms along the chain. The length \(L\), may be taken as equal to \(2m \times I\) where \(I\) is bond length of the chain elements; the average bond length, \(I\), has taken as 1.3 angstrom on the basis of approximations considered by Kuhn\textsuperscript{150-151}. The electron gas stretches by length, \(\alpha L\), on both sides of the each terminal nitrogen atom. Thus, a more satisfactory value of \(L\) is given by
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\[
\Delta E = \frac{h^2(m+2)^2}{8m_eL^2} - \frac{h^2(m+1)^2}{8m_eL^2} = h^2(2m+3)8m_eL^2 \\
\lambda_{\text{max}} = \frac{hc}{\Delta E} = \frac{m_e}{\hbar L^2/(2m+3)}
\]

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\[ L = 2m \times 1 + 2 \alpha \times 1 = 2(1 + \alpha) \]

Now according to eqn. 7

\[
\lambda_{\text{max}} = 8m_e c/h \times 4l^2(m + \alpha)^2/(2m + 3)
= 127(m + \alpha/2)^2/(m + 3/2) \text{ nm}
\]

Equation ......8

In the conjugation polyenes, symmetrical cyanines and their analogues, Kuhn\textsuperscript{152} has calculated the stretching of the electron gas to both sides of each terminal atom, as 1.5 angstrom, on the basis of vibration treatment. As the length \( \alpha l \) on both the ends is approximately 1.5A. This may be considered that \( \alpha = 1 \). The value \( \alpha = 1 \) has already been used of \( \alpha \) is the treatment of the dye molecule, F.XVII. It has been found that the value of \( \alpha \) is dependent on the end groups, and thus in a homologous series of dyes \( \alpha \) is constant for all the members of the series. If strongly polarizable groups in increasing orders are introduced in the terminal atoms, the value of \( \alpha \) also increases. On the basis of above considerations the calculated value \( \lambda_{\text{max}} \) of the said dye with \( m=2,3,4,5,6 \) and 7 are in excellent agreement with experimental data\textsuperscript{153} of these carbocyanines.

The free electron method has also been used\textsuperscript{154} to determine longest wavelength of absorption of a number of basic dyes and to compare the influence of a central nitrogen atom in a conjugated system. In the simplest case the linear compound A is compared with the aza derivative B in which the central carbon atom has been replaced by nitrogen. This atom contributes one electron to the total pi system and since it is more electronegative than carbon atom that it replaces, there will be decrease in the HOMO energy level in the ground state.

\[
(CH_3)_2 N = CH \cdots CH = CH - N(CH_3)_2, \quad (H_3 C)_2 N = CH - N = CH - N(CH_3)_2
\]

A \quad \quad \quad \quad \quad B

In the first excited state of both A and B, there is vibration node at the central atom and the energy level in both the cases is equivalent. Consequently the excitation energy \( \Delta E \) involved in the transition will be greater for azo derivative, which therefore possesses a \( \lambda_{\text{max}} \) at a shorter wavelength. In general, when centrally situated \(-CH=\) group is replaced by \(-N=\) in a resonating system between terminal nitrogen atoms, a hypsochromic shift is observed if there is an even number of double bonds
and a bethchromic shift is seen when the number of double bonds is odd. This is because the value of the energy levels in the excited state depends on presence of a node or an anti node at the central atom.

The displacement of a given energy level caused by the nitrogen substitution may be quantitatively assessed by a perturbation treatment and is given by the equation.

\[ \Sigma = A \Psi^2 \quad \text{Equation \ldots 9} \]

Where A is an electronegativity constant, characteristic of the heteroatom and is equal to \(3.9 \times 10^{-20}\) erg cm for the \(-N=\) atom, \(\Psi\) is the normalized wave function at the heteroatom. It can be shown that \(2/L\) give the square of the normalized wave function, where L is again the length of the potential well. It follows that for a state with an anti node at the central atom.

\[ \Sigma = -Ax^2/L = -2A/2(M + \alpha)l \quad \text{Equation \ldots 10} \]

Where \(M\) is the number of double bonds and is the mean carbon–carbon bond distance. The factor \(\alpha\) is introduced, as said before, to account for the extension of constant well potential beyond the terminal atoms of the conjugated system.

The potential well diagram of the simplified free electron model is modified by the presence of electronegative atom to that shown in figure XVIII.

The nitrogen atom is situated at the center of the well and where \(b\), the mean C–N distance, is small compared to the total well length, the probability of finding electron in the trough is \(\Psi^2b\). The reduction, \(\varepsilon\), in the total energy of the state \(n\) is, therefore, \(-V\Psi^2b\) where \(V\) is the negative potential due to the nitrogen atom. It follows from equation 9 that \(A = Vb\) or in other words the electronegative constant is the product of the potential energy drop and the bond distance between the hetero atom and its neighbor.

A comparison of the spectra of Michler’s Hydrol Blue and Bindschedler’s Green, the structures of which are shown in figure XIX, shows that the observed value of \(\lambda_{\text{max}}\) are 603 and 725 nm respectively. If the \(\Delta E'\) is the excitation energy of the aza dye, then,

\[ \Delta E' = \Delta E + \Sigma \quad \text{equation \ldots 11} \]
for the excited state possessing a central antinode the $\Delta E'$ is the excitation energy of the parent unsubstituted molecule (a) in the said figure and

$$E = \frac{hc}{\lambda_{\text{max}}} = 6.62 \times 10^{-27} \times 3.00 \times 10^{10} / 6.03 \times 10^{-5}$$

$$= 3.30 \times 10^{-12} \text{ erg}$$

in equation 11 can be calculated from equation 10 since the values of all the constants, with the exception of $\alpha$ are known. This factor $\alpha$ may be determined by calculating the value of $L$ when observed value $\lambda_{\text{max}}$ for the parent molecule is substituted in equation 3. Comparison of this value of $L$ with the value calculated from the number of double bond and the mean bond length, as shown by Kuhn$^{154}$, gives $\alpha = 0.55$. The number of double bonds is five from equation 10,

$$\varepsilon = -(3.9 \times 10^{-20} / (5 + 0.55)(1.39 \times 10^{-8}))$$

$$= -0.5 \times 10^{-12} \text{ erg}$$

The values of $\Delta E'$ is the sum of these energy terms.

$$\Delta E' = 3.30 \times 10^{-12} - 0.5 \times 10^{-12}$$

$$= 2.80 \times 10^{-12} \text{ erg}$$

Expressing this energy in wave length terms give a wave length of maximum absorption for Bindschedler’s Green (figure XIXb) at 709 nm, a calculated shift of 106 nm, in reasonable agreement with the observed shift of 122 nm on replacing the central $-\text{CH}_2-$ group. Similarly, Michler’s Hydrol Blue may be compared with Acridine Orange, figure XX.

The electronegativity constant for A for N $-\text{CH}_3$ at the position 12 in this compound is $6.0 \times 10^{-20}$ erg cm. In the normal state of the molecule the seven pairs of pi electrons, contributed from the five double bonds and uncharged nitrogen atoms, fill the seven highest occupied energy levels. A free electron model treatment as above gives a calculated value $\lambda_{\text{max}}$ for acridine orange of 471 nm compared with an observed value of 491 nm. The absorption spectra of acridine, oxazine, thiazine, azine and xanthene dyes have all been compared by this method$^{154}$ with some degree of success.

Equation 3 predicts that the absorption band with the lowest energy should be displaced to longer wavelength when an increasing number of ethylenic linkages is introduced into the molecule since $L^2$ is proportional to the wave length. However, with linear polymers, the wavelength of
absorption tends to a maximum as the number of double bonds is increased. The assumption of a constant pi electron potential in the simple free electron model has been shown\textsuperscript{155} to be incorrect and a regular variation in bond length occurs along the chain if it is sufficiently long. Such a varying energy along the box increase the gap between the occupied and the unoccupied orbital so that $\lambda_{\text{max}}$ tends to limit the chain length increases. In terms of resonance theory explanation is that in long chains of this type, the number of idealized structures contributing to the stability of the excited state increases to a greater extent than the contribution each makes to the stability of the ground state. Consequently, the energy difference increase with the increasing chain length.

The FEMO theory has certain feature in common with the qualitative interpretation of the special shifts associated with Burawoy’s K-band theory\textsuperscript{156} in triaryl methane dyes and thiobenzenophenone derivatives\textsuperscript{157}, particularly in its application to the basic dyes, where the electronegative atom situated in a conjugated system can act as an electron sink. The intense K-bands (Burawoy’s nomenclature – K-konjugierte) are attributed to $\pi \rightarrow \pi^*$ excitation when a conjugated molecule contains both an electron donating and electron withdrawing group, a shift of the K-band to a longer wave length occurs which is greater than the additive effect of both group when acting separately. Changes in the nature of the terminal groups in such systems which cause an increase in polarity or polarizability, or the dissolution of the compound in more polar solvents, cause further shift of the K-bands to the longer wavelengths. The presence of the side chain groups also effects the position of the K-band, opposing the electron migration from terminal groups, e.g. from A to B in figure XX1a, where A and B may be N(CH$_3$)$_2$ and $-N^+(CH_3)_{2}$ respectively and assisting it in the new system of groups X (which may be e.g. OH or $-NH_2$) and group B. This replacement of K-band is therefore to shorter wavelength with thiobenzene and triarylmethane cations which are symmetrically substituted, the side chain is also conjugated. The absorption spectra show only one band but should in fact consist of two superimposed bands, i.e. originating from K$_1$ and K$_2$ in figure XX1b.

These bands become apparent when the absorption spectra of non-symmetrically triarylmethane chromophores are examined. When A, A’ and A” are identical and are either –OCH$_3$, –SCH$_3$ or –NCH$_3$, (Crystal Violet) then only one band is observed at 480, 577 and 587 nm respectively. Replacement of one substituents in each of these compounds by hydrogen, (e.g. changing crystal violet to malachite green) cause the emergence of a second band K$_2$ at shorter wavelengths. Simultaneously,
the $K_1$-band undergoes a bathochromic shift of between 20 and 40 nm. Lewis and Bigeleisen\textsuperscript{158} have also made similar observations for crystal violet and the sodium salts of Rhodamine B and Fluorescein.

Kuhn has used the branched pi electron gas model to treat other dyes in a similar manner and the concept of branching leads to a simple explanation of even such characteristic compounds as deep colour of the low molecular weight Wurster's Blue and azulene\textsuperscript{159}.

It is of interest to consider the application of the free electron theory to closed ring systems having conjugation similar to that occurring in porphyrins, azaporphines and phthalocyanines. The free electron theory has been applied to the metal free porphins\textsuperscript{160}, cyclic polyenes\textsuperscript{161} and phthalocyanines\textsuperscript{162-165}, using a circular box model, and by taking into account the perturbation factor calculated from atomic shielding constants\textsuperscript{164}, better agreement\textsuperscript{165} has been found with the experimental data\textsuperscript{166}.

Labhart\textsuperscript{167} further refined free electron theory by taking into account the interaction between the pi electrons and the elastic sigma skeleton. He showed that even for very long polyenes a difference in single and double bond length was of the same order of magnitude as in shorter polyenes was to be expected. Olszewaki\textsuperscript{168} used a linear free electron model with electron-electron and electron-core interaction for the calculation of lowest excited singlet-triplet separation in polyenes, twisting frequency of ethylenes and location of absorption maxima in cumulenes. He also calculated the absorption maxima in the spectra symmetrical cyanine dyes and polyenes by ASFEMO-Anti-Symmetrical Free Electron Molecular Orbital method. An improvement of the theoretical $\lambda_{\text{max}}$ values for cyanines was obtained by introducing resonance barrier\textsuperscript{169} in the free electron model. Spectra of cyanine dyes and cata-condensed hydrocarbons were analyzed by Araki and Huzinaga\textsuperscript{170-171}, Basu\textsuperscript{172}, Dey\textsuperscript{173} and by Rout et al\textsuperscript{174}. who applied suitably modified FEMO method. A part from spectral analysis, the refined FEMO has also been used for the calculation of optical rotatory power\textsuperscript{175} of the organic molecule. The model gave a method for rapid evaluation of electric and magnetic transition moments and was further used for a better understanding of the skew conformation of butadiene. Shuler\textsuperscript{176} used the free electron model for calculating the stability constants and absorption spectra of pi molecular complexes. Mueller\textsuperscript{177} examined theoretically the bimolecular exchange reaction.

\[ \text{H}_2 + \text{H}_2 \rightarrow \text{H}_2 + \text{and} \; \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \]
Via activated complex by free electron model. Bonham et al\textsuperscript{178}, and Basu\textsuperscript{179} treated the electrophilic substitution in molecules by the FEMO method. The treatment is based on the fact that any aromatic substitution reaction proceeds through the formation of the activated complex. Nathan\textsuperscript{180} successfully employed the FEMO method for the theoretical investigation of diamagnetism of aromatic hydrocarbons.

**B.8 Two-dimensional free electron gas model:**

The two-dimensional free electron gas model\textsuperscript{183} is closely related to the branched electron model described earlier in this chapter. Each state of interest in the two dimensional model corresponds to a state in the one-dimensional model. In the two dimensional model for a system with resonating structure, the plane of the center of the atoms is chosen as the xy-plane of the xyz-coordinate system. It is assumed that the pi electrons are in potential field $V(z) + V(xy)$, where $V(z)$ is a certain function of $z$. $V(xy)$ is the potential of the pi electron averaged over $z$ and is the sum of the contributions of the carbon atoms. The contribution of the carbon atom can be obtained by nuclear charge and shielding considerations. The $z$ part of the wave function of an electron in the potential $V(z) + V(xy)$ can be separated from the $xy$ part, and the problem of finding eigen functions $\phi_n(x,y)$ and eigen values $E_n$ of the Schrodinger wave equation.

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + 8\pi^2 m \left[ E_n - V(x,y) \right] / \hbar^2 = 0$$

can be solved by using an analog computer. The two dimensional method can be applied to polyenes and polyacetylenes. Using the observed values of bond distances, the position of the strong absorption bands was calculated and the results were found to be in good agreement with those of one-dimensional treatment and with the observed data\textsuperscript{184}. Two dimensional models may also be applied to dye molecules of any complicated shape.

**C. Phthaleins: Their Colour and Constitution:**

An entirely different series of dyes, the phthalein dyes, figure XXIII, XXIV and XXVI may be obtained by simply replacing N-CH$_3$ by more electronegative oxygen atom at the position 12 H at position 6 by –C$_6$H$_5$COO$^-$ in acridine orange figure, XX. Derivative of pyronines, these phthaleins may be considered to be intermediates between fuschone Figure XXII and benzaurine figure XXV.
Colour responsibility of these acid dyes, the phthaleins, is attributed
to the anionic portion, which thus becomes more important part of the dye
molecule. It has been established for a well studied representative of the
phthalein, that in the neutral medium it bears a lactone structure and thus is
then colourless, figure XXVI, while in alkaline solution (pH 8.4) it
undergoes ring opening producing intense red divalent anion, figure
XXVII, having longest wave length band of \( \lambda_{\text{max}} \) at 532 nm with an
extinction coefficient of 31,000. Further, the well known property of
phenolphthalein as an indicator is \( \lambda_{\text{max}} \) actually attributed to this very
intense red divalent anionic form which actually is a hybrid of figure
XXVIII and a number of its possible intermediate resonating structures.
The divalent anion transforms to carbinol, figure XXX, a trivalent anion,
when excess alkali is added, and thus loses the colour.

An analogue of phthalein is fluorescein, figure XXIII that differs
only in the presence of an oxygen bridge. Both phenolphthalein and
fluorescein in alkaline medium exhibit bathchromic shift. In each case,
alkali produces an ion that can be represented by two equivalent resonating
structures. Thus the alkali produces ions that are stabilized by resonance
and this leads to absorption at longer wavelengths. Fluorescein has two
equivalent resonating structures shown in XXXIa and XXXIb in the alkali
medium.

Fluorescein, as expected, absorbs at shorter wavelengths than
phenolphthalein. The fluorescein anion is red (\( \lambda_{\text{max}} \) in water 500nm)
where as phenolphthalein anion is magenta (\( \lambda_{\text{max}} \) in water 552nm).
Fluorescein absorbs at shorter wave length because in it, charge distribution
between two oxygen atoms is decreased due to the oxygen bridge of the
pyrone ring, which is capable of forming a double bond with the ring
acquiring some of the available charge. Fluorescein is characterized by a
strong green fluorescence and many of its derivatives are also fluorescent.

Eosin, figure XXXII, having bromine atoms at ortho positions to
pyrone oxygen, electron density of carbon atoms of pyrone is increased
and consequently it hinders oxygen to take up part of the oscillating
charge. It is evident from the structure of phthalein, figure XXVII and
XXIX and also from the above considerations that only part of the
molecule which is shown above the dotted line plays important part in the
light absorption as regards the main absorption band of the molecule. The
removal of the carboxyl group in the compounds, figure XXXIII to
XXXVI doesn’t affect the position of the absorption maxima in
compounds, figure XXXVII to XL. A number of workers have
studied the effect on light absorption by making changes in lower part
(below the dotted line) of the molecule figure XXIII and XXVI, and could find so significant changes in \( \lambda_{\text{max}} \) thus confirming the previous observations. Ghatak and Dutt\(^{206}\) have prepared phthaleins of the type XLI in which two hydroxyl molecules are dissimilar. They also prepared asymmetric fluoresceins where the substituents in the two sides of the fluoron nucleus are not identical, figure XLII and XLIII.

Recently, Gupta, Beg, Ali et al. have prepared and studied the chemistry of some novel analogues of phthalein and succinein dyes; specially their synthesis and colour. The present investigations are in continuation of the work that has already been done by Beg et al.
XXX

XXXIa

Fluorescein

XXXIb

XXXII

Eosin
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