COLOUR AND CONSTITUTION

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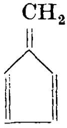
1. *Introduction* [1]

The birth of the organic dye industry with the discovery of mauve by Perkin in 1856 made possible attempts at the correlation of the colour of an organic compound with its chemical constitution. The first observation was made by C. Graebe and C. Liebermann [2] twelve years later. These writers pointed out that all the coloured compounds known at that time became colourless on reduction. Their conclusion was that the colour of a compound was in some way due to a close linking between the C, O, and N atoms contained in it. O. N. Witt [3] in 1876 introduced the conceptions that have formed the basis of all subsequent theories. According to his theory, before colour can appear in a compound, two conditions have to be satisfied. First, the molecule must possess a potentiality for colour; secondly, there must be a salt-forming group present for developing the colour potentiality. A group of atoms possessing the potentiality for colour is known as a *chromophore*, the molecule containing it being a *chromogen*. The group responsible for developing the colour is known as an *auxochrome*. Typical chromophores are $-NO$, $-NO_2$, $-N{=}N-$, $C{=}C$, and $C{=}O$, and auxochromic groups are represented by $-OH$, $-NH_2$, $-NHR$, and $-NR_2$. Some chromogens are themselves coloured, for example nitrosobenzene (I), fulvene (II), and diacetyl (III). But it is of interest to note that none of the chromogens possesses dyeing properties. Thus Witt's concept of the function of an auxochrome was not only to develop the colour latent in the chromogen, but also to develop its dyeing propensities.

(I.)



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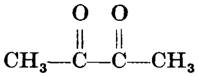


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(III.)

H. E. Armstrong [4] in 1888 advanced the view that many organic dyes either contained the quinonoid grouping, or could be modified in such a manner as to contain it. This view was probably arrived at from a consideration of the recently discovered phenomenon of tautomerism. That the quinonoid theory was not sufficient to account for all the facts is seen

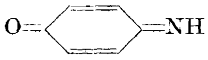
[1] An excellent account of the development of colour theory up to 1918 is to be found in Watson's "Colour in Relation to Chemical Constitution," Longmans Green & Co., London, 1918.

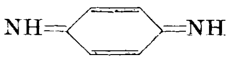
[2] *Ber.*, 1868, **1**, 106.

[3] *Ibid.*, 1876, **9**, 522.

[4] *Proc.*, 1888, **4**, 27.

from a consideration of iminoquinone (IV) and di-iminoquinone (V), both


(IV.)


(V.)

of which possess the quinonoid structure but are colourless. Then again a number of coloured substances are known to which a quinonoid structure cannot possibly be assigned. However, the quinonoid theory was of great importance both because of the impetus it gave to experimental work and because of its practical application in the hands of dye chemists.

In attempting to correlate the data on the triphenylmethane dyes R. Nietzki [5] in 1879 postulated that the colour of a dye may be deepened by adding groups so as to increase the molecular weight, the deepening being roughly proportional to the increase in molecular weight. M. Schütze [6] in 1892 subjected this rule to a careful scrutiny and was able to point out many exceptions. He was able to show that the chemical nature of the added group was of importance and introduced the terms *bathychromic* and *hypsochromic*. The former refers to a group the addition of which to a molecule gives rise to a deepening of the colour, the latter referring to a group which has the opposite effect. The term depth of colour will be defined later.

Although the colour of organic compounds is one of their most striking properties, yet it was realised early in this century that it is unsatisfactory to attempt to base a theory of colour merely upon visual observation. The human eye is only sensitive to the spectral region from about 4000 A. to 7500 A., and this physiological fact places a severe limitation upon the range of observation. The recognition that the ultra-violet region is merely a continuation of the visible made possible an explanation as to how an apparently small change of structure might convert a colourless substance into a yellow one. This view was well expressed in the *Annual Reports* for 1907 : " It is now generally recognised that a more precise meaning must be given to the idea of colour than has often been the case. The production of physiological colour, due to the occurrence of absorption in the visible spectrum, is more or less an accidental circumstance. Absorption bands may occur in the ultra-violet of equal importance with those in the visible spectrum. In some cases a change in the frequency of the absorbed rays may cause a band to move from the ultra-violet into the visible region without any change of form. A colourless substance may therefore be converted into a coloured one without any real change in constitution having taken place. . . . The quantitative study of the absorbing power of a substance . . . makes an exact comparison of different derivatives possible, and relationships are made evident which would escape notice if the examination were confined to visual observation of colour." This realisation of the importance of objective measurements of colour enabled the basis of the physicochemical theory of colour to be laid. However, this theory

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[5] *Verhandl. Vereins Beförd. Gewerbefleisses,* 1879, **58,** 231.

[6] *Z. physikal. Chem.,* 1892, **9,** 109.

is dependent upon quantum concepts, and did not develop until some thirty years later.

The colour of an organic compound is due to its having one or more absorption bands in the visible region of the spectrum. The relationship between the wave-length of the absorbed light and the colour of a compound is shown in Table I. This table is strictly only applicable to a substance which has a single narrow absorption band between 4000 and 7500 A. High intensity of absorption often implies a wide absorption band, which may invalidate conclusions drawn from the table. Also, colour is a subjective phenomenon. In view of these complications the desirability of representing the colour of a compound by an objective method becomes obvious.

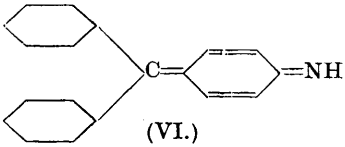
TABLE I

Absorption Wave-length and Colour

Wave-length, A.	Colour absorbed.	Visible colour.
4000—4350	violet	yellow-green
4350—4800	blue	yellow
4800—4900	green-blue	orange
4900—5000	blue-green	red
5000—5600	green	purple
5600—5800	yellow-green	violet
5800—5950	yellow	blue
5950—6050	orange	green-blue
6050—7500	red	blue-green

The term depth of colour, which has been used in a number of senses, may now be defined. In the following, one substance will be said to have a deeper colour than another if the wave-length of maximum absorption is greater for the former than the latter. As the absorption moves towards the red, the colour is said to deepen.

An important observation was made by A. Baeyer [7] in 1907. He noted that the introduction of an amino-group into fuchsonimine (VI) to give Doebner's violet (VII) led to the development of colour, and he attributed



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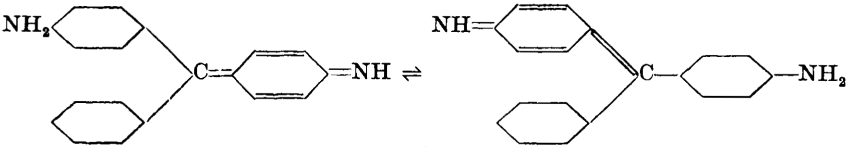

(VII.)

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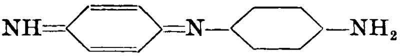
[7] *Annalen*, 1907, **354**, 152.

this to an oscillation of the quinonoid condition between the two benzene nuclei. However, here again not all coloured compounds could be classified as of this type. R. Willstätter,[8] as a result of his observations on the quinhydrones, came to a similar conclusion, namely, that colour is due to an oscillation by which two benzene nuclei alternately become quinonoid.

Following investigations on the colour of azo-compounds, J. T. Hewitt and H. V. Mitchell [9] in 1907 concluded that the colour of a substance is deeper the longer the conjugated chain. This view was modified in 1916 by A. C. Sircar,[10] who suggested that the important factor was the length of the conjugated chain in the part of the molecule containing the auxochrome. In 1913, E. R. Watson [11] propounded the view that dye molecules which are quinonoid in all possible modifications will have a deep colour. Thus indamine (VIII) is blue while 4 : 4′-diaminoazobenzene (IX) is yellow.



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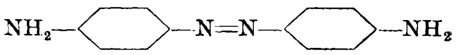
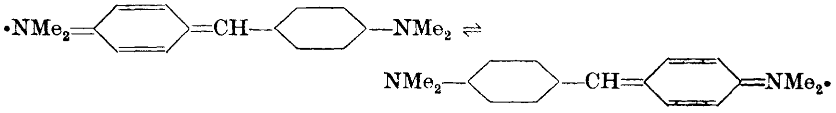


(IX.)

Two years later E. R. Watson and D. B. Meek [12] suggested that the colour is deeper the longer the conjugated chain reversed in the tautomeric change. These authors were led to distinguish two cases. The first was that in which the substance was ionised and the oscillation consisted merely "in a rhythmic rearrangement of strain within the molecule," which was responsible for the deeper and more intense colour ; thus for Michler's hydrol (X) the oscillation was represented by :



(X.)

The second case was concerned with hydrogen atom tautomerism.

Another phase of colour theory was initiated in 1910 by P. Pfeiffer,[13] who, from a study of free aryl radicals, concluded that the tervalent carbon atom was the essential chromophore. W. Dilthey [14] in 1920 went further and regarded chromophoric properties as being associated with atoms rather than with groups of atoms as Witt had postulated. The roots of chromophoric activity in atoms lay in their "co-ordinative unsaturation." Thus while the carbon atoms in diamond or in a paraffin have all their valencies satisfied, in ethylene, benzene, and graphite this is not so. Thus the carbon atoms in the latter substances can act as chromophores. Similarly in the triphenylmethyl cation (XI) the carbon atom marked with a dot (in Dilthey's

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[8] *Ber.*, 1908, **41,** 1458, 3245.

[9] *J.*, 1907, **91,** 1251.

[10] *J.*, 1916, **109,** 757.

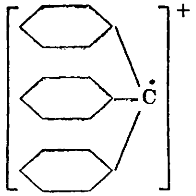
[11] *Proc.*, 1913, **29,** 348 ; *J.*, 1914, **105,** 759.

[12] *J.*, 1915, **107,** 1567.

[13] *Annalen*, 1910, **376,** 292.

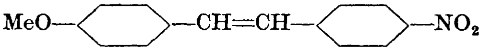
[14] *Ber.*, 1920, **53,** 261.

nomenclature) possesses chromophoric activity. Dilthey also observed that in non-polar compounds chromophoric activity is often weak, but becomes strengthened on conversion into an ionic form.



(XI.)

R. K. Wizinger [15] in 1926–27 emphasised the fact that the action of auxochromes was most observable in kationic chromogens. This led to the concept of *anti-auxochromes*, which function in the opposite sense to the auxochrome in that they behave in an anion in the same way as do auxochromes in a cation. Such anti-auxochromes are —NO, $—NO_2$, —N=N—, and >C=O. The colour of electrically neutral molecules in the Dilthey–Wizinger theory is due to the presence of an intramolecular ionoid state between auxochrome and anti-auxochrome. In the case of *p*-nitro-*p*′-methoxystilbene (XII) the chromophore, auxochrome, and anti-auxochrome are respectively the >C=C<, —OMe, and $—NO_2$ groups.



(XII.)

J. Stieglitz [16] approached the problem of colour from the viewpoint of oxidation–reduction. Reduction of a dye, as noticed by Graebe and Liebermann, usually destroys its colour, while gentle oxidation will restore it. Strong oxidation, on the other hand, may completely destroy it. The concept of a dye being in an intermediate state of oxidation led Stieglitz to identify chromophores and auxochromes with groups capable of oxidation and reduction respectively. The colour of a compound is then due to a type of intramolecular oxidation–reduction.

The importance of the intensity as well as the wave-length of maximum absorption was emphasised by N. Q. Chako.[17] He pointed out that a number of the bands which were responsible for the colours of organic compounds were relatively weak, and by applying the classical theory of the light absorption process he was able to calculate a fundamental measure of the intensity of absorption in the so-called oscillator strength. Some interesting relationships between the oscillator strength and structure of related compounds emerged, although no readily interpretable dependence of band width, the other constant of the classical theory, and structure came out.

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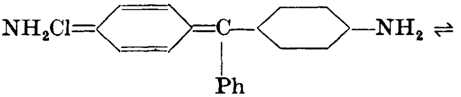
[15] " Organische Farbstoffe," Ferd. Dummlers Verlag, Berlin u. Bonn, 1933.

[16] *Proc. Nat. Acad. Sci.*, 1923, **9**, 303.

[17] *J. Chem. Physics*, 1934, **2**, 644.

The development of quantum mechanics in the years following 1926 made possible a more detailed theory of colour in terms of molecular energy levels. C. R. Bury [18] suggested that the basis of the colour of an organic compound might lie in the quantum-mechanical resonance phenomenon, and he was able to translate many of the older ideas on colour into modern terms. Thus Baeyer [7] had postulated that the colour of Doebner's violet was due to an oscillation between (XIII) and (XIV), whereas Bury pointed out that the oscillation was only structural, resonance theory providing a mechanism for the "rhythmic rearrangement" suggested by Watson and Meek. The function of the auxochrome, then, was to realise the possibility of resonance. The same type of mechanism holds for the case of acidic dyes such as benzaurin (XV). However, Bury was at a loss to provide the mechanism for neutral dyes like indigo (XVI).



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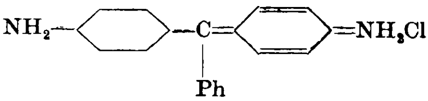

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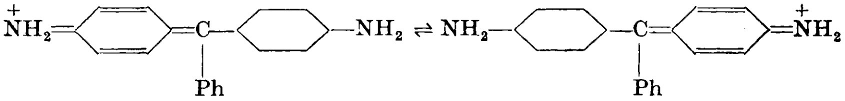

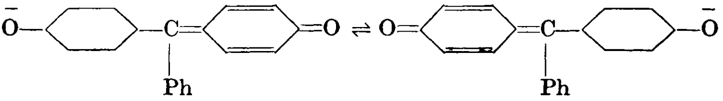

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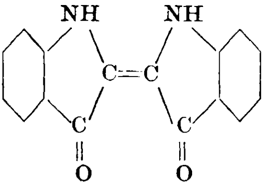

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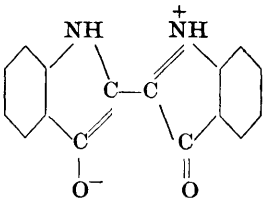

(XVII.)

Before 1937, quantum-mechanical calculations had aimed at determining the energy of the ground state of a molecule, and thus its resonance energy. However, in that year, A. L. Sklar [19] realised the importance of the excited states of a molecule for the light-absorption process, and was able to calculate the absorption bands of a number of unsaturated hydro-

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[18] *J. Amer. Chem. Soc.*, 1935, **57**, 2115.

[19] *J. Chem. Physics*, 1937, **5**, 669.

carbons. In the next year this work was extended by Th. Förster.[20] The attack on the quantum-mechanical problem of the colour of dyes was sketched out by L. Pauling [21] in 1939. As well as outlining the general solution of the acid and basic dyes problem, Pauling was able to account qualitatively for the absorption bands of neutral dyes such as indigo in terms of resonance between the classical valency structures and dipolar structures of higher energy such as (XVII). This problem was also considered by F. Arndt and B. Eistert.[22] Since 1939 this work has been followed up by R. S. Mulliken, Th. Förster, A. L. Sklar, K. F. Herzfeld and others. It is of interest to note that whereas the older theories were concerned with complex molecules and were inadequate to deal with simple systems, quantum mechanics has reversed this position, and having started with the simple systems is now developing methods of attack for the more complex.

G. N. Lewis and M. Calvin [23] in 1939 set out "to re-examine the data of light absorption and to see whether, by applying the more inductive methods of chemistry together with such general results of quantum theory as are applicable to all systems, we may obtain a better understanding of the data. Starting with the idea that in the absorption of light the energy is taken up by electronic oscillations, we have considered these oscillations as analogous to classical oscillations but subjected to the rules of simple quantisation." This quasi-classical theory has correlated a great deal of data, and has stimulated some extremely interesting experimental investigations.

From this point this article will be primarily concerned with a more careful scrutiny of the development of the theory of colour that has taken place in the last decade or so.

2. *The Classical Theory of Light Absorption* [24]

The classical theory of the interaction of light with matter, due to Drude, is based upon Maxwell's electromagnetic theory and the concept of electrons. The former theory shows that a beam of light may be considered as consisting of transverse waves, the oscillating entities being the electric vector **E** and the magnetic vector **H**, these two vectors being perpendicular to each other and to the direction of propagation. The plane through the electric vector and the direction of propagation is known as the plane of polarisation. Explicit solution of Maxwell's wave equation shows that a plane monochromatic wave of frequency ν, travelling in the z direction in a medium of refractive index a and polarised in the x direction is given by

$$\begin{aligned}\mathbf{E} &= \mathbf{i}E_x e^{2\pi i\nu(t-az/c)} \\ \mathbf{H} &= \mathbf{j}H_y e^{2\pi i\nu(t-az/c)} \qquad (2.1)\end{aligned}$$

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[20] *Z. physikal. Chem.*, 1938, *B*, **41**, 287.

[21] *Proc. Nat. Acad. Sci.*, 1939, **25**, 577.

[22] *Ber.*, 1939, **72**, 202, 860.

[23] *Chem. Reviews*, 1939, **25**, 273.

[24] (*a*) The treatment of this section closely follows that of Chako (ref. 17). Compare also (*b*) Th. Förster, *Z. Elektrochem.*, 1939, **45**, 551 ; (c) R. A. Morton, *Ann. Reports*, 1941, **38**, 7 ; (*d*) R. S. Mulliken and C. A. Rieke, *Rep. Prog. Physics*, 1941, **8**, 231.

where **i** and **j** are unit vectors along the x and y axes and c is the velocity of the waves in a vacuum.

In order to investigate the interaction of radiation with matter, some hypothesis as to the structure of matter has to be made. It is satisfactory for the present purpose to assume that in a gaseous medium containing N' molecules per c.c. each molecule contains $\bar{f}_j$ electrons bound by an elastic force to an equilibrium position and having a frequency of oscillation ν_j. The electric force acting on a given electron in the molecule is the product of the electric vector and the charge e of the electron. It can be shown that the magnetic force is negligible. The oscillating electric field of the light wave will cause forced vibrations of the electrons, the equations of motion of the latter being of the form

$$m\ddot{x} + \omega_j^2 mx = eE_x e^{i\omega(t-az/c)} \quad . \quad . \quad . \quad (2.2)$$

where $\omega = 2\pi\nu$, $\omega_j = 2\pi\nu_j$; ν_j is the proper frequency of the electron, and is determined by the elastic force binding the electron to its equilibrium position. A solution of (2.2) together with the solution of Maxwell's equations suffices to evaluate a, the refractive index, usually represented by n. The result is

$$n^2 = 1 + \frac{4\pi e^2 N'}{m}\sum_j \frac{\bar{f}_j}{\omega_j^2 - \omega^2} \quad . \quad . \quad . \quad (2.3)$$

an equation in accord with the experimental results. It can be seen that for $\omega < \omega_j$ the refractive index increases with the frequency of the light, a phenomenon known as normal dispersion.

If the frequency of the light coincides with one of the electronic proper frequencies, the refractive index becomes infinite. The analysis may, however, be carried through if it is assumed that the electrons are subject to a "damping force," proportional to their velocities. The equation of motion then becomes

$$m\ddot{x} + mg_j\dot{x} + \omega_j^2 mx = eE_x e^{i\omega(t-az/c)} \quad . \quad . \quad . \quad (2.4)$$

The refractive index may be determined by the same procedure as before and is given by

$$a^2 = 1 + \frac{4\pi e^2 N'}{m}\sum_j \frac{\bar{f}_j}{\omega_j^2 - \omega^2 + ig_j\omega} \quad . \quad . \quad . \quad (2.5)$$

Thus the motion of the light wave in the medium is governed by a complex refractive index. Writing

$$a = n(1 - i\kappa) \quad . \quad . \quad . \quad . \quad . \quad (2.6)$$

and separating real and imaginary parts, we have

$$n^2(1 - \kappa^2) = 1 + \frac{4\pi e^2 N'}{m}\sum_j \frac{\bar{f}_j(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + g_j^2\omega^2} \quad . \quad . \quad (2.7)$$

$$n^2\kappa = \frac{2\pi e^2 N'}{m}\sum_j \frac{\bar{f}_j g_j \omega}{(\omega_j^2 - \omega^2)^2 + g_j^2\omega^2} \quad . \quad . \quad . \quad (2.8)$$

The refractive index thus shows a marked change in the neighbourhood of an electronic proper frequency. If it is assumed that there is a single electronic frequency, then (2.7) shows as the frequency of the light approaches that of the electron, the refractive index increases until a maximum is reached after which it begins to decrease, reaching a minimum, when it again increases. The existence of more than one electronic frequency will complicate this phenomenon, which is known as anomalous dispersion.

To interpret κ, the ratio of the energy of the wave after having traversed a distance z in the medium to its value on entering the medium has to be determined. This treatment leads to

$$I = I_0 e^{2\omega\kappa n z/c} \quad . \quad . \quad . \quad . \quad . \quad (2.9)$$

where I_0 and I are the entrant and emergent intensities. While this law has been derived for the gaseous state, most of the relevant data refer to solutions. For this reason (2.9) will be written in a form appropriate to solutions, and the corrections which are necessitated by this procedure will be discussed later. Thus since κ is proportional to N', (2.9) may be expressed as

$$I = I_0 e^{-\varepsilon' c d} \quad . \quad . \quad . \quad . \quad . \quad (2.10)$$

ε' being a new constant, c being the concentration of the medium, and d the distance through which the light has travelled. Formula (2.10) combines Beer's and Lambert's laws and has received experimental confirmation.

By the use of (2.8), (2.9), and (2.10) the following expression is obtained for ε' :

$$\varepsilon' = \frac{2e^2N \times 10^{-3}}{cmn} \cdot \frac{\bar{f}_j \gamma_j \nu^2}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2\nu^2} \quad . \quad . \quad . \quad (2.11)$$

where $\gamma_j = g_j/2\pi$ and N is Avogadro's number. From (2.11) it follows that if ν is markedly different from ν_j, ε' is essentially zero. The curve of ε' against ν is bell-shaped, ε' reaching a maximum at $\nu = \nu_j$. The substance is said to have an absorption band at ν_j.

The integrated intensity over the whole band may be obtained in the following way. If the band in question is a weak one, removed from the strong bands that are responsible for dispersion, then its contribution to n may be neglected, and for n may be written the value due to all other bands at ν. In addition, if the band is sufficiently narrow, it can be shown that

$$\int \varepsilon' . d\nu = \frac{\pi e^2 N \times 10^{-3} \bar{f}_j}{cmn} \quad . \quad . \quad . \quad . \quad (2.12)$$

Up to the present it has been assumed that the absorbing substance is in the gaseous state. To test the effect of a solvent which does not absorb in the region in question, the Lorentz–Lorenz forces acting on the absorbing molecule due to the polarisation of surrounding molecules have to be taken into account. This treatment leads to

$$\int \varepsilon' . d\nu = \frac{\pi e^2 N \times 10^{-3}}{cm} \left(\frac{(n_0^2 + 2)^2}{9n_0} \right) \bar{f}_j \quad . \quad . \quad . \quad (2.13)$$

for a dilute solution, n_0 being the refractive index of the solvent at frequency ν. This constitutes a correction to the integrated intensity as measured in solution, to give the value for the gaseous state. Chako has tabulated $\bar{f}_j$, $\bar{\bar{f}}_j$, and also f_j which is obtained from (2.12) by setting $n = 1$. With regard to the solvent correction, Chako came to the conclusion " that it is impossible to account for the influence of the solvent through the Lorentz–Lorenz forces." This problem of solvent correction has also been considered by R. S. Mulliken.[24d] Some interesting data which throw light on this question have been recorded by V. Henri and L. W. Pickett [25] for *cyclo*hexadiene, and by L. W. Pickett, E. Paddock, and E. Sackter [26] for *cyclo*pentadiene. For *cyclo*hexadiene the vapour and the solution values agreed very well, but for *cyclo*pentadiene the integrated absorption was about 20% higher for the vapour than for the solution. This effect is the opposite to that which would be predicted from a consideration of the Lorentz–Lorenz forces. On such grounds as these, Mulliken concluded that in the absence of empirical data as to the ratio of vapour to solution intensity, the best procedure is to neglect the correction given by (2.13) and to assume $n = 1$, which would be true for the substance in the gaseous state. The importance of the correction of f values derived from measurements in solution, to f values for the gaseous state, lies in the fact that the latter quantities may be calculated by quantum-mechanical methods, as will be shown in Section 3.

From (2.11) it follows that

$$\varepsilon'_{\text{max.}} = \frac{2e^2N \times 10^{-3}}{cm\gamma_j} f_j, \quad (n = 1) \qquad . \quad . \quad . \quad (2.14)$$

or, by using (2.12),

$$\gamma_j \varepsilon'_{\text{max.}} = \frac{2}{\pi}\int \varepsilon' . d\nu \qquad . \quad . \quad . \quad . \quad . \quad (2.15)$$

If γ_j is constant throughout the band,

$$\Delta\nu = 2\gamma_j \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2.16)$$

where $\Delta\nu$ is the distance between the points at which $\varepsilon' = 1/2\varepsilon'_{\text{max.}}$. The " damping constant " γ_j is equal to the half-width of the band. Both (2.15) and (2.16) were used by Chako to evaluate γ_j. However, no readily interpretable relationship was found between γ_j and the chemical constitution of the substance or the nature of the solvent.

Equation (2.14) allows an estimate to be made of the magnitude of $\varepsilon'_{\text{max.}}$. For if it is assumed that $f_j = 1$, *i.e.*, that there is one electron per molecule concerned in the absorption process, and that $\gamma_j \sim 2000$ cm.$^{-1}$, then substitution in (2.12) shows $\varepsilon'_{\text{max.}}$ to be of the order of 100,000. However, for many molecules $\varepsilon'_{\text{max.}}$ is much smaller.

Experimental results are usually expressed in terms of ε or E defined by

$$I = I_0 10^{-E} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2.17)$$

$$E = \varepsilon cd \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2.18)$$

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[25] *J. Chem. Physics*, 1939, **7**, 439.

[26] *J. Amer. Chem. Soc.*, 1941, **63**, 1073.

E is known as the extinction, while ε, the extinction for unit concentration and distance, is known as the molecular extinction coefficient, c being the molar concentration. The data are conveniently represented by plotting E or ε, or their logarithms, as abcissa, the ordinate being either the wavelength or the frequency. In the former case either Ångstrom units (A.; 1 A. $= 10^{-8}$ cm.) or millimicrons (mμ; 1 mμ $= 10^{-7}$ cm.) are used, while in the latter the frequency (ν) in sec.$^{-1}$ or the wave-number ($\tilde{\nu} = \lambda^{-1} = \nu/c$) in cm.$^{-1}$ is employed. The frequency is conveniently expressed in fresnels, one fresnel being equal to a frequency of 10^{12} sec.$^{-1}$.

To determine the f value of a band, the method usually employed is to measure the area under the curve obtained by plotting ε as a function of $\tilde{\nu}$; f can then be calculated from (2.12), allowance being made for the change of base of the logarithms. Thus

$$f = 4{\cdot}31 \times 10^{-9}\int \varepsilon . d\tilde{\nu} \quad . \quad . \quad . \quad . \quad (2.19)$$

While Lambert's law—that the proportion of light absorbed by a substance is independent of the incident intensity but directly proportional to the logarithm of the distance travelled—always holds, Beer's law is not of such universal applicability. Beer's law states the proportionality between the light absorbed and the number of molecules of the absorbing substance through which the light passes. It does, however, apply where chemical reaction either between solute molecules or between solute and solvent molecules does not occur.

A more detailed picture of the electronic proper frequencies and the oscillator strengths is afforded by Bohr's adaptation of the old quantum theory to the discussion of the energy states of atoms and molecules. Bohr showed that atoms and molecules exist in radiationless stationary states of constant energy, known as *energy levels*. When the electron jumps from a stationary state of energy E_1 to one of energy E_2, light is absorbed or emitted according as $E_1 \lessgtr E_2$, the frequency being

$$\nu = \frac{E_2 - E_1}{h} \quad . \quad . \quad . \quad . \quad . \quad (2.20)$$

where h is Planck's constant. The electronic proper frequencies are the values of ν given by (2.20), and $E_2 - E_1$ is the *transition energy*. In the molecular case, the vibrational–rotational energy of the molecule as a whole is quantised as well as the electronic energy. As the order of magnitude of these energies is usually $E_{\text{rot.}} \ll E_{\text{vib.}} \ll E_{\text{elec.}}$ the internal energy of the molecule (*i.e.*, excluding translational energy) may be written

$$E = E_{\text{rot.}} + E_{\text{vib,}} + E_{\text{elec.}}$$

Three types of spectra can be distinguished, *viz.*, rotational spectra occurring in the far infra-red, vibration–rotation spectra in the near infra-red, and electronic spectra in the visible and ultra-violet. Molecular spectra are distinguished from atomic spectra in that the latter consist of a number of lines, whereas the former consist of bands, except at very high resolution in the gas phase, when the bands are seen to consist of closely and regularly spaced lines. The bands arise from the fact that, concurrently with an electronic transition, there are vibrational and rotational transitions. The spectrum of a molecule in the gas phase is thus very complex, and a great deal of work has been published dealing with the interpretation of the fine structure of molecular spectra. However, this lies outside the scope of the present review.[27] In solution, owing to intermolecular interactions, the fine structure of the electronic bands is largely lost, and smoothed off regions of relatively large width appear. Vibrational structure may still remain, as is shown for benzene in Fig. 1.[28] The vibrational energy levels obtained from the electronic absorption spectra will be those of the excited state, since most of the absorbing molecules will be in the lowest vibrational level of the normal electronic state. Because of the complications produced by vibrational structure, it is not surprising that Chako found no correlation between the half-widths of absorption bands and the nature of the absorbing molecule or of the solvent.

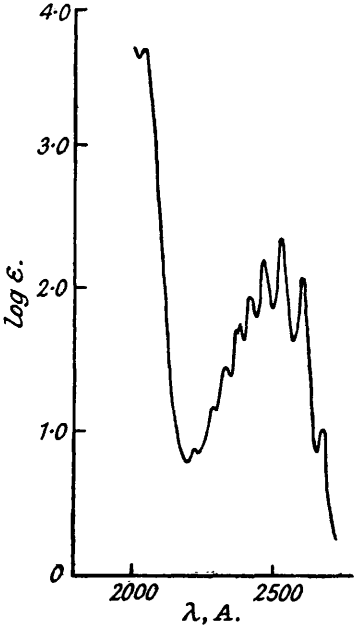

FIG. 1

The absorption spectrum of benzene in ethyl-alcoholic solution, showing the fine structure.

The old quantum theory also provides an explanation of the low values of f ($\sim 0{\cdot}0001$) which are sometimes observed for molecules. On the classical theory, the explanation would be naïve, namely that only one in 10,000 molecules was of a kind capable of absorption. The old quantum theory interprets f as the probability of transition for a given molecule. This view makes possible fractional f numbers but no further information as to their magnitude could be obtained, apart from the fact that $\Sigma_j f_j$ was equal to the total number of electrons in the molecule. On the basis of dispersion theory the f_j are known as *oscillator strengths.*

The procedure adopted in obtaining the f value of a band is equivalent to comparing it with a single line in an atomic spectrum. Where the band shows vibrational structure, the analogous case would be an atomic line showing fine structure. The justification for this procedure has been examined by R. S. Mulliken.[29]

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[27] This field is reviewed by H. Sponer and E. Teller, *Rev. Mod. Physics*, 1941, **13**, 75.

[28] W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.*, 1935, *A*, **152**, 299.

[29] *J. Chem. Physics*, 1939, **7**, 14.

3. *The Quasi-classical Theory of Lewis and Calvin* [30]

This theory is based on the concept that the energy absorbed during the interaction of a molecule with radiation is taken up by electronic oscillations within the molecule. The oscillations are regarded as being analogous to classical oscillations, but quantum methods are used to determine a set of energy levels. One of the simplest molecules that can be considered is ethane, which shows continuous absorption below 1600 A. Indeed, it is characteristic of most simple molecules that absorption commences only in the far ultra-violet. The oscillating unit is taken to be the pair of electrons constituting the C–C bond. Since electronic motion is very rapid compared with nuclear motion, no difficulty arises from taking the nuclei as being fixed in space. The electronic oscillations may be interpreted in terms of the following resonance structures for ethane:

$$\mathrm{H_3\overset{+}{C}\quad :\overset{-}{C}H_3} \qquad\qquad \mathrm{H_3C{-}CH_3} \qquad\qquad \mathrm{H_3\overset{-}{C}:\quad \overset{+}{C}H_3}$$

(XVIII.) (XIX.) (XX.)

It is not necessary to assume a complete transition from (XVIII) to (XX), an approach towards these structures from (XIX) being all that is required. If now a restoring force proportional to the displacement of the electron pair from its equilibrium position is assumed, the energy levels of the system are given by

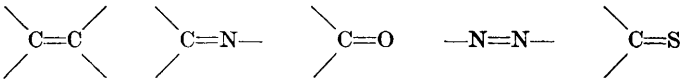
$$E_n = (n + 1/2)h\nu, \quad n = 0, 1, 2, \ldots \qquad (3.1)$$

where ν is the frequency of the electronic oscillation related to the restoring force/unit distance (k) by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (3.2)$$

and n is the quantum number specifying the energy level. Absorption then corresponds to a change in n from 0 to 1, the frequency of the light absorbed being ν, as given by the Bohr frequency condition (2.20). Even when the oscillator is in the state $n = 0$, there is a certain energy associated with it, the zero-point energy.

The authors next consider a series of double bonds



arranged in order of decreasing force constant by the following argument. Simple compounds containing a carbon–carbon double bond absorb in the region of 2000 A., those containing a carbon–oxygen double bond at about 2800 A., while the absorption characteristic of the azo-group lies at about 3500 A. Although the spectra of simple compounds containing carbon–nitrogen or carbon–sulphur double bonds have not been studied, the positions of these groups can be assigned from their behaviour in more complex compounds. Assuming that the double bond is the essential chromophore,

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[30] Reference 23.

i.e., neglecting the lone pairs on the nitrogen, sulphur, and oxygen atoms, it follows that the force constant diminishes in the series from $>C{=}C<$ to $>C{=}S$. The extreme structures to which the electronic oscillations tend are represented by (XXI) and (XXII), (XXIII) being the classical

$$\overset{+}{A}{-}{:}\overset{-}{B} \qquad \overset{-}{A}{:}{-}\overset{+}{B} \qquad A{=}B$$

(XXI.) (XXII.) (XXIII.)

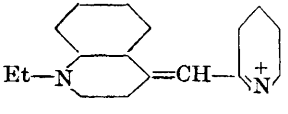
structure. If the oscillations are simple harmonic, a series of parabolæ representing the potential energies of the electron pair in the various nuclear frameworks can be plotted. For this type of potential function, the selection rules lay down that $\Delta n = \pm 1$, *i.e.*, the oscillator can only jump from a given state to an adjacent one. However, if the potential function becomes non-parabolic at large displacements, the transition $\Delta n = 2$ becomes allowed, the intensity varying with the degree of departure from the parabola.[31] In the case of a conjugated molecule, as well as there being a possibility of overtones, there is also the possibility of the molecule possessing a band which is relatively insensitive to the structure of the molecule as a whole. These considerations led Lewis and Calvin to propose the following classification of absorption bands.

(*A*) Fundamental Bands :

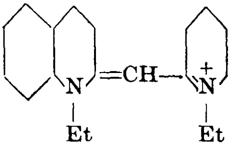
- (1) First order, n changes from 0 to 1.
- (2) Second order, n changes from 0 to 2.

(*B*) Bands of Partial Oscillation.

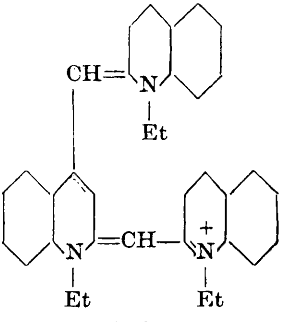
Whereas type *A* are characteristic of the molecule as a whole, type *B* are the result of a localised oscillation. This classification may be illustrated by the compounds (XXIV), (XXV), and (XXVI). Although the absorption



(XXIV.)



(XXV.)



(XXVI.)

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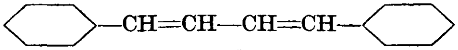
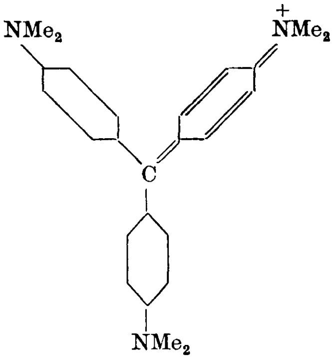
[31] The second-order bands are further dealt with by G. N. Lewis and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2107.

curves of (XXIV) and (XXV) are closely similar, that of (XXVI), while showing a band similar to that of (XXV), also shows an entirely new band at longer wave-length. The former band can be considered as due to partial oscillation, the latter being characteristic of the molecule as a whole.

A further classification comes from a consideration of the geometry of the molecule. In the case of a diphenylpolyene such as (XXVII), the oscillation may be thought of as following an approximately linear path. However, in a molecule such as crystal-violet (XXVIII) the positive charge can be placed on any of the three nitrogen atoms, and so the oscillation can be resolved into two component oscillations at right angles. In this case the oscillation frequencies in the two directions will be equal, but, if there is a marked dissymmetry in the molecule, this degeneracy will be removed. Similarly, if the absorbing molecule possesses extension in three dimensions, there will be the possibility of a third component oscillation. In this way the fundamental bands of a molecule can be classified as



(XXVII.)



(XXVIII.)

(*a*) *x* Bands. One-dimensional oscillator.
(*b*) *x* and *y* Bands. Two-dimensional oscillator.
(*c*) *x*, *y*, and *z* Bands. Three-dimensional oscillator.

By convention, the band of longest wave-length characteristic of the molecule as a whole is taken to be the *x* band.[32]

The nature of the electronic oscillations may be enquired into in further detail. The polyenes form one extreme class. If as a first approximation the effect of the end groups is neglected, these systems can be represented by

$$\mathrm{R—[CH{=}CH]}_n\mathrm{—R}$$

the extreme structures being

$$\mathrm{R—\overset{+}{C}H—[CH{=}CH]}_{n-1}\mathrm{—\underset{\bullet\bullet}{\overset{-}{C}}H—R} \quad \text{and} \quad \mathrm{R—\underset{\bullet\bullet}{\overset{-}{C}}H—[CH{=}CH]}_{n-1}\mathrm{—\overset{+}{C}H—R}$$

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[32] Additional evidence for *y* bands is afforded by Lewis and Bigeleisen, *ibid.*, p. 2102.

The normal state of the molecule will be non-polar. However, in the presence of an electric field of strength E, a moment (μ) will be induced in each $>\mathrm{CH}=\mathrm{CH}<$ unit given by

$$\mu = ex = \alpha E \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.3)$$

x being the displacement of the charge and α the polarisability of the molecule. When the electrons are displaced, the electric force acting on them must be balanced by the restoring forces. Thus :

$$eE = kx \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.4)$$

From (3.3) and (3.4) it follows that the force constant is given by

$$k = e^2/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.5)$$

If the molecule now be placed in the field of a light wave whose wave-length is long compared with the dimensions of the molecule, individual oscillations are set up in the units of the chain, the displacements being the same for each unit. On the assumption that in the excited states of the molecule the oscillations are of the same character as the induced oscillations discussed above, the dependence of frequency on chain length can be investigated. If m is the mass of the effective electrons in each unit, then for a chain of n units, the vibration frequency will be determined by the force constant k, and the mass nm. It is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{nm}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.6)$$

or

$$\lambda^2 = k'n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.7)$$

k' being a new constant. This treatment predicts a linear relationship between λ^2 and the number of units in the chain. However, the effect of the end groups cannot be predicted to this approximation.

In the above treatment it is assumed that, while the individual units vibrate in phase, there is little interaction between them. Even in the excited state of the molecule, the electrons may never get far from their mean positions. However, a second extreme type of oscillator is illustrated by the carbocyanines, the essential structures being

$$>\overset{+}{\mathrm{N}}=\mathrm{CH}\text{—}[\mathrm{CH}=\mathrm{CH}]_n\text{—}\mathrm{N}< \qquad >\mathrm{N}\text{—}[\mathrm{CH}=\mathrm{CH}]_n\text{—}\mathrm{CH}=\overset{+}{\mathrm{N}}<$$

In this case, even in the normal state, the charge is distributed through the whole molecule. The restoring force on each electron pair is dependent on the position of the other electrons. Lewis and Calvin liken the oscillations of such a system to the longitudinal oscillations of a stretched string, and conclude that the wave-length of absorption should be proportional to the length of the chain, or

$$\lambda = k''n \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.8)$$

The two types of molecules just discussed represent extreme cases. In between these extremes, intermediate types of behaviour may be expected. The determining factor is the mobility of the electrons within the molecule. When the normal state of a molecule can be represented by a formula without any formal charges, the mobility will be small. However, as the normal state of the molecule departs from the classical formula, so will the mobility increase, becoming greatest when two structures can be written down, differing only in the position of the charge.

4. *The Quantum Theory of Light Absorption* [33]

Although the Bohr theory led to a general understanding of the light-absorption process, it was left to quantum mechanics to elucidate the details. The quantum-mechanical treatment of organic molecules goes back to 1927, when Heitler and London put forward their theory of the hydrogen molecule. Heisenberg had shown in 1926 that if a number of structures can be written down for an atomic or molecular system of equal or nearly equal energy, then the actual state of the system is more stable than any of the hypothetical states represented by the structures. The system is said to be stabilised by resonance. The principle of indeterminacy expressed the fact that electrons could not be rigidly located, and Heitler and London were able to account for the stability of the hydrogen molecule by casting off the concept of localised electrons. The resonance phenomenon, rather than being fundamental, is a legacy from classical chemistry, which thought in terms of particle electrons and rigid bonds, and which guided the choice of structures used in the quantum-mechanical calculations.

Before considering in more detail the Heitler–London approach to the hydrogen molecule, it is necessary to consider the quantum-mechanical description of the hydrogen atom. The starting point is the Schrödinger equation :

$$\mathrm{H}\psi = E\psi \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where H is a differential operator, E the energy of the system, and ψ a function of the co-ordinates, which specifies the state of the system ; H can be obtained from the classical mechanical expression for the total energy of the system by substituting certain differential operators for the co-ordinates and momenta of the particles comprising the system. If now it is stipulated that ψ shall be single valued and continuous and such that

$$\int \psi^*\psi d\tau = 1 \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

where ψ^* is the conjugate complex of ψ, $d\tau$ being a generalised volume element, then these conditions can only be satisfied for certain values of E. These values of E are known as *eigenvalues*, the corresponding ψ's being the *eigenfunctions* or *wave functions*. The " space " of which $d\tau$ is an infinitesimal element is not ordinary three-dimensional space, except in the

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[33] The following papers review the quantum mechanical treatment of molecules: (*a*) " The Quantum Theory of Valence," J. H. van Vleck and A. Sherman, *Rev. Mod. Physics*, 1935, **7**, 167. (*b*) " The Quantum Mechanics of Molecules," G. J. Kynch and W. G. Penney, *Ann. Reports*, 1936, **23**, 37. (*c*) " Grundzüge der Theorie ungesättige und aromatischer Verbindungen," E. Hückel, *Z. Elektrochem.*, 1937, **43**, 752. (*d*) " The Theory of Molecular Structure," W. G. Penney, *Rep. Prog. Physics*, 1939, **6**, 212. (*e*) " The Quantum Theory of the Chemical Bond," C. A. Coulson, *Proc. Roy. Soc. Edin.*, 1941—43, *A*, **61**, 114. (*f*) C. A. Coulson, this vol., to appear.

case of a system comprising a single particle, but has dimensions equal to the number of co-ordinates required to describe the system. The quantisation of the energy of the system then arises as the result of placing certain limitations on the solution of (4.1). A justification of the foregoing conditions is provided by the interpretation of ψ, namely, that

$$\psi^*\psi d\tau \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.3)$$

measures the probability of the system being in the " volume element " $d\tau$. The normalising condition (4.2) ensures that the probability of finding the system somewhere in " space " is unity. In the case of a single electron,

$$\psi^*(r, \theta, \phi)\psi(r, \theta, \phi)d\tau$$

may be interpreted as the probability of finding the electron in the element of volume $d\tau$ in the neighbourhood of (r, θ, ϕ) or, if multiplied by e, the quantity of charge in an infinitesimal region surrounding the point.

As well as being a function of the co-ordinates the wave function of an electron in a spherically symmetrical field depends upon four parameters known as *quantum numbers* :

$$\psi = \psi_{n, l, m, s}(r, \theta, \phi)$$

The first, n, is known as the *principal quantum number*, and determines the energy of the electron. The second and third, l and m, are known as the *azimuthal* and *magnetic quantum numbers*, and determine respectively the total orbital angular momentum and the orbital angular momentum in the direction of an external magnetic field, not strong enough to affect the energy of the electron. The fourth quantum number, s, the *spin quantum number*, describes the spin momentum of the electron, which can be orientated parallel with, or antiparallel to, the magnetic field. All the quantum numbers except s are integers, and are subject to

$$l \leqslant n - 1, \qquad -l \leqslant m < l$$

The spin quantum number can only have the values $\pm 1/2$. The *Pauli exclusion principle* stipulates a condition on the quantum numbers describing the electrons in an atom. It states that no two electrons in an atom can have the same four quantum numbers. Thus the maximum number of electrons in an atom with specified n, l, m is 2 ; the number with specified n, l is $2(2l + 1)$, while the number with a given n is $2n^2$. A more general statement of the exclusion principle is that the wave function of an atom must change sign (be antisymmetric) when the co-ordinates of two electrons are interchanged. While the individual angular momenta of the electrons in a many-electron atom are not constants, the total angular momentum of all the electrons is. As the total angular momentum is related to the values for the individual electrons, these latter still provide a useful means of classification. A wave function specified by n, l, m is known as an *atomic orbital* (A.O.). By the exclusion principle, each orbital can contain a maximum of two electrons and these must have their spins opposed. For purposes of classification, it is sufficient to specify the electrons of an atom in terms of n, l. Electrons with $l = 0, 1, 2, \ldots$ are known as $s, p, d \ldots$ electrons, an electron with $n = 2$, $l = 1$, being represented by $2p$. In this way the electron structure of the carbon atom may be represented by $1s^2 2s^2 2p^2$, the superscripts indicating the number of electrons of the given type.

Once the Schrödinger equation has been solved, all information concerning the state of the system can be obtained. In general, the mean value of a property of a system represented by the operator F, for a system in the state ψ_n, is given by

$$\bar{\mathrm{F}} = \int \psi^*_n \mathrm{F} \psi_n \mathrm{d}\tau \qquad . \quad . \quad . \quad . \quad (4.4)$$

However, most of the systems of chemical interest are too complex to admit of a solution of the Schrödinger equation. Recourse has then to be had to approximate methods. It usually happens that the wave-equation may be solved for the system if some simplifying assumptions are made. The wave functions thus found can be taken as a starting point for an improved calculation. A theorem of very great utility states that the energy of a system calculated with an approximate wave function is always greater than the true energy, the difference decreasing as the approximate wave function approaches the true one. If a system were considered as possibly existing in n structures represented by $\psi_1, \psi_2 \ldots \psi_n$, an approximate wave function of the form

$$\psi' = a_1\psi_1 + a_2\psi_2 + \ldots + a_n\psi_n \qquad . \quad . \quad . \quad (4.5)$$

could be used. The a_i are then determined so as to make the energy of the system a minimum. This minimising process gives rise to the quantum mechanical *secular equation*

$$\begin{vmatrix} E_{11} - S_{11}E, & E_{12} - S_{12}E & \ldots & E_{1n} - S_{1n}E \\ E_{21} - S_{21}E, & E_{22} - S_{22}E & \ldots & E_{2n} - S_{2n}E \\ \ldots\ldots & \ldots\ldots & \ldots & \ldots\ldots \\ E_{n1} - S_{n1}E, & E_{n2} - S_{n2}E & \ldots & E_{nn} - S_{nn}E \end{vmatrix} = 0 \qquad (4.6)$$

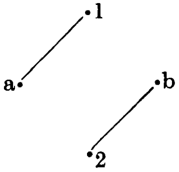
where

$$E_{ij} = \int \psi^*_i \mathrm{H} \psi_j \mathrm{d}\tau$$

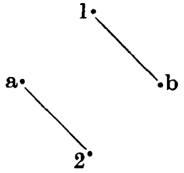
$$S_{ij} = \int \psi^*_i \psi_j \mathrm{d}\tau$$

The energies of the structures are $\frac{E_{ii}}{S_{ii}}$, $\frac{E_{ij}}{S_{ij}}$ being the interaction energies between these structures ; E is the approximation to the energy of the system. This equation is an algebraic equation of the nth degree, the n roots $E_1, E_2, \ldots E_n$ being the approximations to the energy levels. The approximations to the states of the system are found by substituting the values of a_i corresponding to the required energy level into (4.5).

In the case of the hydrogen molecule, two possible structures present themselves, (XXIX) and (XXX) ; (XXIX), for example, represents electron 1 being attached to nucleus a and electron 2 to nucleus b. This was the method used by Heitler and London. It is essentially the theory of the

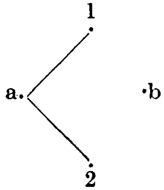


(XXIX.)

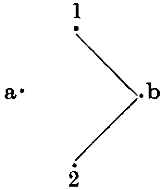


(XXX.)

homopolar molecule, ionic structures like (XXXI) and (XXXII) playing no part.



(XXXI.)



(XXXII.)

The wave functions representing (XXIX) and (XXX) are

$$\psi_a(1)\psi_b(2), \qquad \psi_a(2)\psi_b(1)$$

and the approximate wave function is

$$\Psi = a_1\psi_a(1)\psi_b(2) + a_2\psi_a(2)\psi_b(1) \quad . \quad . \quad . \quad (4.7)$$

The wave-mechanical computation shows that the correct linear combinations are

$$\Psi_S = A_S[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \quad . \quad . \quad . \quad (4.8a)$$

$$\Psi_A = A_A[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \quad . \quad . \quad . \quad (4.8b)$$

the corresponding energies being E_S and E_A. These quantities are functions of R, the internuclear distance, and computation shows that whereas $E_S(R)$ possesses a minimum, $E_A(R)$ does not. Hence (4.8*a*) corresponds to the formation of a stable molecule. The subscripts S and A refer to symmetry or asymmetry with respect to the interchange of electrons. When electron spin is taken into account, four spin wave functions present themselves. If $\alpha(1)$ represents electron 1 with $s = \frac{1}{2}$ and $\beta(2)$ represents electron 2 with $s = -\frac{1}{2}$, they are $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)$, $\alpha(2)\beta(1)$, $\beta(1)\beta(2)$. These four wave functions can be combined to give four new functions, one of which is antisymmetric and the other three of which are symmetric with respect to interchange of electrons. In order to satisfy the exclusion principle, (4.8*a*) must be multiplied by the antisymmetric spin function, and (4.8*b*) by the symmetric spin function to give the complete wave function of the molecule. As E_S represents the stable state and as the antisymmetric spin function is made up from $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$, it follows that the electrons forming a chemical bond have opposed spins.

The second method of treating molecular structure was developed by Hund, Lennard-Jones, Mulliken, and Hückel. It involves the building up of a *molecular orbital* (M.O.) from the wave function of a single electron moving in the potential framework of the nuclei and the other electrons. The energy of their molecular orbitals may in principle be determined by a rigorous solution of the Schrödinger equation. Each molecular orbital can contain two electrons, and so to determine the molecular energy, the electrons are fed two at a time into the orbitals of lowest energy. Rather than rigorously solve the Schrödinger equation, the L.C.A.O. method assumes that the M.O. is given by a *linear combination of atomic orbitals*. The molecular orbital for the hydrogen molecule to this approximation would be

$$\Psi = a_1\psi_a(1) + a_2\psi_b(1) \quad . \quad . \quad . \quad . \quad (4.9)$$

The correct linear combinations are found to be

$$\psi_g = A_g[\psi_a(1) + \psi_b(1)] \quad . \quad . \quad . \quad . \quad (4.9a)$$

$$\psi_u = A_u[\psi_a(1) - \psi_b(1)] \quad . \quad . \quad . \quad . \quad (4.9b)$$

The subscripts g and u indicate symmetry and asymmetry with respect to inversion of the orbital in the centre of symmetry. Quantal calculation shows (4.9a) to be the orbital of lowest energy (ψ_g is said to be a bonding orbital, while ψ_u is antibonding). Hence the molecular wave function is

$$\Psi = A_g^2[\psi_a(1) + \psi_b(1)][\psi_a(2) + \psi_b(2)] \quad . \quad . \quad . \quad (4.10)$$

If this expression is multiplied out, it is seen to contain two terms corresponding to (4.8a) together with two additional terms of the type

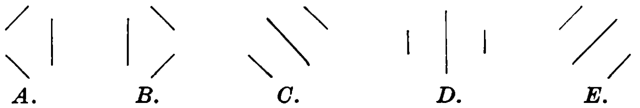
$$\psi_a(1)\psi_a(2) \qquad \psi_b(1)\psi_b(2) \quad . \quad . \quad . \quad . \quad (4.11)$$

which are the wave-mechanical transcription of (XXXI) and (XXXII). Thus the molecular orbital treatment gives as much weight to the ionic structures as to the purely homopolar ones considered in the Heitler–London treatment. Both of these methods when generalised so as to apply to complex organic molecules suffer from limitations : the Heitler–London or *valence-bond* (V.B.) method on account of its neglect of ionic structures : the M.O. method because of its treatment in terms of a single electron, with consequent neglect of interelectronic interaction. However, both methods may be modified to overcome these deficiencies.

The Heitler–London treatment of the hydrogen molecule shows that the pair of electrons forming a chemical bond have their spins opposed. This suggests that the valency of an atom is equal to the number of electrons with unpaired spins that it possesses. Thus carbon in the state $1s^22s^22p^2$ would be bivalent, the two p electrons being capable of forming bonds. It is of interest to enquire into the directional properties of valence bonds. To do this requires a qualitative discussion of the nature of the s and p electron distributions. The solutions of the Schrödinger equation for an electron in a spherically symmetrical field show that, while the charge distribution of s electrons is spherically symmetrical, those of p, d, . . . electrons exhibit maxima in certain directions. In the case of the p electrons the maxima are mutually perpendicular and so they can be classified as p_x, p_y, or p_z. If the formation of a chemical bond is regarded as the building up of a charge between bonded atoms, then an atom with two p electrons would tend to form bonds directed at right angles, with two other atoms. Returning to the case of carbon, in order to obtain a quadrivalent state it seems reasonable to assume that a $2s$ electron is promoted to the $2p$ state, giving the structure $1s^2 2s 2p^3$, in which case there are four electrons with unpaired spins. If, however, these orbitals are used for bond formation, a model comprising three mutually perpendicular bonds, with the fourth symmetrically disposed with respect to the other three, would be obtained. On this basis methane would not possess the symmetry of a regular tetrahedron, a structure which has been amply confirmed by physicochemical studies. However, as has been seen, a better approximation to the system can be obtained by taking four linear combinations of the four orbitals. This was the method used by Pauling, who took as his criterion in the formation of linear combinations the principle of maximum overlapping. This assumes that a bond between two atoms will be stronger the greater the degree of overlapping of the orbitals forming the bond. Pauling defined the strength of bonds formed by s orbitals as 1, and of those formed by p orbitals as $3^{1/2}$. By linear combination of the $2s$ and the three $2p$ electrons he was able to form four bonds directed tetrahedrally with the maximum strength of 2. Similarly, the strongest bonds that can be formed from the configuration sp^2 are inclined at 120°. The latter process gives rise to the trigonal bonds of great importance in the discussion of conjugated systems. This process involving the mixing of s and p electron wave functions is known as *hybridisation.*[34]

Hückel was the first to apply these ideas to unsaturated molecules. In the case of benzene, for example, he assumed that the s, p_x, p_y electrons were hybridised to give the trigonal bond system already referred to, the three σ orbitals being used in forming the C–C and C–H bonds. He was then able by both methods to determine the energy of the p_z or π electrons and hence the energy over and above that of the framework bonds.

While the L.C.A.O. treatment of conjugated systems is relatively straightforward, the valence-bond treatment introduced several new concepts. The latter method employs the fact that, for a conjugated system, the electron spins of the various p_z electrons may be coupled in a number of different ways, corresponding to different structures or bond diagrams. A useful theorem due to Rumer limits the number of bond arrangements that have to be considered. He showed that for a system of n bonds ($2n$ electrons) any conceivable structure can be represented in terms of a fundamental set of $\dfrac{(2n)!}{(n)!\,(n+1)!}$ structures. These are known as a *canonical set.* For benzene, the now famous structures are



(4.12)

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[34] For a more complete discussion of this process, see Reference 33 (*f*).

Structures *C*, *D*, *E*, containing a para-bond, are said to be *excited.* The number of canonical structures increases very rapidly with the number of bonds ; for anthracene there are 429. The number of structures containing formal bonds (bonds between non-adjacent atoms) also increases with the number of bonds. A structure containing no formal bonds is said to be unexcited, with one formal bond, first excited, and so on. It is unfortunate that the same term " excited " is used to refer both to the structures and to the actual states of a molecule. However, the context usually makes clear the sense in which it is used.

Largely as the result of work by Slater, Pauling, and Eyring, simplified methods were evolved for setting up the secular equation in terms of the canonical structures. These methods were then employed to calculate the resonance energies of a large number of conjugated molecules.

Before 1937, attention had been focused upon the lowest root of the secular equation, *i.e.*, on the ground states of molecules. However, in that year Sklar[35] calculated the differences in energies between the ground and the first excited states of a number of molecules, and was able to show that this energy difference or transition energy corresponded to their long wave-length absorption bands. Rather than to use explicit expressions for the atomic orbitals, his method was to determine the energy difference between the states in terms of a quantum-mechanical parameter, α. He obtained the value of this parameter from purely thermochemical data. His results for benzene are given in Fig. 2(*a*), and these are to be compared with the experimentally determined values shown in Fig. 2(*c*). With a value of α equal to 1·92 v.e., the long wave-length absorption band of benzene is found to lie at 2470 A. compared with the experimentally determined band

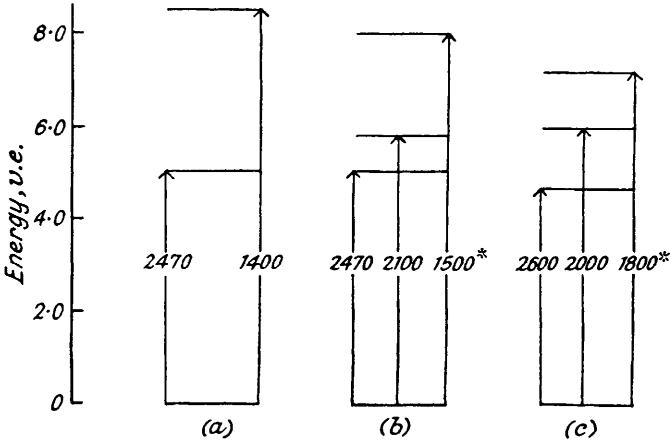

FIG. 2

The electronic energy levels of benzene by (a) *the valence bond,* (b) *the antisymmetrised molecular orbital method,* (c) *experimental. The allowed transitions are shown with an asterisk.*

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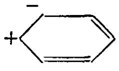
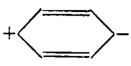
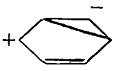
[35] Reference 19.

at 2600 A. The attempt to calculate the position of the shorter wave-length bands by this method led to results in poor agreement with experiment. Sklar attributed this breakdown to the neglect of excited ionic structures, such as (XXXIII), (XXXIV), and (XXXV). Because of the large number


(XXXIII.)


(XXXIV.)


(XXXV.)

of these structures he was only able to incorporate the twelve of type (XXXIII). The calculations show that while the ionic structures interact only slightly with the lower states of the molecule, they become of great importance when the highly excited states are considered.

The problem may also be approached from the molecular orbital viewpoint. Calculation shows that the energies of the various molecular orbitals for benzene are given by

$$W_1 = 2\beta \cos (2\pi/6)l \qquad (l = 0, \pm 1, \pm 2, 3) \quad . \quad . \quad . \quad . \quad (4.13)$$

where β is the resonance integral, which may be evaluated empirically. The energy of the orbitals increases with $|l|$. Thus two electrons are placed in the orbitals with $l = 0$ and four in those with $|l| = 1$. The total energy is then 8β. In the first excited state one electron is raised from $|l| = 1$ to $|l| = 2$. This state is fourfold degenerate, since the odd electron in the $|l| = 1$ level may have $l = \pm 1$, while the electron in the $|l| = 2$ level may have $l = \pm 2$. The energy of the first excited level is 6β, the energy difference corresponding to the long wave-length band being 2β. Since estimates of β by different workers differ considerably, all that can be said of this calculation is that it gives a value of the right order of magnitude.[36]

In order to refine the molecular orbital method, M. Goeppert-Mayer and A. L. Sklar [37] utilised a modification suggested by Mulliken. It is known as the method of *antisymmetrical molecular orbitals.* One of the main sources of error in the L.C.A.O. method (molecular orbitals formed as a linear combination of atomic orbitals) is the neglect of the interelectronic repulsions. These interactions are responsible for removing the degeneracy previously discussed. But, as has been seen, the molecular wave function, which is the product of the appropriate molecular orbitals, allows many electrons to congregate around a given nucleus. Because of this, the introduction of the interelectronic repulsion may lead to results in worse agreement with experiment. However, if the molecular wave function is multiplied by an appropriate spin function and the whole antisymmetrised in the co-ordinates of the electrons, all terms which represent an accumulation of more than two electrons on a single nucleus vanish. By means of this refinement, the limitations of the molecular orbital method are largely overcome. In addition, the expression for the energy levels may be obtained

[36] R. S. Mulliken and C. A. Rieke, *Rev. Mod. Physics*, 1942, **14**, 259.

[37] *J. Chem. Physics*, 1938, **6**, 645; A. L. Sklar and R. H. Lyddane, *ibid.*, 1939, **7**, 374; F. London discusses some of the approximations involved in the method (*ibid.*, 1945, **13**, 396).

in terms of certain integrals, which are calculable analytically, the only empirical data used being the internuclear C–C distance. In this way the results shown in Fig. 2(*b*) were obtained. The calculated values are seen to be in good agreement with experiment.

In 1939 R. S. Mulliken,[38] in a series of papers, developed methods for calculating the intensity of a band quantum mechanically. The transition (electric) moment is defined as

$$(\mathbf{er})_{mn} = \int \Psi^*{}_n(\sum_i e\mathbf{r}_i)\Psi_m \mathrm{d}r \quad . \quad . \quad . \quad . \quad (4.14)$$

where the summation is taken over all the electrons and $\mathbf{r}_i$ is a vector defining the position of the *i*th electron. The theory of radiation now relates the *transition moment* or the *dipole strength* $(r)^2{}_{mn}$ with the oscillator strength of dispersion theory. The relationship is

$$f_j = \left(\frac{8\pi^2 mc}{3h}\right)\bar{\nu} r_j^2 \quad . \quad . \quad . \quad . \quad (4.15)$$

where the subscript j refers to the transition $m \longrightarrow n$. It is often convenient to consider the components of $\mathbf{r}_j$, namely, x_j, y_j, z_j. If it so happens that $x_j, y_j, z_j = 0$, then to this degree of approximation $f_j = 0$, and the transition is said to be forbidden.

Mulliken's method may be illustrated by his treatment of the hydrogen molecule. From the L.C.A.O. viewpoint, the ground state is represented by

$$\Psi_N = \psi_g(1)\psi_g(2) \quad . \quad . \quad . \quad . \quad (4.16)$$

while the first excited state to which transition is allowed is given by

$$\Psi_E = \frac{1}{\sqrt{2}}[\psi_g(1)\psi_u(2) + \psi_g(2)\psi_u(1)] \quad . \quad . \quad . \quad (4.17)$$

The transition corresponding to absorption is that of an electron from a bonding M.O. to an antibonding one. If the molecular axis is taken as the z direction, then $x_j = y_j = 0$. Expression (4.14) thus reduces to

$$(z)_{NE} = \int \Psi_E(z_1 + z_2)\Psi_N \mathrm{d}r \quad . \quad . \quad . \quad (4.18)$$

This expression, on substitution for Ψ_E and Ψ_N, becomes after reduction

$$(z)_{N,E} = \frac{1}{\sqrt{2(1 - s^2)}}\left[\int \psi_a z \psi_a \mathrm{d}r - \int \psi_b z \psi_b \mathrm{d}r\right] \quad . \quad . \quad (4.19)$$

Now $\int \psi_a z \psi_a \mathrm{d}r$ is simply the average value of z for atomic orbital a, and as the internuclear distance $R = z_\mathrm{A} - z_\mathrm{B}$,

$$(z)_{N,E} = \frac{R}{\sqrt{2(1 - S^2)}} \quad . \quad . \quad . \quad . \quad . \quad (4.20)$$

The factor $[2(1 - s^2)]^{-\frac{1}{2}}$ is related to A_g and A_u of (4.9*a*) and (4.9*b*). From the V.B. point of view it can be shown that

$$(z)_{N,E} = \frac{SR}{\sqrt{1 - S^4}} \quad . \quad . \quad . \quad . \quad . \quad (4.21)$$

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[38] *J. Chem. Physics*, 1939, **7**, 14, 20, 121, 339, 353, 364, 570.

the transition being that from an essentially non-polar ground state to an essentially ionic excited state. Substitution of the known values for R and S gives $f = 0{\cdot}68$ from (4.20) and $0{\cdot}49$ from (4.21). The agreement between the two values is excellent in view of the approximations involved.

The theory of groups can be applied to simplify the calculation of the energy states of a molecule, and to decide the question as to whether a given transition is allowed or not. For benzene, which has the symmetry of a plane regular hexagon, it can be shown that transitions from the ground state to the two lowest excited states are forbidden. This is in qualitative agreement with the experimental data, which show a weak band at 2500 A., a stronger one at 2000 A., and a very intense band at 1800 A. The appearance of the weak long wave-length band is due to a distortion of the symmetry of the molecule by vibrations. The intensity of the forbidden band at 2000 A. is probably related to its proximity to the allowed transition at 1800 A.[39] An interesting study has been the effect of the distortion of the benzene symmetry by the gentle method of replacing the hydrogen atoms

FIG. 3

The absorption spectrum of solid hexamethylbenzene : (1) electric vector in the plane of the ring ; (2) electric vector perpendicular to the plane of the ring.

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[39] H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Physics*, 1939, **7**, 207.

by deuterium[40] or by the more drastic method of replacing them by F,[41] OH,[42] NH_2,[43] or CH_3.[44]

For the conjugated molecules to be discussed in the present review it is assumed that the energy levels of the π electrons are concerned in the long wave-length spectra. That ultra-violet absorption can arise in other ways is shown by saturated molecules such as ethane for which absorption starts at about 1600 A. The recent work of G. Scheibe, St. Hartwig, and R. Müller[45] strikingly demonstrates the part played by the π electrons in the long wave-length spectrum of hexamethylbenzene. This molecule possesses a layer structure in the solid state, and so a known orientation of a crystal implies a known orientation of the molecular planes.[46] The absorption spectrum can then be determined by using polarised light with the electric vector parallel and perpendicular to the plane of the molecule. If the π electrons are responsible for the absorption, the extinction in the latter case should be very small. The results are shown in Fig. 3. The extinction with the electric vector perpendicular to the plane of the molecule is a tenth of that with the electric vector parallel, thus confirming the rôle of the π electrons. Other examples of the directional properties of light absorption are discussed by R. A. Morton.[47]

5. *Some Qualitative Applications of the Resonance Theory*[48]

The problem of the relationship between the colour of an organic compound and its chemical constitution has been approached from two directions. The first was along the lines of classical organic chemistry, and consisted in the examination of a series of related molecules in order to find the effect upon the absorption maximum of the parent substance caused by changes in constitution. Unfortunately, much of the early work is marred by the neglect of "subsidiary" changes in constitution which may have had a greater effect than the change which was to have been investigated. The second approach is the calculation of the wave-length and intensities of absorption by quantum-mechanical methods. The quantal treatment, however, is limited to relatively simple molecules, although qualitatively the theory of resonance is capable of providing much valuable information. The present section will deal with the applications of the resonance concept, and the last section with the results of the quantal calculation.

The relationship between the resonance energy of a compound and its light absorption is of interest. In Section 4 it has been shown that, if more than one structure can be written for a molecule, interaction between the

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[40] C. A. Beck and H. Sponer, *J. Chem. Physics.*, 1942, **10**, 575.

[41] S. H. Wollman, *ibid.*, 1946, **14**, 123.

[42] F. A. Matsen, N. Ginsberg, and W. W. Robertson, *ibid.*, 1945, **13**, 309.

[43] N. Ginsberg and F. A. Matsen, *ibid.*, p. 167.

[44] N. Ginsberg, W. W. Robertson, and F. A. Matsen, *ibid.*, 1946, **14**, 511.

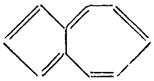
[45] *Z. Elektrochem.*, 1943, **49**, 372.

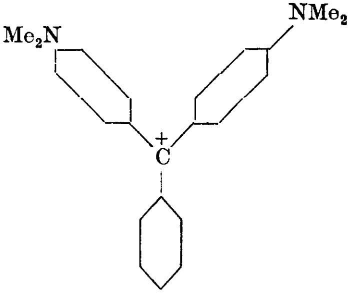
[46] K. Lonsdale, *Proc. Roy. Soc.*, 1929, *A*, **123**, 494.

[47] Reference 24 (*c*).

[48] A discussion of the colour of organic compounds from the M.O. viewpoint is given by E. J. Bowen, *Ann. Reports*, 1943, **40**, 12.

structures will give rise to a set of states which will be better approximations to the actual molecular states. The energy difference between the lowest state found in this way and the structure of lowest energy is the resonance energy of the molecule, whereas the energy difference between the two lowest molecular states is equal to the energy corresponding with the long wave-length absorption band, provided of course that the transition is allowed. In the diphenylpolyenes (XXVII), the resonance energy increases with addition of each successive vinylene group, while the absorption maxima move towards the red. However, an increase in the resonance energy does not always imply a bathychromic effect, as a consideration of the isomeric molecules naphthalene and azulene (XXXVI) shows. For while naphthalene has a greater resonance energy than azulene, the former molecule absorbs at a much shorter wave-length than the latter. Another example comes from the work of G. Schwarzenbach *et al.*,[49] who have studied the spectra of indicators capable of undergoing several colour changes. These authors concluded that the most highly coloured form of the indicator was the most stable. However, chemical evidence would suggest that malachite-green (XXXVII) has a smaller resonance energy than crystal-violet (XXVIII), while the wave-lengths of absorption are 6230 and 5900 A., respectively.[50] The bathychromic effect, together with the increase in resonance energy observed in the case of the polyenes as the series is traversed, can be understood on the following basis. The successive additions of vinylene groups cause a rapid increase in the number of excited structures, there being only one unexcited structure, corresponding to the classical formula, in each case. Thus on proceeding up the series the ground state of the molecule is lowered, corresponding with an increased resonance energy, but the first excited state is still further lowered, corresponding with a shift of the absorption towards the red. Although the prediction of the relationship between the resonance energy and light absorption may safely be made for a related series of molecules, yet great care has to be exercised when the argument is extended to molecules outside the series.


(XXXVI.)



(XXXVII.)

For closely related molecules, the greater the extent of the resonance

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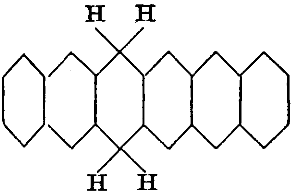
[49] *Helv. Chim. Acta*, 1937, **20**, 1591.

[50] Reference 23.

system, the longer the wave-length of absorption. This is clearly shown by the phenomenon of *insulation* of chromophores. The spectrum of 6 : 15-dihydrohexacene (XXXVIII) is almost identical with the sum of the spectra of naphthalene and anthracene.[51] The extent of the resonance system is reduced, and the spectrum of the molecule reverts to the spectra of the two systems formed by the insulating effect of the two methylene groups. The insulating effect may be achieved by more subtle methods, as has been shown by the work of L. W. Pickett, G. F. Walter, and H. France on some substituted diphenyls.[52] The long wave-length band of diphenyl is very similar in position to that of benzene, but has a greatly increased intensity ($\varepsilon_{\text{max.}}$ 18,000, compared with 200 for benzene). Yet the spectrum of 2 : 2′ : 4 : 4′ : 6 : 6′-hexamethyldiphenyl, for example, approximated to that of mesitylene. This phenomenon is understandable in terms of resonance theory. The structures for diphenyl are the four classical structures and excited ones such as (XXXIX), and the corresponding ones with a formal bond between the *pp′* positions. The question of the relative importance of the ionic and the formal bonded structures will be discussed in Section 6. For the maximum interaction between structures of this type, the two rings must be coplanar.[53] This follows from the principle of maximum overlapping, since the π orbitals of atoms *a* and *a′* have their maxima perpendicular to the plane of the rings. Thus, any effect which tends to force the rings far out of the coplanar condition will decrease the contributions of the above structures, and the spectrum of the molecule will revert to that of the corresponding benzene derivative.



(XXXVIII.)

(XXXIX.)

So far the discussion has been mainly concerned with chromogens. According to Bury [54] the function of an auxochrome is to provide a greater possibility of resonance. Thus in aniline, as compared with benzene,

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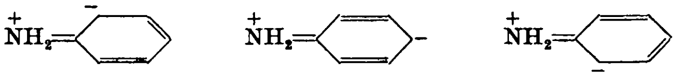
[51] E. Clar, *Ber.*, 1942, **75,** 1283.

[52] *J. Amer. Chem. Soc.*, 1936, **58,** 2296.

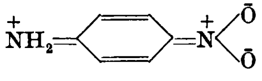
[53] For a discussion of the structure of diphenyl, see J. Karle and L. O. Brockway, *ibid.*, 1944, **66,** 1974.

[54] Reference 18.

structures such as (XL) participate, as well as the two Kekulé and the p-bonded types. Confirmation of this view comes from a comparison of the spectrum of aniline with that of the anilinium ion, for which structures of the type represented by (XL) become highly improbable. The two spectra are very different, that of the anilinium ion being practically identical with that of benzene. The anti-auxochromes of Wizinger can be interpreted in a similar fashion. Thus, in p-nitroaniline the possibility of resonance becomes further enhanced, limiting structures such as (XLI) playing a part.

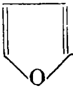


(XL.)



(XLI.)

Some very interesting results have been recorded showing the relationship between the spectra of members of a series of compounds. In particular may be mentioned the work by K. W. Hausser *et al.*[55] on certain polyenes, and the attack on the cyanine dyes initiated by N. I. Fisher and F. M. Hamer,[56] and extended by L. G. S. Brooker and his co-workers.[57] Other data have been obtained by A. E. Gillam and D. H. Hey [58] for two series of polyphenyls, and by E. Clar *et al.*[59] for certain polycyclic aromatic compounds. Only the first two series will be discussed here, as they are illustrative of the general method of approach.

The polyenes are members of a vinologous series which can be represented by the general formula (XLII). The compounds considered were of the following types : R,R′ = CH_3, CHO ; CH_3, CO_2H ; , CHO ; and , . Of particular importance is the tabulation of the integrated intensities of the bands, for, as was shown in Section 2, the integrated intensity or the related f value constitutes the best measure of the intensity of absorption. The tabulation of $\lambda_{max.}$ and $\varepsilon_{max.}$ is unsatisfactory, since f is a function of both $\varepsilon_{max.}$ and γ, the half-width of the band. In Table II are given the results obtained for the diphenylpolyenes, the data referring to benzene solution.

$$R\text{—}[CH{=}CH]_n\text{—}R' \qquad (XLII.)$$

$$R\text{—}\overset{-}{C}H\text{—}[CH{=}CH]_{n-1}\text{—}\overset{+}{C}H\text{—}R \qquad (XLIII.)$$

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[55] *Z. physikal. Chem.*, 1935, *B*, **29**, 363, 371, 378, 384, 391.

[56] *Proc. Roy. Soc.*, 1936, *A*, **154**, 703 ; 1937, *A*, **163**, 138.

[57] *Rev. Mod. Physics*, 1942, **14**, 275.

[58] *J.*, 1939, 1170.

[59] E. Clar, " Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1941 ; see also R. N. Jones, *Chem. Reviews*, 1943, **32**, 1.

TABLE II

The diphenylpolyenes

n . . .	0	1	2	3	4	5	6	7
$\lambda_{max.}$ . .	2515	3190	3520	3770	4040	4240	4450	4650
f . . .	0·41	0·58	0·77	1·26	1·39	1·41	1·58	1·90

The other series show the same general type of behaviour. In terms of the resonance theory the structures are the classical structure (XLII) and excited ones, such as (XLIII). There are of course many other contributing structures, involving smaller separation of charge. If it is assumed that structures of the type (XLIII) are of main importance for the excited state, then a bathychromic effect would be expected upon ascending the series, and this is observed. Since all the polyene series examined show the same type of dependence of absorption maxima upon n, the end groups may as a first approximation be neglected. Fig. 4 shows the resonance energy over and above that of the four phenyl groups, and the transition energy as a function of n. The increase in intensity with increase in n may be accounted for qualitatively since the transition moment will be greater the longer the chain.

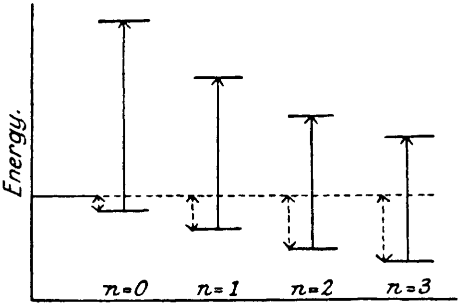

FIG. 4

The resonance energies (←- - - →) and transition energies (——→) of some diphenylpolyenes.

This series of compounds formed the first type of linear oscillator in the sense of Lewis and Calvin. The relationship derived (3.7) indicates that a plot of λ^2 against n should give a straight line. This is shown in Fig. 5, the agreement being excellent. This series also affords evidence of the existence of a " second-order band," as the polyenes all show a second band at shorter wave-lengths. The ratio of λ_1 to λ_2 approaches 2 as the length of the chain increases, as is to be expected for a second-order band.

The light absorption of an important series of polyenes, the carotenoids, has been discussed by L. Zechmeister, L. Pauling, *et al.*[60] Of particular

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[60] *J. Amer. Chem. Soc.*, 1943, **65**, 1941 ; see also R. S. Mulliken, *J. Chem. Physics*, 1939, **7**, 364.

interest is the existence of steric isomers, due to the possibility of different arrangements around the double bonds. Quantal calculations show that, for a polyene in the all-*trans*-configuration, transitions are allowed from the ground to the first and the third excited states, but forbidden to the second.

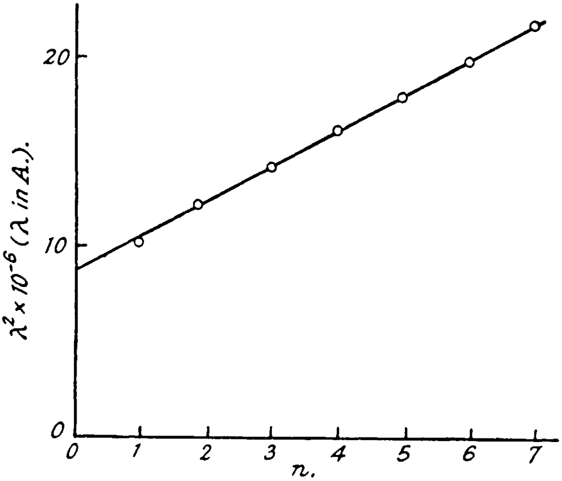


FIG. 5

The linear relationship between λ^2 *and* n *in the diphenylpolyenes.*

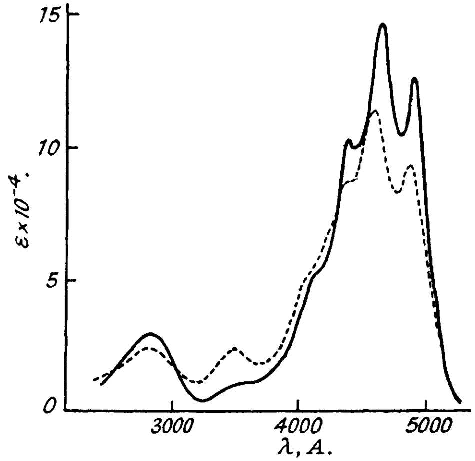
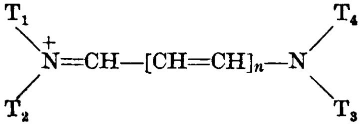


FIG. 6

The development of the " cis-*peak* " *in carotene :* ——— *all* trans-*carotene ;* – – – – *equilibrium mixture of isomers.*

If, however, the molecule possesses a *cis*-arrangement about some of the double bonds, transition to the second excited state becomes allowed. This accounts for the third peak characteristic of the *cis*-carotenes. Fig. 6 shows the development of the " *cis*-peak " in γ-carotene.

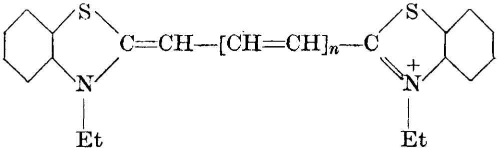
The cyanine series, investigated by N. I. Fisher and F. M. Hamer, can be represented by the general formula (XLIV), T_1, T_2, T_3, T_4 being atoms in a heterocyclic molecule. Molecules of this type form another example of a vinologous series. The cyanines may be divided into two classes, the symmetrical cyanines, for which the two end groups are the same, and the unsymmetrical ones in which the end groups differ. Three general relationships emerge from this work. In the first place there is a bathychromic shift as n increases, and secondly the intensity of the long wave-length band increases with n. The third conclusion that may be drawn is that in many cases the wave-length of absorption of an unsymmetrical cyanine can be calculated as the mean of the wave-lengths of absorption of the two related symmetrical compounds.



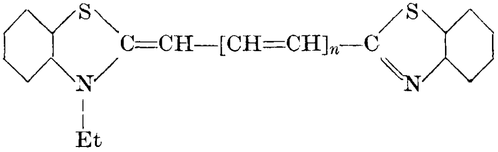
$$(T_1)(T_2)\overset{+}{N}=CH-[CH=CH]_n-N(T_4)(T_3)$$

(XLIV.)

The colour of dyes has been extensively investigated by L. G. S. Brooker and his collaborators. The first point of interest lies in a comparison of the spectra of a series of cyanines (XLV) with those of the related anhydro-bases (XLVI). The data are given in Table III, the solvent being methyl alcohol.



(XLV.)



(XLVI.)

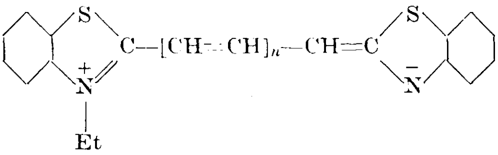
TABLE III

Comparison of the Spectra of a Series of Cyanines with those of the Corresponding Anhydro-bases

n.	Cyanines.		Anhydro-bases.	
	$\lambda_{max.}$	$\epsilon_{max.} \times 10^{-4}$.	$\lambda_{max.}$	$\epsilon_{max.} \times 10^{-4}$.
0	4230	8·45	3960	5·85
1	5575	14·8	4580	5·65
2	6500	22·9	4900	6·4
3	7580	24·6	5100	6·8

For the cyanines, $\lambda_{\text{max.}}$ is approximately linearly related to n, the behaviour to be expected from "linear oscillators of the second type" in the Lewis and Calvin sense. The increase in intensity on ascending the series is also to be expected on this view. However, an entirely different state of affairs exists for the anhydro-bases. In the first place $\varepsilon_{\text{max.}}$ is approximately constant for all members of the series, and secondly, whereas a change in n from 0 to 1 causes a bathychromic shift of 620 A., yet the change in n from 2 to 3 only causes a shift of 200 A.

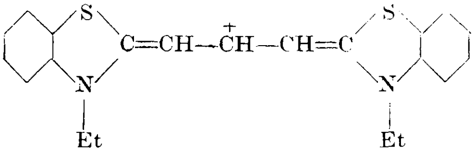
The marked difference between the behaviour in these two cases enables Brooker to classify the spectra of series of compounds on the grounds of convergence or non-convergence. The former series is non-convergent, while the latter is convergent. This author attributes the difference in behaviour in the two cases to the degeneracy or non-degeneracy of the *extreme structures*. This term will be used to signify structures with the charge placed at the end of the chain. Whereas in the cyanines there exist two extreme structures of equal energy, for the anhydro-bases there is a single low-energy classical structure, together with two extreme structures such as (XLVII). In both there are additional intermediate structures,



(XLVII.)

but it is not necessary to consider these for the present argument. For the cyanine series a degeneracy exists among the extreme structures, whereas in the anhydro-bases the classical structure differs widely in energy from the ionic structures. This degeneracy, according to Brooker, is a prerequisite for the non-convergence of a series.

The variation in $\lambda_{\text{max.}}$ of a symmetrical cyanine of given chain length, with alterations in the end groups, can be explained by the consideration of intermediate structures such as (XLVIII). Pauling has pointed out the



(XLVIII.)

necessity for taking into account structures of this type, since the extreme structure represented by (XLV) and the corresponding one with the charge on the left-hand nitrogen atom will not by themselves interact. Brooker concludes that the greater the energy difference between (XLV) and (XLVIII), the less the resonance splitting of the degenerate levels and the longer the wave-length of absorption. Fig. 7 [61] shows approximately the ground and the first-excited levels for a series of symmetrical cyanines. Evidence for the decrease in resonance energy as *n* increases is afforded by the work of V. K. LaMer and G. H. Burrows.[61] These authors investigated the acidity required to decolorise a series of symmetrical cyanines and found that it decreased with *n*. If it is assumed that the process involves the addition of a proton to the chain, and thus the loss of resonance stabilisation, the decrease in this quantity with increasing *n* is verified.

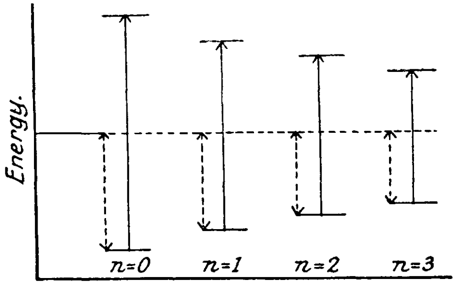
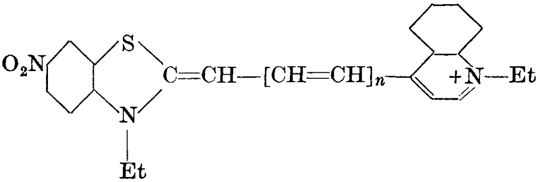


Fig. 7

The resonance energies (←- - -→) *and transition energies* (——→) *of some symmetrical cyanines.*

Non-degeneracy may also be observed in the unsymmetrical cyanines if the basicity of the two heterocyclic nuclei are different. In this case there would be a stabilisation of the extreme structure with the positive charge on the more basic nitrogen atom. For the compound (XLIX) there is a marked convergence, the absorption maxima for $n = 0$, 1, and 2 being 5045, 6170, and 6800 A., respectively.



(XLIX.)

The non-convergence makes itself apparent in another fashion. It had been noted by Fisher and Hamer that the wave-length of absorption of an unsymmetrical cyanine could be calculated from the mean of the values for the two related symmetrical compounds. This relationship must obviously break down if the series of the symmetrical cyanines are non-convergent while that of the unsymmetrical compound is convergent.

Brooker has used the deviation $\lambda_{\text{calc.}} - \lambda_{\text{obs.}}$ as a measure of the relative basicity of heterocyclic nuclei. For a given value of *n*, one of the end groups is kept constant, while the other is varied. The greater the deviations in

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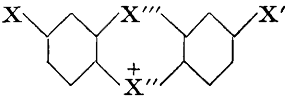
[61] L. G. S. Brooker, " Resonance and Organic Chemistry," " Frontiers in Chemistry," Vol. 3, Interscience Publishers, Inc., New York, 1945.

such a series of compounds, the greater is the difference in basicity between the two end groups. Consistent results for the order of basicities have been obtained by Brooker from measurements both in the cyanine and in the styryl dye series.

G. N. Lewis[62] has recently published a classification of dyes based upon the concepts of the Lewis and Calvin theory, together with rules for estimating their long wave-length absorption bands. The parent molecule considered is (L), and the various families of dyes are obtained by specifying



(L.)

X'', X''' and the auxochromic groups X and X'. For example with $X'' = N$, $X''' = O$, the oxazine dyes are obtained. X''' may be absent, as in the triphenylmethyl dyes. The positive charge, formally represented as residing at X'', is distributed through the molecule owing to resonance. The " electronic oscillation " responsible for the colour is supposed to take place between X and X', the auxochromic groups. The simplifying assumption is made that the effects due to alterations in X, X', X'', and X''' act independently, and the direction of these effects is calculated by the use of the following rule. " If the colour of a compound is associated with an oscillation of positive charge along a given path, the frequency of absorption will be increased by anything that diminishes the amount of positive charge, and decreased by anything that increases it." Thus the bathychromic effect of $X,X' = NR_2$ as compared with $X,X' = OH$, and the hypsochromic effect of $X''' = O$ as compared with a molecule in which X''' is absent, can be accounted for on this basis. Malachite-green being taken as the standard molecule, the effect of constitutional changes upon the colour can be determined empirically as additive effects. Lewis has considered a large number of dyes, and the agreement between $\lambda_{\text{obs.}}$ and $\lambda_{\text{calc.}}$ is very good, the mean error being 30 A. In the acridine family, $X'' = CR$, $X''' = N$, the agreement is very poor, and this is interpreted as indicating that the long wave-length band of such compounds corresponds to a " vertical oscillation."

The foregoing are typical of the arguments used in the application of resonance theory to a correlation of the absorption spectra of organic molecules. The value of such treatment will be discussed at the end of the next section.

6. *The Application of Quantal Methods*

The calculation of the colour of an organic compound, besides having an intrinsic importance, also has a utilitarian importance outlined by Sklar :[63] " The determination of the structure of a natural product, perhaps

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[62] *J. Amer. Chem. Soc.*, 1945, **67**, 770.

[63] Reference 19.

a hormone, is a matter of many years' work in which many guesses are made and later rejected. One could calculate the spectrum of a proposed structure, check it against the experimental one, and so keep on the right track." Although at the present time this desirable vista is still distant, considerable progress has been made towards it.

Sklar considered the four molecules butadiene, benzene, fulvene, and azulene, and was able to calculate the transition energy for each molecule by the valence-bond method in terms of a quantum-mechanical parameter α. Rather than evaluate α analytically, recourse was had to thermochemical data, which led to an empirical value for the constant. The results of the calculations, together with some results obtained by other authors, are shown in Table IV.

TABLE IV

Application of the Valence-bond Method

Molecule.	$\lambda_{\text{max.}}$, A.		Obs.
	Calc. (Sklar).	Calc. (Förster).	
Butadiene [a]	1900	—	2100
Hexatriene [b]	2570	—	2600
Octatetraene [b]	3120	—	3020
Fulvene [a]	3650	—	3650
Benzene [a, c]	2470	2450	2600
Styrene [d]	2570	—	2850
*cyclo*Octatetraene [e]	3320	3860	~ 4000
Azulene [a, d]	6910	7800	7000
Naphthalene [c, d]	2680	2950	2750
Diphenyl [d]	2570	—	2515
Anthracene [c]	—	3650	3700
Phenanthrene [c]	—	3000	3400 [d]
Naphthacene [c]	—	4500	4600
Pyrene [c]	—	3450	3300
Pentacene [c]	—	5450	5800

[a] A. L. Sklar, Reference 19.

[b] M. Kovner, *Acta Physicochim. U.R.S.S.*, 1944, **19**, 385; cf. *Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **35**, 54.

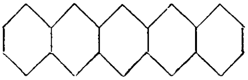
[c] Th. Förster, Reference 20.

[d] G. W. Wheland, "The Theory of Resonance," Wiley, New York, 1944.

[e] A. Maccoll, *Nature*, 1946, **157**, 695. The difference between the values quoted in the table and those in the reference is due to the choosing in the present case of values of the parameter α to conform with the values used by Sklar and Förster.

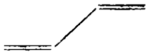
Unless explicit references are given, the sources of the experimental data are taken from the papers which record the results of the calculations.

In setting up the secular equations for butadiene, benzene, and fulvene, Sklar included all the canonical structures. Since the number of these rapidly increases as the number of electrons increases, the method becomes unmanageable for a molecule such as azulene. In this case only the two unexcited structures and the first excited ones were considered. This can be justified on the grounds that the highly excited structures will make only a small contribution to the ground and the first excited state. Even with this approximation, the work involved in the calculations for complex molecules becomes very great, and so Förster [64] in 1938 went a step further and neglected all but the unexcited structures in setting up the secular equation. This method is obviously only applicable to molecules for which more than one unexcited structure exists. Förster was able to treat molecules such as pentacene (LI) and pyrene in this way.

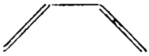


(LI.)

As well as the assumption discussed above, a number of others of a more fundamental nature are made in the treatment of the states of molecules by the V.B. method. A justification of these assumptions is indicated *a postiori* by the success of the method in calculating the resonance energies of molecules. However, a much more serious criticism of the results obtained comes from a consideration of the intensities of the calculated absorption bands. Kovner [65] has shown in the case of butadiene that the valence-bond method leads to the conclusion that the long wave-length transition is forbidden for the model with a *trans*-arrangement about the single bond (LII).



(LII.)



(LIII.)

As this transition becomes allowed for the model with a *cis*-arrangement (LIII), Kovner concluded that butadiene must possess the *s-cis*-arrangement. (This term has been introduced by Mulliken [66] to denote *cis*- and *trans*-isomerism about a single bond.) Kovner's conclusion is in direct conflict with the work of Mulliken,[67] using the molecular orbital method. Even if butadiene possessed the *s-cis*-configuration, it is doubtful whether a sufficiently large transition moment could be obtained by considering, as Kovner did, only homopolar structures. The same type of argument applies to many of the molecules listed in Table IV. That this argument is correct is borne out by the calculations of Sklar [68] for benzene, where, in order to obtain a reasonable value for the position of the first allowed transition, ionic structures had to be taken into account. There exists the anomaly that, while the positions of the absorption bands of molecules listed in Table IV show good agreement with the experimental values, there is little reason to assume that the treatment would lead to agreement in the intensities. The case of *cyclo*octatetraene is hardly a fair test, insofar as a planar configuration was assumed and the effects of strain neglected.

A great deal of theoretical work in recent years has been concerned with the bond lengths in conjugated systems. Thus Pauling *et al.*[69] and

[64] Reference 20.

[65] Reference *b*, Table IV.

[66] *Rev. Mod. Physics*, 1942, **14**, 265.

[67] Reference 24 (*d*).

[68] Reference 19.

[69] L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2705.

W. G. Penney [70] have adapted the valence-bond method, and J. E. Lennard-Jones [71] the molecular orbital method, to deal with such problems. The simple valence-bond treatment assumes, in the first place, that all the bond lengths are the same in a conjugated system, and secondly, that the bond lengths in the excited state of such a system are the same as those in the ground state. Both these limitations have been removed by G. J. Kynch and W. G. Penney,[72] who have taken explicit account of the variation of the quantum-mechanical parameter in calculating the light absorption of butadiene, hexatriene, and benzene. Results calculated on this basis show good agreement with experiment, and, in particular, the high value of the resonance energy of benzene, which is implied by Sklar's treatment, is brought into line with the observed value. Mulliken, however, has criticised this treatment, in particular the identification of the calculated absorption band with the observed.

F. S. Shifrin [73] has examined the valence-bond treatment of the colour of organic compounds, and has pointed out that one of its limitations is the restriction of the calculations to hydrocarbons. He extended the calculations to certain heterocyclic molecules by assuming that a nitrogen atom in a heterocyclic molecule contributes one π-electron, and that the nitrogen atom can be considered as a CH group. On this basis he arrives at the results shown in Table V. The calculated values have been altered from those in the paper referred to, in order to take account of the fact that the values for benzene and pyridine are obtained by Sklar's method, whereas the remainder were obtained by Förster's method. The case of naphthalene is not straightforward, as it seems likely that the band observed at about 3100 A. should be used for the comparison.

TABLE V

	Benzene.	Pyridine.	Naphthalene.	Quinoline.	Anthracene.	Acridine.	Phenazine.
$\lambda_{\text{max.}}$(calc.)	2450	2450	2950	2950	3650	3650	3650
$\lambda_{\text{max.}}$(obs.)	2600	2650	2750	3150	3700	3600	3750

Evidence against the treatment of nitrogen atoms simply as CH groups comes from a study of the gaseous absorption spectra of benzene, pyridine, and pyrimidine. The observed 0–0 transitions are respectively 2600, 2900, and $\sim$ 3100 A., indicating a bathychromic effect upon the replacement of a CH group by a nitrogen atom.[74] Shifrin has also considered the case of pyrrole, indole, and carbazole, pointing out that the NH groups in these compounds possess a lone pair of electrons which may interact with the ring electrons. On this basis, the spectra of the above-mentioned compounds would be expected to resemble benzene, naphthalene, and anthracene respectively.

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[70] *Proc. Roy. Soc.*, 1937, *A*, **158**, 306.

[71] *Ibid.*, p. 280.

[72] *Ibid.*, 1941, *A*, **179**, 214.

[73] *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 27.

[74] A. Maccoll, *J.*, 1946, 670.

The calculation of the intensities of transitions for conjugated systems by the M.O. method has been investigated by R. S. Mulliken.[75] The transitions arise from the transfer of a π-electron from a bonding molecular orbital to a non-bonding one, corresponding in valence-bond nomenclature to the transition from a mainly homopolar ground state to a largely ionic upper state. The calculations are made by the method outlined in Section 4. As the L.C.A.O. method leads to values for $\tilde{\nu}$ in disagreement with experiment, Mulliken calculated a " semi-theoretical " f. This was done by using the experimental value for $\tilde{\nu}$ in equation (4.15). Some of the results obtained are shown in Table VI. The agreement is seen to be reasonably satisfactory, although it must be borne in mind that the values listed under f (calc.) were obtained from the theoretical values by multiplication by an empirical correction factor. In general, the method leads to results which are greater than the experimental values ; this being probably connected with the overemphasis that the L.C.A.O. treatment places on ionic structures.

TABLE VI

f Values Calculated by the M.O. Treatment

	Model.	$\tilde{\nu}_{max.}$(obs.).	f (calc.).	f (obs.).
Ethylene	—	61,000	0·30	—
Butadiene	*trans*	47,700	0·52	0·53
	cis	—	0·43	—
β-Carotene	*trans*	22,000	7·0	2·69
	intermediate	—	4·8	—
Benzene	—	56,000	0·71	—
Diphenyl	—	41,000	0·41	0·41
Stilbene	*trans*	32,000	0·55	0·62
	cis	37,000	0·33	0·39
1 : 4-Diphenylbutadiene	*trans*	30,000	0·85	0·84
1 : 8-Diphenyloctatetraene	*trans*	26,000	1·57	1·42

The antisymmetric molecular orbital method has been employed by Sklar [76] to investigate the intensities of the long wave-length transitions in substituted benzenes.

The study of the directing power of substituents in a benzene ring as regards further substitution has led to two mechanisms whereby the symmetrical charge distribution of benzene may be altered in an isolated molecule. The first is known as the *inductive* effect and arises from the electrostatic influence of the substituent upon the π-electrons of the benzene ring ; the second is the *mesomeric* effect which is brought into play by a migration of charge from the substituent into the ring or *vice versa*.[77] Groups such as Cl, OH, NH_2, which possess a lone pair of electrons, are capable of transferring an electron to the ring ; whereas groups such as NO_2, CHO, CO_2H, which are electron deficient, can accept an electron from the ring. It is found experimentally that a substituent which has a strong directing power also exerts a marked intensifying effect on the forbidden transition of benzene

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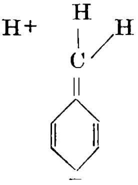
[75] Reference 24 (*d*).

[76] *J. Chem. Physics*, 1939, **7**, 984 ; 1942, **10**, 135.

[77] C. K. Ingold, *Chem. Reviews*, 1934, **15**, 225.

at 2600 A. Whereas the NH_2 group in aniline possesses a lone pair of electrons capable of migration into the ring, this possibility no longer exists for the anilinium ion. This means that the only effect left to the ion is the inductive effect. Experimentally, the absorption curves of the anilinium ion and benzene are almost superimposable, whereas in aniline the shape of the curve is markedly altered and the intensity of the long wave-length band greatly increased. On these grounds Sklar assumes that migration effects will be mainly responsible for intensity changes.



(LIV.)

The case of toluene is of interest insofar as the migrating electrons must be conceived as coming from a C–H bond. This effect is known as *hyperconjugation*.[78] On the valence-bond view the effect can be represented in terms of structures such as (LIV). That this effect is negligible for the anilinium ion is explained on the basis of the increased ionisation potential of $\overset{+}{N}H_3$.

The transition moment was calculated in terms of a parameter which determined the extent of migration of a radical electron into the benzene ring. The parameter was then determined by minimising the energy. The results obtained are shown in Table VII, in which the *f* values are uncorrected for the solvent effect. The value for fluorobenzene is estimated from the work of S. H. Wolleman.[79] On the whole, the agreement is good, considering the uncertainty in the solvent correction. It follows from the treatment that a radical will produce a large intensification effect if it has a low ionisation potential, a lone pair of electrons, and not too great a ring–radical distance. Sklar has also dealt with polysubstituted benzene derivatives.

TABLE VII

Migration Moments of Monosubstituted Benzenes

	f (theor.).	*f* (obs.).
Toluene	0·0005	0·0013
Aniline	0·015	0·0246
Phenol	0·006	0·0197
Fluorobenzene	0·0003	∼ 0·001

The colour of organic dyes has been investigated by Th. Förster,[80] along the lines suggested by Pauling.[81] Using the V.B. method, he considered two idealised systems (LV) and (LVI), representing the cyanine and triphenylmethyl type dyes respectively. The A groups represent auxochromes. In both, calculations show that an increase in chain length or an increase in the strength of the auxochrome groups will cause a bathychromic shift, such as is found experimentally. System (LVI) is related to (L) which G. N. Lewis took as the basis of his classification of dyes. The empirical relationships

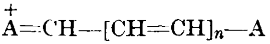
[78] Reference 66.

[79] Reference 41.

[80] *Z. physikal. Chem.*, 1940, *B*, **47**, 245; *B*, **48**, 12.

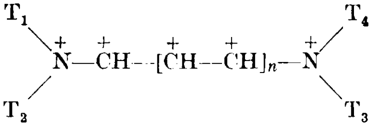
[81] Reference 21.

observed by this author receive a quantum-mechanical foundation on the basis of Förster's work.

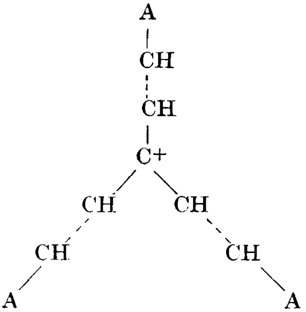


$\overset{+}{A}=CH-[CH=CH]_n-A$

(LV.)



(LVII.)



(LVI.)

K. F. Herzfeld and A. L. Sklar,[82] independently of Förster, have examined the cyanine dyes in greater detail, by both the V.B. and the L.C.A.O. method. The structures used in the V.B. treatment have already been discussed in Section 5. There will be $(2n + 3)$ of them for the system represented by (XLIV), corresponding to the $(2n + 3)$ atoms on which the positive charge may be placed. The secular equation is of degree $(2n + 3)$, and the difference between the two lowest roots is the energy corresponding with the long wave-length transition of the molecule. On the L.C.A.O. view, the problem is that of finding the energy of an electron in the field of the framework (LVII) and of the $(2n + 2)$ other electrons. The secular equation gives the energies of $(2n + 3)$ molecular orbitals, and the $(2n + 2)$ electrons are fed into the $(n + 1)$ molecular orbitals of lowest energy. The long wave-length transition then corresponds with the removal of an electron from the highest filled to the lowest unfilled molecular orbital. The secular equations obtained by these two methods are formally similar, although the various terms occurring in them have a different interpretation in the two cases. On carrying out the calculations, which involve a number of approximations, it is found that both treatments predict that the absorption wave-lengths of the members of the series will go to infinity as n increases. However, only the L.C.A.O. method gives a linear relationship between $\lambda_{\text{max.}}$ and n, as is observed experimentally. For the unsymmetrical ions, the V.B. method is superior, predicting the convergence of the $\lambda_{\text{max.}}$ values as n increases.

The present state of affairs in the field of colour and constitution may now be examined. Dealing first with the Lewis and Calvin theory, it is found that the simple concept of the two types of linear oscillators is not sufficient to explain the behaviour of certain series of compounds. Thus, with the *p*-polyphenyls [83] the convergence is too rapid to give a linear plot of λ^2 against n. This behaviour may be accounted for *a postiori*, but such a state of affairs is not very satisfactory. It must be pointed out, however,

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[82] *Rev. Mod. Physics*, 1942, **14**, 294 ; *J. Chem. Physics*, 1942, **10**, 508, 521.

[83] Reference 58.

that the authors regarded the two types of oscillators as limiting cases, but much of the attractiveness of the quantitative treatment is lost when subsidiary assumptions have to be made. Perhaps the greatest achievement of the theory is the broad correlation it has made possible, yielding a panoramic view of the field, rather than a " close-up."

The same conclusions can be drawn from an examination of the results of the qualitative application of the theory of resonance. Here again a broad correlation has been achieved, not only in the field of colour, but in the many other aspects of chemistry that can be accounted for on the resonance concept. The theory has afforded a correlation on the grand scale of the apparently divergent hypotheses introduced by the early works. More specifically, a chromogen may be thought of as a resonating system, the absorption of which does not extend into the visible. Auxochromes and anti-auxochromes are groups capable of extending the resonance system of the chromogen in such a way that the absorption moves into the visible. The importance of the quinonoid structure in producing colour, and in particular the oscillation of the quinonoid condition become intelligible with the aid of resonance concepts. The limitations of the early theories were largely due to their derivation in terms of specific systems ; the power of the resonance treatment lies in its general applicability.

Finally, there remain the quantal calculations. Here again the position leaves much to be desired. On the one hand, the V.B. treatment has been very successful in predicting the position of the absorption bands for a number of compounds, but at present there exists no guarantee that the calculated absorption bands refer to those actually observed. Only by an investigation of the intensities of the transitions can this point be settled, and such an investigation would have to take account of ionic structures, which greatly complicate the calculations. Very little evidence can be adduced from the literature as to the importance of ionic structures. On the other hand, the L.C.A.O. method has had reasonable success in computing the intensities of absorption bands, but only with the aid of the observed wave-length of absorption. It is still to be shown that the bands for which the intensities are calculated are the observed bands. In both these methods the approximations made are rather disconcerting, although some justification may be obtained from the success of similar approximations in the treatment of the ground states of molecules. The most satisfying treatment is with the use of antisymmetrical molecular orbitals, but here the labour involved restricts, at present, the treatment to relatively simple molecules. Many loose ends are apparent in the quantal treatment, and only the passage of time will show how successfully they may be tied.

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