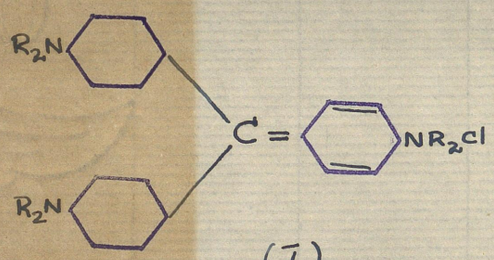
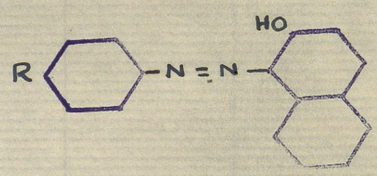
N=N and CO groups. He regarded auxochromes as weakly salt-forming groups, e.g. NH_2, NHR, NR_2 and OH; and strongly salt-forming groups, whether they are acidic or basic (e.g. SO_3H, COOH, NR_4), were considered to have no auxochromic properties, and in fact to diminish the colour. A compound containing a chromophore or an auxochrome may be coloured, but unless both are present, it will not function as a dye towards a textile fibre (cf. benzene, trinitrobenzene and picric acid). Witt called a chromophore-containing compound a chromogen. The colour of a chromogen, as elaborated by later users of Witt's theory, depends on the nature, number and position of the auxochromes. The influence of the first factor is shown by the colours of



(I)



(II)

Pararosaniline (red), Crystal Violet and Aniline Blue (I; NR_2 = NH_2, NMe_2 or NHPh). Increasing the number of amino groups from one to two to three (4, ~~2~~2:4, and 2:4:2[1]) changes the yellow colour of aminoazobenzene to orange and red-brown. Watson[1] has tabulated the colours of the hydroxyanthraquinones and their salts in illustration of the fact that chromogens possessing the same number of a given auxochrome can be differently coloured*. Further, the dyeing properties of a chromogen containing an auxochrome may be completely altered by the introduction of other groups; thus benzeneazo-β-naphthol (II) is an insoluble azo colour produced on the fibre, or an acid colour, or a basic colour according as R is absent, is SO_3Na or NMe_2. Liebermann and Kostanecki (1885) distinguished between colour and dyeing properties when they stated their "rule" that at least one hydroxyl ortho to a chromophoric group is necessary for giving a substance mordant dyeing properties.

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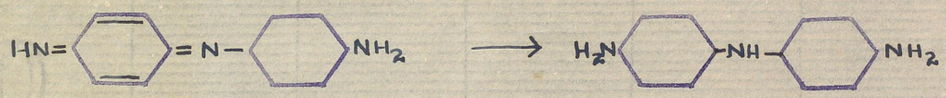
[1] loc. cit.

* if they are differently orientated in the nucleus.

The quinonoid theory.- In 1888 H. E. Armstrong postulated that dyes are derivatives of quinones in which one or both the oxygen atoms may be replaced by other atoms or groups, and the colour of dyes is due to the quinonoid structure. Although the quinonoid theory consisted essentially in a new and closer definition of Witt's chromophore, it serves to explain in a simple and rational manner some of the important empirical facts of dyestuff chemistry. The majority of coloured organic compounds and dyes in particular can be represented in quinonoid forms. Many dyes are sensitive to reduction, the reaction being similar to the conversion of yellow benzoquinone to colourless hydroquinone; such dyes undergo reduction to their leuco-compounds, e.g. the blue indamine (III) to the colourless diaminodiphenylamine



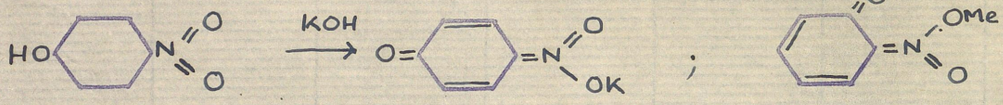
(III) (IV)

(IV). The quinonoid hypothesis leads to a distinction to be anticipated between o- and p-quinonoid types of dyes. The leuco-compounds of some groups of dyes (e.g. azines, acridines) are readil reoxidised, even by atmospheric oxygen, like catechol in alkaline solution. The leuco-compounds of certain other dyes (e.g. triphenylmethane derivatives, indamines, indophenols) require more powerful oxidising agents (dichromate, persulphate, etc.) for regeneration of the original quinonoid dye, thus simulating the behaviour of hydroquinone and p-benzoquinone. Such behaviour on reduction and reoxidation is indeed one of the fundamental reactions on which schemes for the identification of dyes are based.

Apart from its obvious limitation that it makes no attempt to explain why a quinone should be coloured, the quinonoid theory has well known exceptions and difficulties: the colour of azobenzene, the behaviour of anthraquinone derivatives on reduction and reoxidation, the tautomerisation of some dyes between o- and p-quinonoid forms, etc.

Hantzsch (1907) explained the deepening of colour on the very conversion of o- or p-nitrophenol into its alkali salt as being

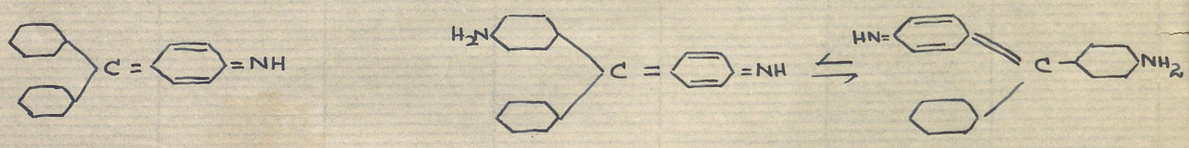
connected with the structural change of the phenol (V) to the quinonoid "aci "-form (VI). In confirmation of his view regarding the tautomerisation of the nitrophenols, Hantzsch was able to



(V) (VI) (VII)

isolate coloured (red) alkyl ethers corresponding to the aci-form (e.g. VII) in addition to the colourless ethers, the former being unstable and readily isomerising to the colourless form. Hantzsch took the view that colour is an additive property, and that since the simultaneous presence of the ~~nitro~~ NO_2 and ONa groups produce visible colour, which neither produces separately, there must be an interaction between the two groups, resulting in a new structure for the molecule. He therefore regarded change of colour as evidence of change of structure, and he termed the phenomenon "chromo-isomerism". In the case of the diphenylviolurates for instance he assigned specific bands in the absorption spectra to the nitroso and isonitroso forms[1].

The applications of the quinonoid theory might be illustrated in the case of the triphenylmethane dyes, which will be considered again in terms of resonance. Baeyer[2] explained the conversion of the colourless fuchsonimine ⟿ to the deeply coloured Döbner's Violet ⟿ (by the introduction of an amino-group) as being due to the oscillation of the quinonoid



(Colourless fuchsonimine) (Döbner's Violet)

condition between the two benzene rings.

While triphenylmethane (VIII), triaminotriphenylmethane (IX) and triaminotriphenylcarbinol (X) are colourless, a red colour

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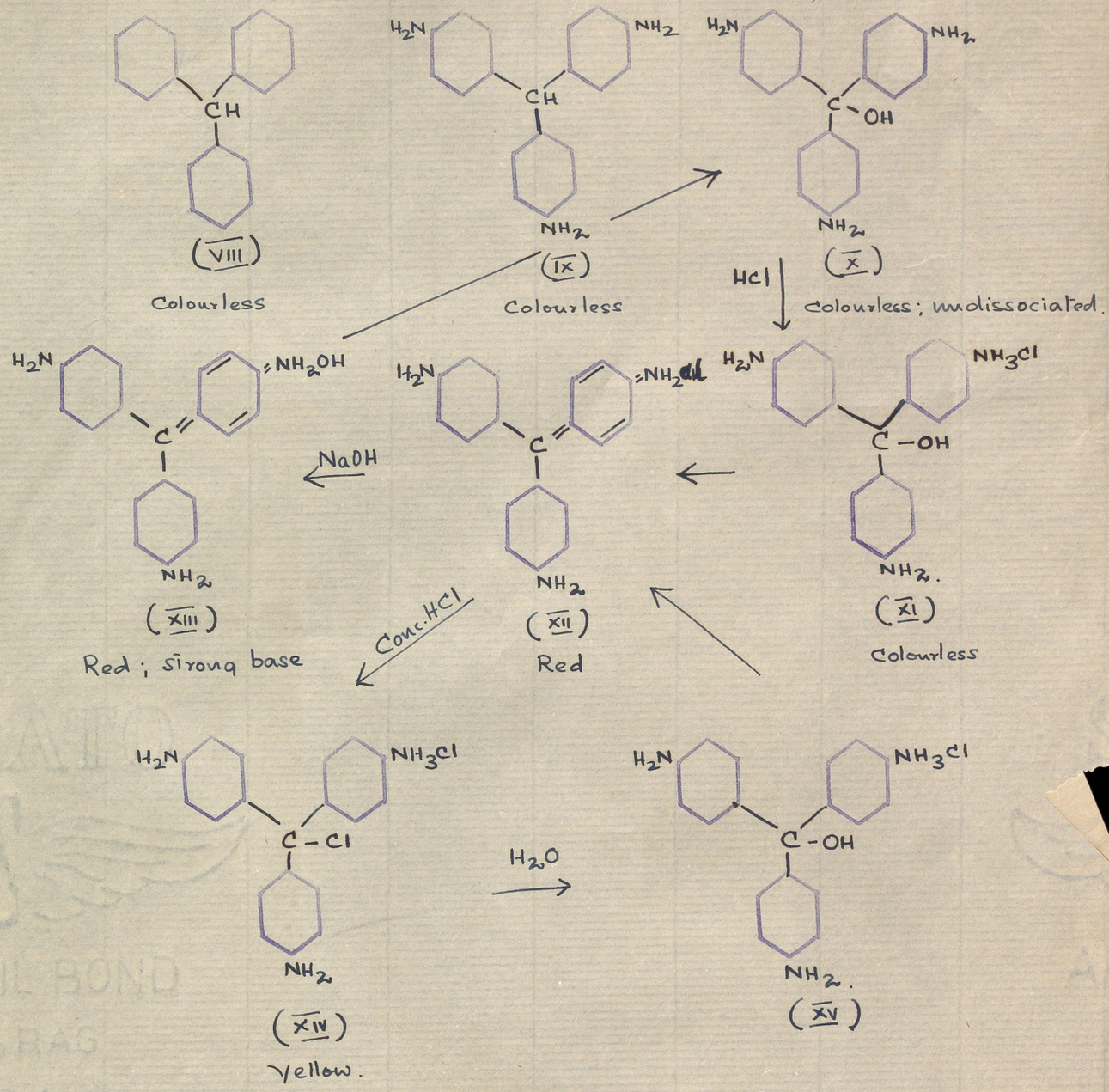
[1] Ber., 43, 666(1910).

[2] Ann., 354, 152(1907).

develops on the addition of dilute acid, the coloured quinonoid salt (XII) being formed via the colourless salt (XI). When the



red acid solution is neutralised with caustic soda, an amorphous red precipitate (XIII) is obtained, which gradually (and more rapidly on washing) changes to the colourless crystalline compound (X) with a fall in electrical conductivity. On the addition of concentrated hydrochloric acid to (XII), the colour weakens to a pale yellow on account of the formation of (XIV); the colour is restored on dilution, due to the regeneration of (XII) via (XV). Other members of the rosaniline series undergo similar colour changes, and the colour changes of phenolphthalein were likewise explained by the quinonoid theory.

Soon after Witt's theory (1879) Nietzki's rule stated that the colour of a dye could be deepened (from yellow through red to green) by adding groups to increase its molecular weight. Among the older theories, which have on the whole proved of real value as guides in the discovery of new dyes, and which could be described as inadequate and lacking a physical basis, rather than being erroneous, Nietzki's alone has proved to be completely unstable. It is the nature and not the weight of an added group on which the deepening of colour depends. Aminoazobenzene sulphonic acid (m.w. 277) and Benzo Fast Yellow (m.w. 1160) (XVIII) are both yellow; and yellow dyes of more or less indefinitely high molecular weight could be synthesised. In the homologues series $CH_3(CH_2)_a\text{-}X\text{-}(CH_2)_bCH_3$, in which X is a chromophoric or absorbing group, the depth of the colour is independent of the numbers a and b.

Hewitt and Mitchell[1] made the important observation, on the basis of their work on the absorption spectra of azo dyes, that the "chief oscillation frequency is less, and consequently the colour is deeper, the longer the conjugate chain". Sircar submitted "Hewitt's rule" to extensive experimental tests, and he came to the conclusion that the depth of colour is proportional to the length of the conjugate chain in the part of the molecule containing the auxochrome.

Watson[2] formulated his rule that "dyes which are quinonoid in all possible tautomeric forms have a deep colour, no matter how simple their structure or how small their molecular weight". It was later suggested by Watson and Meek[3] that the colour is deeper the longer the conjugate chain reversed in the tautomeric change. "A pulse passes in one direction along the conjugate

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[1] J. Chem. Soc., 91, 1251 (1907).

[2] Ibid., 105, 759(1914).

[3] Ibid., 107, 1567 (1915).

[4] Du Pont, U.S.P., 2001,737-8

A The dye (XVI)[4], which has a complex composition and a molecular weight of 769·5, is only yellow in colour.

chain... and back again ... this pulse is the vibration which causes the colour of dyes". In ionised dyes, "there is no vibration of the atoms of the molecule, but only rhythmic arrangement of the strains in the molecule. Even when the substance is not ionised, the only atom that must necessarily move is the hydrogen atom concerned in the tautomerism."

Dilthey and Wizinger's theories.- Dilthey and Wizinger[1] define chromophores as coordinatively unsaturated atoms, as distinct from Witt's unsaturated groups; the latter owe their chromophoric properties to the coordinatively unsaturated atoms which they contain. There is a marked increase in light absorption when there is a transition from a coordinatively unsaturated atom to the ionic state, and the most powerful absorbers of light are "ionoid" in character. The hypothesis that a strongly coloured substance must be an ion or an inner salt is unsupported by many facts. Neutral substances such as p-nitroaniline and 4-nitro-4'-aminostilbene, which are yellow to orange-red, lose their colour or become a pale yellow upon the addition of hydrogen ion. PTO */ are coloured to about the same depth and intensity by the addition of neutral substances such as boron trichloride or stannic chloride instead of hydrogen ion[2].

The Stieglitz theory.- The contribution of Stieglitz[3] to colour theory is a bridge between the older theories and the resonance concept of colour. Since many dyes lose their colour both by reduction and by oxidation, he considered them as being in an intermediate state of oxidation. They contained both oxidising and reducing groups, identified respectively with chromophores and auxochromes. The result of the presence of the two in the molecule was intromolecular electron transfer.

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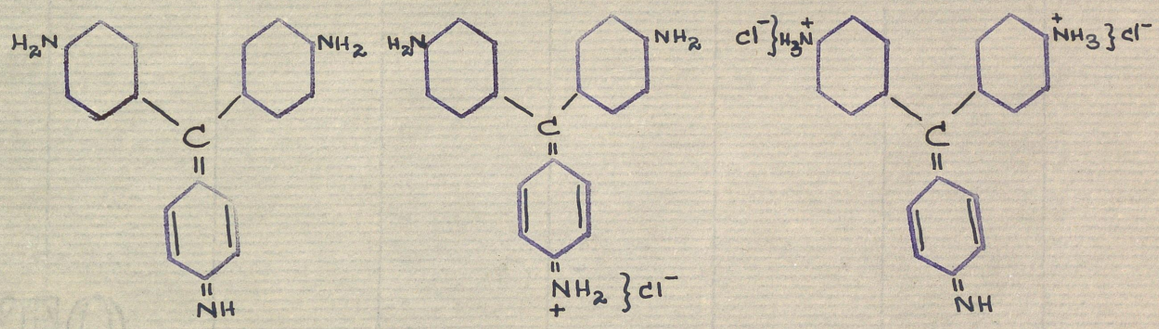
[1] Ber., 53, 261 (1920); Organische Farbstoffe, Ferd. Dummless Verlag Berlin w. Bonn, 1933.

[2] Lewis and Calvin, Chem. Reviews, 25, 304 (1939).

[3] Proc. Nat. Acad. Sci., 9, 303 (1923); J. Franklin Inst., 200, 35 (1925).

* In the phenomenon of halochromism, the neutral organic compounds, which become brilliantly coloured on the addition of hydrogen ion,

Valance electrons were therefore freed from the ordinary atomic restraints, and the absorption bands were shifted from the ultraviolet to lower frequencies, producing visible colour. Colour changes occurring on the addition of acid or alkali, as in the case of the triphenylmethane dyes, were explained by Stieglitz as dependent on the salt formation increasing or decreasing the chromophoric or auxochromic character of the groups concerned. Salt formation of an auxochrome hydroxyl group (e.g. in an indophenol or phenolphthalein) deepens the colour. In the basic dyes such as the rosaniline series, when salt formation occurs by the addition of acid to (XVII) in the oxidising (quinonoid) component of the dye molecule, the colour deepens (XVIII); but when salt formation occurs with an auxochromic



Yellow (XVII). Red (XVIII). Yellow (XIX).

amino group and destroys its reducing power, the depth of the colour is diminished (XIX).

Auxochromes and resonance.- As early as 1914, E. Q. Adams and Rosenstein[1] had suggested that the colour of Döbner's Violet is due to the oscillation of an electron. Bury (1935)[2] applied this idea to a series of dyes representing them in equivalent resonance structures and he stated that "the intense absorption of light that characterises dyes is due to an intimate association of a chromophore and of resonance in the molecule. In the basic dyes the resonance is in the cation, and among the examples quoted by Bury, two are the ions of Döbner's Violet and Acridine

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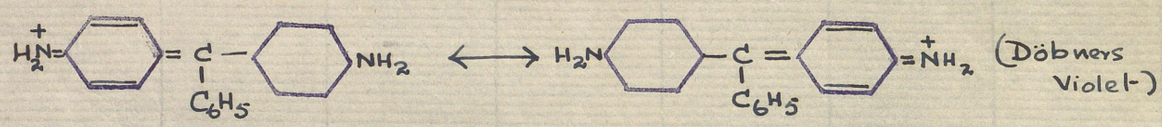
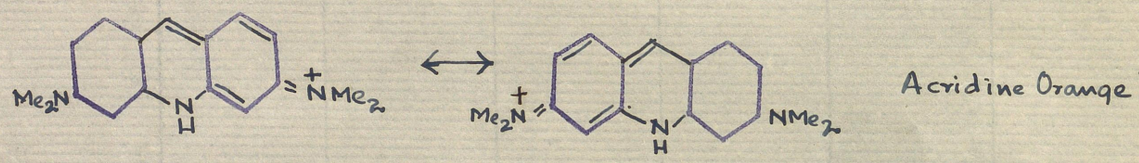
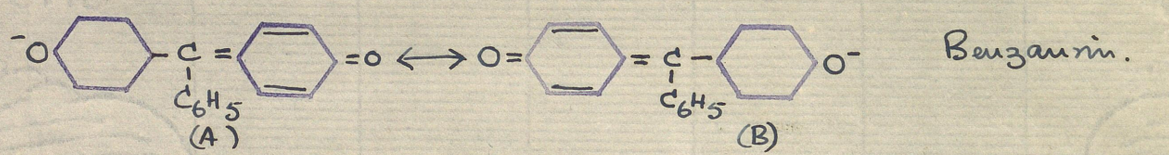
[1] J. Am. Chem. Soc., 36, 1472(1914); see also Baeyer, Ann., 354, 152 (1907).

[2] Ibid., 57, 2115 (1935).

Orange. ~~(I) and (II).~~ In acid dyes such as benzaurin (~~III~~ II) the ~~re~~ resonance is in the anion. Bury explained that the function of







an auxochrome is to introduce the possibility of resonance.

The problem of the colour of dyes is of the utmost complexity, and a true theory of colour has to take into account both the qualitative and quantitative aspects of the colour of all the known types of coloured organic compounds. Acid and basic colours represent two somewhat special types, and even from the purely qualitative aspect, they are apt to lead to an over-simplified and erroneous interpretation of the general relation between colour and structure. Bury for instance has referred to gallacetophenone as a vat dye, and has attempted to ascribe similar structures to this substance and to the anthraquinonoid vat dye, indanthrone. The vast scope of the problem is fully recognised in recent approach to a theory of colour, in which progressive variations of structure ~~of~~ and colour are being carefully studied, commencing with attempts to make quantum mechanical calculations of the absorption of light in the case of simple molecules and conjugated systems and to correlate them with the observed spectra.

Interpretation of absorption spectra.- Attempts to correlate the absorption spectrum of an organic compound, especially a complex dye molecule, with its chemical constitution and its resonance states must be made with caution on account of a variety

of complicating factors. The purity of the compound has to be ensured, and this is by no means an easy matter in dealing with a dye; with a water-soluble azo dye for instance it is a long and laborious process to obtain it in chemically pure form. Having isolated a dye as an analytically pure substance, it may still consist of a mixture of molecular species: cis-trans isomers (e.g. in the case of azo compounds and stilbenes); azophenol-quinone-hydrazone tautomers in the case of o- and p-hydroxyazo compounds; keto-enol, amide-iminoalcohol, and lactam-lactim tautomers; monomers and polymers; etc. The absorption spectra of many dyes are affected by acid, basic and amphoteric addition. Examples of these are quoted in discussing the constitution of the relevant classes of dyes, and the influence of such factors on light absorption is indicated later in this Chapter.

Absorption spectra having usually to be observed in solution, further complications arise. Carefully purified solvents are naturally used, and it is desirable to choose a solvent which has uniform transmission throughout the region under examination and does not interact in any way with the solute. The influence of solvents on the absorption bands of a simple substance is illustrated in Fig. 1. (after Klingstedt)[1]. Solvates are eliminated by the use of a saturated hydrocarbon solvent, e.g. n-hexane, but more often than not, dyes are insoluble in paraffin solvents. The two-electron covalent bond is not activated by light

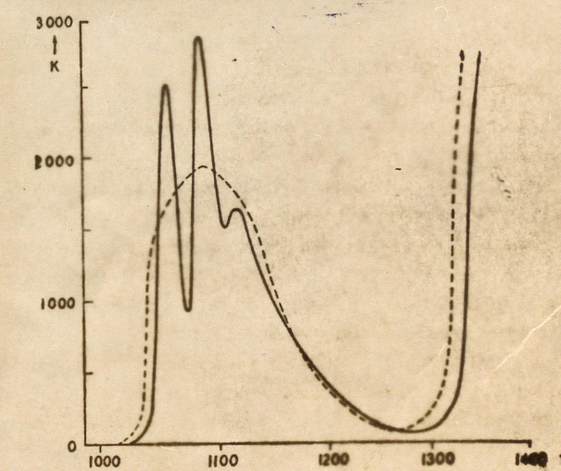


FIG. 1. Influence of solvents on absorption bands. Absorption spectra of phenol in alcohol (- - - -) and in hexane (———). (Klingstedt [C117].)

[1] Compt. rend., 176, 1550 (1923).

of wavelength λ_{max} between 200-1000 mμ, and solvents consisting of saturated molecules such as water, ~~the paraffin hydrocarbons~~, ethanol, cellosolve and dioxane can usually be employed. Using chlorinated aromatic hydrocarbons, nitrobenzene, concentrated sulphuric acid, etc., as solvents, the complications due to the spectral characteristics of the solvents themselves, hydrogen bonding between solute and solvent, oxonium salt formation, and other kinds of interaction leading to new molecular species with absorption spectra different from those of the molecule which we are seeking to investigate, have to be carefully borne in mind. In special cases, such as the triphenylmethane dye ($\overline{\times\times}$) in which the charge on the ion is distributed more on one end of the molecule

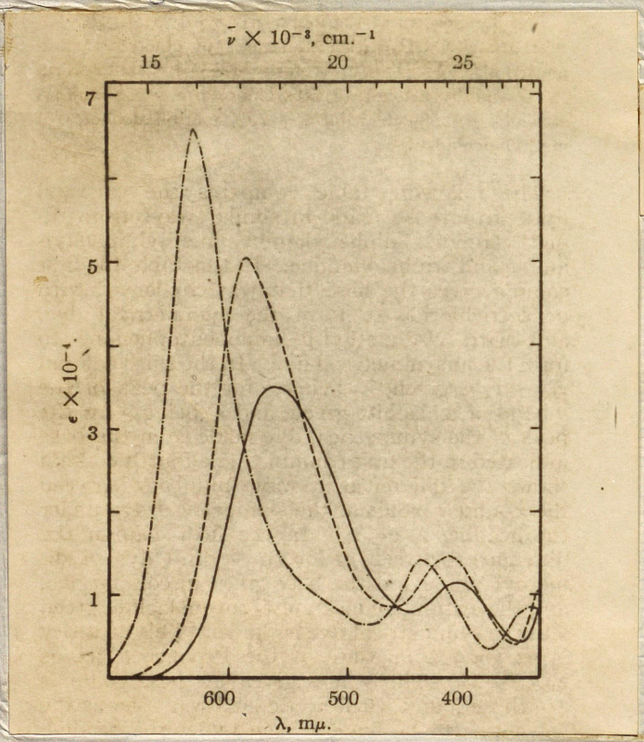
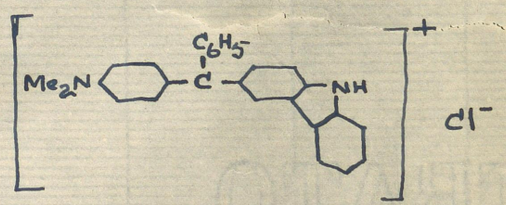


Fig. 2.—Spectra of the monocarbazyl dye $[(C_{12}H_8N)C(C_6H_5)(C_6H_4N(CH_3)_2)]^+$ in various solvents: ——— in water; - - - in methyl alcohol; —·—·— in chloroform.



($\overline{\times\times}$)

than the other, the dielectric properties of the solvents are can have a profound influence on the spectra (cf. Fig. 2)[1]. Methy Blue exists in considerable amount as the dimeric ion in a solve of high dielectric constant such as water; in alcohol the dimer band of Methylene Blue becomes pronounced at low temperatures; and in solvents of low dielectric constant molecular dimers an polymers are formed, the blue colour changing to pink.[2] The

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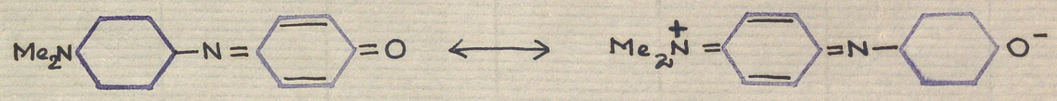
[1] Branch, Tolbert and Lowe, J. Am. Chem. Soc., 67, 1693 (1945).

[2] Lewis et al., Ibid., 65, 1150(1943).

absorption of an unionised dye is strongly affected by the solvent if a polar structure, with which the colour is associated as explained later, is stabilised by the solvent. Thus Phenol Blue gives solutions which vary in colour from reddish violet in cyclo-



(A) Phenol Blue. (B)

hexane to deep blue in water. The values of λmax vary from 552 mμ in cyclohexane to 582 mμ in acetone, 612 mμ in methanol, and 668 mu in water. The bathochromic shift is in the order of increasing dielectric constants of the solvents (2, 21, 31 and 80 approximately). Brooker and Sprague[1] have suggested that the resonance structure B, associated with the deep colour of Phenol Blue, is relatively unstable in the absence of solvent effects, but it is increasingly stabilised by the dipole orientation of the surrounding solvent molecules as the polarity of the solvent is increased.

Using a substance in a single molar form and a non-interacting, non-absorbing solvent, or taking into account the existence of more than one molecular species, separate electronic bands can usually be observed in the absorption spectrum and in the visible and ultraviolet regions, and the objective is to correlate the maxima with transitions between electronic states. Broad electronic bands sometimes show a fine structure, which may be accentuated by working at a very low temperature (cf. Fig. 2). Each electronic state can be associated with many vibrational and rotational states, and the fine structure has been attributed to vibrational activations. The loss of fine structure (i.e. the breadth of a band even when it has been resolved into narrow bands) has been explained as being due to several reasons. There is a "natural width" of the band connected with the uncertainty principle of Heisenberg and in indeterminacy of the energy of the initial excited state. In a complex

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[1] J. Am. Chem. Soc., 63, 3214(1941).

molecule the energy of the electronic activation may be dissipated in the form of many vibrational activations of much smaller energy. This dissipation and the consequent destruction of structure in the absorption bands ~~by loss~~ are facilitated by loading a molecule with saturated groups, halogen atoms, the nitro group and other groups capable of vibrations of low energy. Lewis and Calvin have shown the intimate relationship between the fluorescence of organic compounds and the appearance of fine structure in their absorption bands; the prevention of fluorescence and the disappearance of structure are both to be ascribed to a rapid transfer of the energy of an electronic oscillation to atomic vibrations.

RESONANCE AND THE ABSORPTION SPECTRA OF MOLECULES

Molecules, like atoms, can exist in different electronic states, and spectra arise from transitions between states; but since molecules contain two or more nuclei, they also possess quantised energies of rotation and vibration. Of the two general types of spectra, emission and absorption spectra, the colour of organic compounds is concerned with absorption spectra, in which the substances absorb light and are raised to states of higher energy. The frequency (ν) of the light absorbed is related to the energies (ϵ_1 and ϵ_2) of the molecule in the initial and final states by the Bohr equation, $\epsilon_2 - \epsilon_1 = h\nu$, in which h is Planck's constant. In considering the problem of the colour of dyes, the primary interest is in absorption in the visible region, although ultraviolet absorption is important for studying the effect of constitutive factors which shift the absorption of the organic molecules from the ultraviolet into the visible part of the spectrum. The energy changes which correspond approximately to absorption at 400 mu at the blue end of the visible spectrum and to absorption at 800 mu at the red end are 71 and 35.5 kcal per mole. Among the three types of absorption spectra corresponding to changes in the rotational, vibrational and electronic states, it is in the transitions between electronic states that the energy differences

are large enough for the absorption of light in the ultraviolet and visible region. In spite of our lack of knowledge of the energy levels of complex molecules such as coloured organic compounds, and of the impossibility of submitting dye molecules to rigid quantum-mechanical treatment, there has been some success in calculating the spectra of a few conjugated systems characteristics of dye molecules by a combination of the inductive methods of organic chemistry with quantum mechanical principles.

The equations of wave mechanics predict "selection rules" which define the "permitted" and "forbidden" transitions between levels. A state can "combine" with another state only if the quantum numbers defining each state bear certain relationships. In the wave-mechanical treatment of electrons as a complex of "standing waves", the quantum states are described by means of the wave functions, and the property of "combination" between states depends on symmetry considerations of the wave functions. "Forbidden" transitions may however become partly "permitted", with the occurrence of organic spectra, if the symmetry properties of levels are disturbed by collisions, applied electrical fields, etc.

With the exception of the hydrogen molecule, consisting of two nuclei and two electrons, the problem cannot be solved directly and precisely, and methods of approximation have to be used. Two methods of treatment[1] have been adopted with reference to organic and especially aromatic molecules. The first is based on the Heitler-London treatment of the hydrogen molecule in which the energy of the system is considered when two hydrogen atoms are moved closer and closer to each other from an infinite distance. When they

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[1] For a comparison of these methods and for a full discussion of molecular spectra, see Wheland, J. Chem. Physics, 2, 474(1934); Wheland, The theory of resonance, Wiley, N.Y., 1944; Branch and Calvin, The theory of organic chemistry, Prentice-Hall, New York, 1941; Pauling, The nature of the chemical bond, Cornell Univ. Press, 1940; etc.; Bowen, Annual Reports, Chem. Soc., 40, 12(1943); Price, ibid., 36, 47(1939); for a recent review on Colour and Constitution with special reference to the quantum-mechanical aspects, see Maccoll, Quarterly Reviews, 1, 16(1947); see also Thompson, "Molecular spectra and thermodynamics", Annual Reports, Chem. Soc., 38, 46(1942); Morton, "Absorption Spectra", Ibid., 7.

are brought together, the wave functions combine through resonance, and this coupling by mutual interaction of the two electrons, each of which was originally associated with one proton, cannot be expressed as the sum of the two functions. The stability of the binding is increased, and the energy (E) of the molecule is lower than the energy (E_o) associated with the electrons moving round their respective nuclei, the difference (E_o-E) being the "resonance energy". A similar treatment is applicable to the two-electron or covalent bond in general, and hence its importance in organic chemistry.

In the second or molecular-orbital (or LCAO - linear combination of atomic orbitals) method, due to Hund, Mulliken and Huckel, the molecule is constructed mathematically by locating the nuclei (and the electronic shells not involved in the electronic transitions which give rise to the spectra) at stated distances from each other, and then adding the outer shell electrons*. The benzene molecule for instance is considered with the nuclei of the six carbon atoms arranged as a regular hexagon and the electron sextet as a shell round this core; the symmetries and energies of the states of the six electrons are then calculated by wave-mechanics. The two treatments agree in their broad results, and the organic chemist finds the resonance treatment more convenient for his purposes.

Starting with the result of the Heitler-London treatment that chemical covalency is a shared pair of electrons with opposed spins, and that the strength of the covalent linkage is due to quantum-mechanical resonance between two structures, the concept of resonance in its applications to organic chemistry has been developed by Pauling and his school, and has largely confirmed and extended the electronic interpretations of Ingold, Robinson, Arndt and others. If it is possible to assign to a molecule two or more reasonable electronic structures, and if certain other conditions are satisfied, the normal state of the molecule cannot be represented

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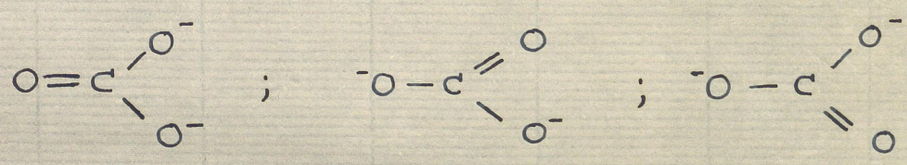
* For a review of the representation of simple molecules by molecular orbitals, see Coulson, Quarterly Reviews, 1, 144(1947).

by any one of the structures alone, but is compounded of all the structures. The molecule is a "resonance hybrid" of the various structures, and is more stable (i.e. has lower energy) than any of the individual structures. The energy stabilising the molecule is the "resonance energy". The main conditions for resonance are that the structures should correspond to the same, or very nearly the same, relative positions of all the atomic nuclei and to the same number of unpaired electrons. The major contributions to the resonance are made by structures of approximately the same stability; structures of lower stability (i.e. higher energy) make correspondingly minor contributions, although these might be of importance, as explained later, from special points of view such as colour and chemical reactivity. The "reasonable" character of a paper structure may be judged in terms of relative stability, which for practical purposes may be roughly computed on the basis of such principles as the following: (1) The hydrogen atom is limited to one covalent bond, except in the case of the "hydrogen bond" which serves to bridge two electronegative atoms in the same or different molecules. The hydrogen bond is important in the chemistry of dyes, especially the mordant dyes, and in the affinity of dyes for fibres, but the nature of the bond is not yet fully understood; according to Rodebush[1], it consists of a covalent linkage with one atom and an ionic linkage with a second donor atom. (2) The octet rule: carbon, nitrogen, oxygen and other atoms in the first row of the periodic table are limited to four covalent bonds; structures in which more than eight valence electrons are assigned to one of these atoms can be neglected, and structures in which an atom has a deficiency in the octet are less stable than the structures in which

[1] The Hydrogen Bond, p. 145 in Advances in nuclear chemistry and theoretical organic chemistry, Interscience Publishers, New York, 1945.

all the eight electrons have been accounted for as bonds or as unshared pairs of electrons. (3) Structures with the largest number of bonds are usually the most stable. (4) As between structures with the same number of bonds, structures in which there are "formal" charges on atoms are relatively unstable, unless the atoms concerned are sufficiently electropositive or electronegative to be capable of forming an ionic bond. The formal charge $F = [n - b - u]$, in which n = the number of valency electrons, b the number of bonds and u the number of unshared electrons. (5) As between two structures in which a negative charge is placed on a more electronegative or less electronegative atom, the former will be more stable.

Examples of resonance structures.- The carbonate ion is a resonance hybrid of three equivalent structures, and x-ray analysis[1] of crystalline carbonates has shown that all the three oxygen atoms are equidistant from the carbon atom and from each other,



and lie in a plane with the carbon atom, which is at the centre of an equilateral triangle. The x-ray data also establish the important fact that in this symmetrical system each of the three carbon-oxygen bonds is of the same length (1.30 A), and shorter than the average of one double bond and two single bonds between carbon and oxygen. In a nonresonating system the interatomic distance in a C-O bond is 1.43A, and in a C=O bond 1.28A. A shortening of bond distances is a characteristic consequence of resonance.

From a study of the spectra of simple molecules the actual electronic distribution may be approximately estimated, and Mulliken has shown that the electronic state of the carbon dioxide molecule is about half way between the homopolar structure

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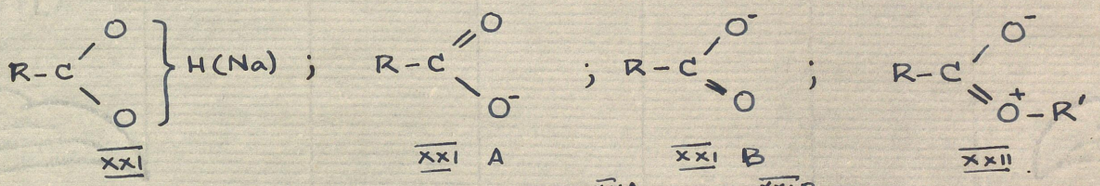
[1] Elliott, J. Am. Chem. Soc., 59, 1380 (1937).

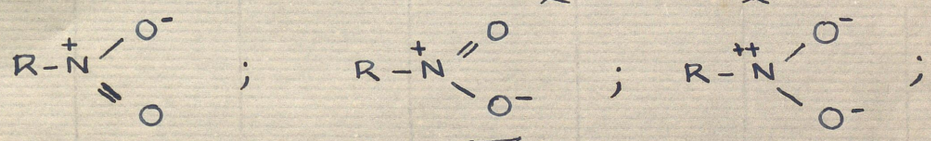
O=C=O and the ionic structure $\overset{-}{O}-\overset{++}{C}-\overset{-}{O}$.

The marked difference in properties between a carboxylic acid and an ester, for instance towards the Grignard reagent, is not obvious from the classical formulation $R-\underset{\underset{O}{\|}}{C}-OR^1$, in which R^1 = hydrogen or an alkyl group. Hantzsch observed that esters absorbed more strongly in the ultraviolet than acids and salts, and since absorption of light indicated unsaturation, he concluded that esters were true carbonyl compounds, while acids and salts could be represented as (XXI). The carboxyl ion is now regarded as



XXI ; XXI A ; XXI B ; XXII.

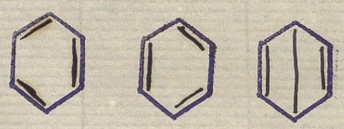
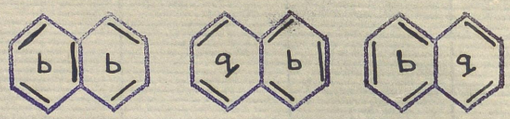
a resonance hybrid of the structures (XXI A) and (XXI B), in which the carbon atom is bound to each of the oxygen atoms by a hybrid shortened link. On account of the stability associated with the resonance, a carboxylic acid displays diminished reactivity in reactions involving addition to the C=O group. Esters also are stabilised by resonance with the structure (XXII), but this is less significant due to the energy required for the charge separation, while in a carboxylic acid ionisation leads to the equivalent structures (XXI A) and (XXI B). Increased resonance in an ion is in fact a driving force for ionisation, not only in carboxylic acids, but also in the case of phenols and nitrophenols, enols, etc. The two oxygen atoms in the nitro group are equivalent on account of resonance between the structures (XXIII A) and (XXIII B) with a



possible small contribution from (XXIII C). In p-dinitrobenzene[1] the nitro groups are coplanar with the benzene ring; the two oxygen atoms of the nitro group are equidistant at 1.23A from the nitrogen atom, in agreement with the resonance mechanism suggested by Pauling in which the two principal structures are (XXIII A and B).

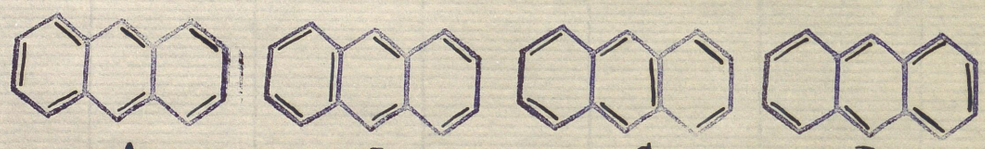
[1] Llewellyn, J. Chem. Soc., 890 (1947).

Resonance in the benzene molecule between the two Kekule structures (XXIV A and B) stabilizes it to the extent of about 37 kcals., and in addition the contribution of less stable structures such as (XXIV C) increases the resonance energy to about 39 kcals. The high stability of aromatic ring systems, as well as

(XXIV)  ;  (XXV)

A B C A B C

their optical and other properties, can be ascribed to their character as resonating molecules. The benzene molecule is known from electron and x-ray diffraction studies to be coplanar; the six carbon atoms lie at the corners of a regular hexagon 1.39A on edge, while the C-C bond distance in ethane is 1.54A, and the C=C bond in ethylene is 1.35A. The main resonance structures for naphthalene, which has a resonance energy of 75 kcals are (XXVI A, B and C), and the chemical evidence indicates that the symmetrical structure (XXV A) makes a larger contribution than B and C in which one ring (b) is benzenoid and the other (q) quinonoid. The resonance energy of anthracene is 105 kcals, there being

(XXVI) 

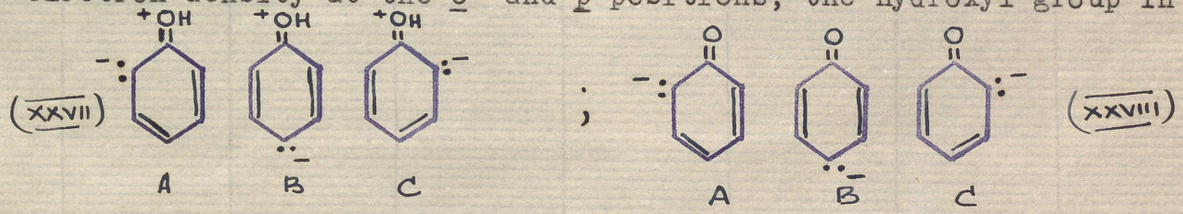
A B C D

four main contributing structures (XXVI A-D).

Inductive and resonance effects.- The displacement of electric charge is important from the point of view of colour and of chemical reactivity, such as substitution in aromatic rings. In addition to the resonance effect (R-effect) which is relayed through a conjugated path of alternate double and single linkages, there is also an inductive effect (I-effect) which can be relayed down a saturated chain or may be regarded as a general field effect, and which leads to a polarisation of the molecule in equilibrium with

its environment[1]. Thus a strongly electronegative atom will tend to pull electrons towards itself. The I-effect will undergo progressively rapid damping with increasing distance from the atom or group producing the effect.

The I- and R-effects of a substituent in an aromatic ring influence the electron distribution at other positions, and therefore the optical and other properties. The R-effect operates in the o- and p-positions, and it may reinforce or be opposed to the I-effect; in the latter case the R-effect predominates. These effects are clearly seen in aromatic substitution, and in the electronic interactions between groups (auxochrome-chromophore effects) in a dye molecule which determine its colour. In aromatic substitution, the common attacking atoms and groups (e.g. the NO_2, SO_3H and diazonium groups; and $:\ddot{\underset{\cdot\cdot}{Cl}}:$ which in a nuclear chlorination seeks to complete its octet, leaving the second chlorine atom in the chlorine molecule as the ion with a complete octet) are electro$^{\curvearrowright}$seeking (electrophilic or cationoid) and they are attracted to sites of comparatively high electron density. In phenol for instance the structures (XXVII A, B and C) make a significant contribution to the Kekule resonance, and on account of the increased electron density at the o- and p-positions, the hydroxyl group in



phenol is o-p-directing. In the phenolate ion, the resonance energy is about 8 kcals more than in phenol on account of the much larger contributions made by the structures (XXVIII A, B and C), and o-p-substitution takes place very readily. While aniline behaves similarly to phenol on account of similar resonance (e.g. XXIX), the

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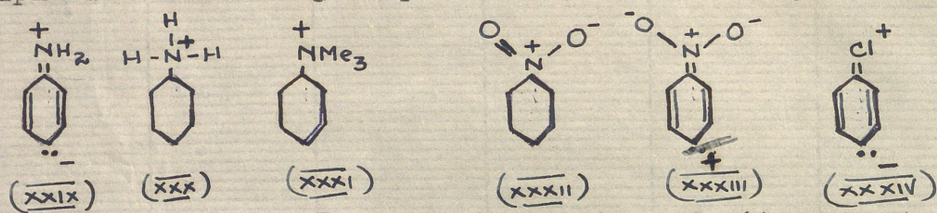
[1] For a full account, see Branch and Calvin, and Wheland, loc. cit.; Remick, Electronic interpretations of organic chemistry, Wiley, New York, 1943; Watson, Modern Theories of Organic Chemistry, 2nd ed., Oxford Univ. Press, Robinson, Outlines of an electrochemical theory of the course of organic reactions, Institute of Chemistry, London.

anilinium ion (XXX) (e.g. aniline in presence of a large excess of sulphuric acid during sulphonation) behaves very differently from



(XXIX) (XXX) (XXXI) (XXXII) (XXXIII) (XXXIV)

the phenolate ion. The positively charged nitrogen atom in (XXX) cannot enter into resonance interaction with the benzene ring, and the inductive effect is to attract electrons from the ring. The electron deficiency is felt more in the o- and p-positions, and in comparison with them the m-position is less deactivated, so that substitution takes place in the m-position. The phenyltrimethylammonium ion (XXXI), in which the nitrogen atom carries a much stronger positive charge than in (XXX), is more powerfully m-directing. It is obvious at the same time that groups which tend to withdraw electrons will tend to deactivate the ring as a whole with reference to substitution by electrophilic reagents, so that m-substitution is much less facile than o-p-substitution.

In nitrobenzene the main contribution to the ~~xxxxxx~~resonance are structures such as (XXXII), in which the inductive effect of the positively charged nitrogen atom is in the same sense as in (XXXI); but there are also small contributions from structures such as (XXXIII) due to resonance interaction of the nitro group with the benzene ring, and this effect reinforces the inductive effect. In chlorobenzene the electrophilic inductive effect of the chlorine atom is opposed and overcome by the resonance effect (e.g. XXXIV), so that o-p substitution takes place. The contribution of structures such as (XXXIV) to the resonance of chlorobenzene is indicated by the C-Cl bond distance of 1.69A in comparison with 1.76A for the pure bond.[1]

There is a parallelism between the op -directing activity of substituents and their effect on light absorption. Thus in a series of substituted nitrosobenzenes the absorption maximum is displaced

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[1] Brockway and Palmer, J. Am. Chem. Soc., 59, 2181(1937)

towards greater wavelengths in the order p > o > m-Me, I > Br > Cl[1]

The effect of "acidifying substituents" on chromophoric systems has been examined by Eistert[2]. There is no simple relationship between the position of the absorption bands of the anion and the acid-strengthening effect of the substituent. The SO_2R group affects absorption by its inductive effect, while the nitro group exerts also a secondary electromeric effect on the stability and structure of the anion. 4:4'-Dinitrotriphenylmethane is colourless, but gives an intense violet salt with caustic soda; while the analogue containing $-SO_2Me$ in place of $-NO_2$ is colourless both in the neutral and alkaline solution. This is due to the small inductive effect of $-SO_2Me$ on the methane carbon, and the large mesomeric effect of the nitro groups.

Dipole moments and resonance.- Dipole moments are important in the consideration of the colour of organic compounds, especially with regard to the intensity of absorption bands. When a substance is placed in an electrical field of unit strength, the total molar polarisation (P) measured by the dielectric constant (ϵ) is the sum of the induced polarization (P_α) and the polarization (P_μ) due to the polar character of the molecule (i.e. the presence of a permanent dipole in the molecule). These relationship are shown in equations (i), in which M is the molecular weight and d the

$$P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{d} = P_\alpha + P_\mu = \frac{4\pi}{3} N\alpha + \frac{4\pi}{3} N \frac{\mu^2}{3KT} \quad \ldots\ldots (i)$$

density, α the polarizability of the molecule, N the Avogadro number, μ the dipole moment of the molecule, k the molecular gas constant (Boltzmann constant) and T the absolute temperature). The polarizability (α) represents essentially the ease with which the electrons in a molecule may be displaced from their normal positions, since for the present purpose the displacement of atomic nuclei may be

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[1] Tsuzuki, Uemura and Hirasawa, Ber., 74, 616 (1941).

[2] Z. Elektrochem., 47, 35 (1941).

neglected on account of their much greater mass. There are several methods[1] by which the polarizability (α) and the dipole moment (μ) may be separately computed.

Experimental measurement gives the total dipole moment of a molecule, but ~~in dual~~ individual bond moments can be inferred, especially in the case of simple molecules ~~and in~~ such as water and ammonia. For a diatomic molecule obviously, the bond moment is identical with the measured dipole moment. The symmetrical character of molecules such as CCl_4, CO_2 and CS_2 is shown by the absence of a permanent dipole moment. On the other hand water and hydrogen sulphide have dipole moments, showing that the three atoms do not lie in a straight line and the moments of the two dipoles do not cancel each other. While a bond may be essentially ionic or essentially covalent depending on the relative stability of the ionic and covalent structures, resonance occurs between the two types of structures and their relative contributions are reflected by the bond moment. The dipole moment of the molecule can then be regarded as the vector sum of the moments of all the bonds in the molecule, and any difference between the observed and calculated dipole moments can be correlated with the resonance interactions between atoms and groups in the molecule.

In alkyl and aryl chlorides the dipole moment vector is directed along the R-Cl axis, but chlorobenzene has a moment of 1.55 D (D is a Debye unit of 10^{-18} e.s.u.) in comparison with 1.86 for methyl chloride[1]. The reduction is due to the contribution of resonance structures such as (XIV); for the same reason the chlorine atom in chlorobenzene is less reactive than in methyl chloride. In nitrobenzene the inductive and resonance effects (cf. XII and XIII) operate in the same direction, so that unlike the case of chlorobenzene, nitrobenzene has a moment of 3.95 which is about 0.64 above the value for nitroparaffins.

Benzene has no dipole moment, and the sign of the dipole in a substituted benzene, which represents the direction of displacement

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[1] Sutton, Trans. Faraday Soc., 30, 789(1934).

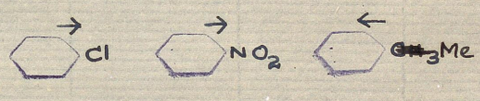
of electrons, is indicated by the additivity of the bond or group moments in disubstituted benzenes (Table I). By this method

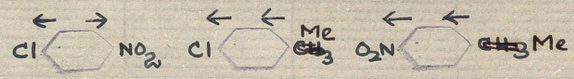
Table I

Dipole moments of substituted benzenes[1]

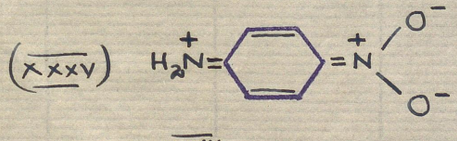
	Observed	Calculated
$C_6H_5-CH_3$	0.4	-
C_6H_5-Cl	1.55	-
$C_6H_5-NO_2$	3.95	-
$C_6H_5-NH_2$	1.52	-
C_6H_5-OH	1.61	-
p-Cl-$C_6H_4-CH_3$	1.90	1.95
p-$O_2N-C_6H_4-CH_3$	4.4	4.35
p-Cl-$C_6H_4-NO_2$	2.5	2.40
p-$O_2N-C_6H_4-NH_2$	6.10	5.47
p-$O_2N-C_6H_4-OH$	5.04	5.56

The negative sign of the moment in nitrobenzene follows from the dipole character ($-\overset{+-}{NO_2}$) of the nitro group. By this method atoms and groups may be arranged in a series according to their electronegativity, and may be compared with their influence on the strength of acids and bases.





When an electron-donor group and an electron-acceptor group are present in p-positions as in p-nitroaniline, the dipole moment of the molecule is greater than the sum of the moments of the monosubstituted benzenes on account of the resonance with structures



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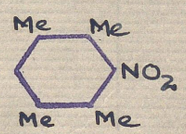


(XXXVI)

such as (XXXV). The steric effect of such resonance is to produce coplanarity, and conversely, evidence of the steric inhibition of resonance is provided by a decrease in the dipole moment of

[1] Birtles and Hampson, J. Chem. Soc., 10 (1937); Ingham and Hampson, ibid., 981(1939).

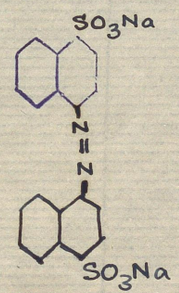
nitrodurene (~~XVI~~ XXXVI), which is 3.39 in the neighborhood of the value for the nitroparaffins. The o-methyl groups prevent coplanar configuration, so that the resonance of the benzene ring with the nitro group is less than in the case of nitrobenzene.

Chromophores and auxochromes: definitions.- Saturated molecules ordinarily do not absorb light except in the far ultraviolet, and the action of a chromophore is to shift the absorption to lower frequencies. All coloured organic compounds are unsaturated in character, and a chromophore may be defined as a group containing one or more multiple bonds. The definition therefore is merely a more precise restatement of Witt's idea of a chromophore. A single chromophoric group, such as the vinylene (-CH=CH-) group, absorbs in the ultraviolet[1], and to produce visible colour, two or more chromophores conjugated with each other are necessary. Further, unsaturation in dye molecules is usually associated with oxygen and nitrogen atoms in a manner which enables ready reversal of the linkages in the conjugate chain, so that dye molecules are resonance hybrids. It then becomes necessary to speak of a chromophoric system or systems in a dye molecule, rather than single chromophores. Colour may be deepened and intensified progressively by the multiplication of chromophores, and by the replacement of weaker by stronger chromophores, as explained later.

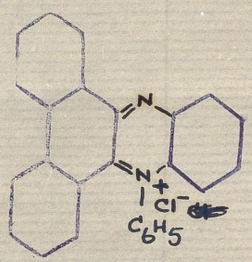
Auxochromes are more difficult to define than chromophores, and there has been some confusion regarding the nature and function of auxochromes. It will be recalled that Witt employed the term for groups, such as hydroxyl and amino, which were "weakly salt-forming" and imparted dyeing properties to a coloured substance, and which also intensified the action of the chromophore. These two effects are distinct and separate, and need to be considered separately. In the sense of salt-forming groups auxochromes have one function. With the exception of methods in which an insoluble dye is applied to textiles as a pigment incorporated in a ~~review~~

[1] For a review of data on ultraviolet light absorption and its empirical correlation with molecular structure, see Braude, Annual Reports on the progress of Chemistry, p. 105-130, Chem. Soc., London, 1946.

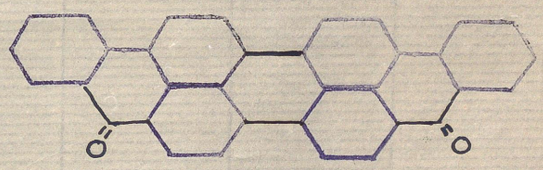
resin binder, dyes are applied to textile fibres from an aqueous medium; a dye molecule therefore must contain a group which will render it soluble in water (under neutral, acidic or alkaline conditions), directly or after suitable chemical treatment such as reduction with hydrosulphite-alkali or sodium sulphide. Dyes therefore contain salt-forming groups, or groups which can be converted before dyeing into salt-forming groups, ~~xxxxxxxx~~ Examples of the former are Witt's auxochromes, to which must be added sulphonic, carboxyl, quaternary ammonium groups, etc., which have the function of enabling a coloured compound to be applied as a dye, and whose influence on the colour of the molecule may be variochromic (cf. Wizinger's positive and negative auxochromes). Two dyes of interest in this connection, as dyes not containing auxochromes in the Witt sense, are 1:1'-azonaphthalene-4:4'-disulphonic acid (~~XVII~~ XXXVII) which dyes wool an orange, and Havinduline (~~XVIII~~ XXXVIII) which is a basic dye for tannin-mordanted cotton. Dyes of ~~the~~ second type, which contain no auxochrome in the original solid state and in which auxochromes are introduced during the process of solubilisation prior to dyeing, are exemplified by the vat dyes. Dibenzanthrone (~~XIX~~ XXXIX) is an intense blue dye which does not contain an auxochrome; on treatment with hydrosulphite-alkali it is reduced to a dihydro-compound, which has two phenolic hydroxyl groups functioning as auxochromes.



(XXXVII)



(XXXVIII)



(XXXIX)

Auxiliary groups, which are not "salt-forming" and which therefore do not fall within the category of Witt's auxochromes, may be introduced in dye molecules for the purpose of increasing the affinity for textile fibres, or "substantivity". In this sense they may also be included among auxochromes. ⟶

An example is the amide (-CO-NH-) group. The phenomenon of substantivity for textile fibres and theories of dyeing are however discussed in Chapter ___, although they are in some ways associated with the problem of colour, and it is found that bathochromic and hyperchromic effects, especially the latter, sometimes run parallel to increasing substantivity.

~~The~~ From the standpoint of the colour of organic compounds an ~~auxin~~ auxochrome is best defined as a substituent atom or group which increases the intensity (ϵ) of the absorption of light due to a chromophore. An auxochrome may (and usually does) increase the wavelength of maximum absorption ($\lambda_{max.}$) in addition to increasing the intensity (ϵ), just as a second chromophore conjugated with the first may (and usually does) increase the intensity of absorption in addition to shifting it to lower frequency. There are however adequate theoretical and practical reasons for associating chromophores with a bathochromic effect and auxochromes with a hyperchromic effect as invariable effects, which may or may not be accompanied by a hyperchromic effect in the first case and a bathochromic effect in the second. A given auxochrome may exercise this positive effect only in the case of certain chromophores, and only when it is situated in a suitable position with reference to the chromophore; the same substituent may decrease the absorption in the case of other chromophores. An auxochromic effect is thus more significant as a term than an auxochrome, since an atom or group functions as an auxochrome only under certain conditions. For this reason the effect of auxochromes and chromophores must be considered in conjunction with each other, and Brooker[1] has made the acceptable suggestion of a composite term, auxochromophoric system, to express the combination of auxochromes and chromophores.

The distinction between an auxochrome[2] and a chromophore with reference to the absorption of light is one of degree, rather than of kind, since auxochromes with the exception of alkyl groups and

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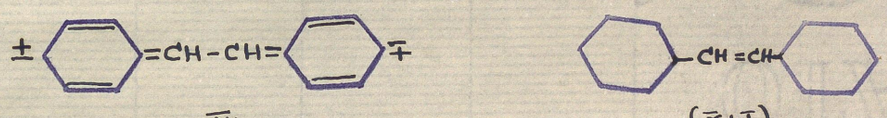
[1] loc. cit.

[2] For a discussion of auxochromic properties in relation to the position of the substituent element in the periodic system, see Bowden, Braude and Jones, J. Chem. Soc., 948(1946).

chlorine atoms, which have unique features and are discussed separately, produce high intensity absorption, in the ultraviolet; and a multiplication of auxochromes in conjugated positions increases the absorption. Nevertheless, it is convenient to distinguish between auxochromes and chromophores on the basis of the electron distribution in the two types of groups, and of the specific effect of auxochromes, as now suggested, of increasing the intensity of absorption. While chromophores are groups containing multiple bonds and in general are electron-attracting, auxochromes are singly bound atoms or groups with unshared pairs of electrons. In an auxochromophoric system therefore, electron mobility, leading to the absorption of light, results from the electronic interaction between auxochromes and chromophores, by which the contribution of highly conjugated and polarised structures to the resonance of the molecule is increased.

For stilbene resonance structures such as (XL), which are associated with the absorption of light, may be considered as contributing to the normal state of the molecule (XLI), but only to a small extent on account of the high energy of charge



(XL) (XLI)

separation; the interatomic distance (1.44A) by the x-ray method indicates about 18% double bond character for the bonds between the

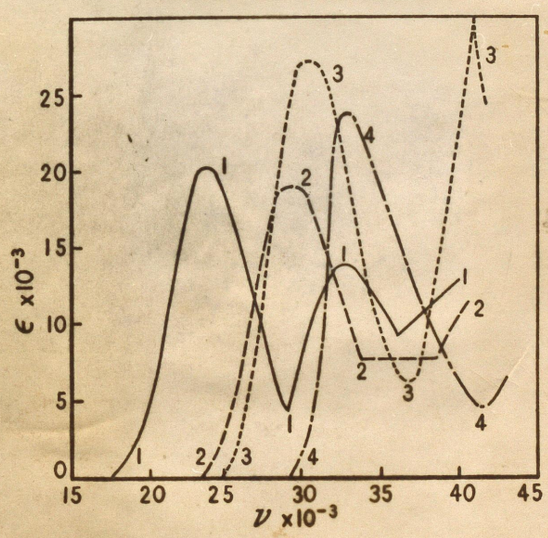
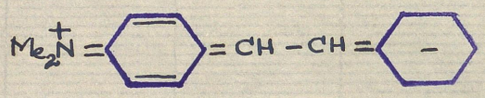
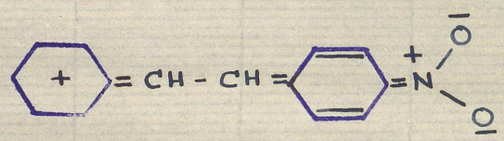


Figure 13. Absorption curves of four stilbenes in alcohol. Curve 1, *p*-nitro-*p'*-dimethylaminostilbene; curve 2, *p*-nitrostilbene; curve 3, *p*-dimethylaminostilbene; curve 4, stilbene.

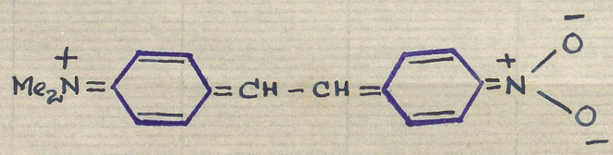
benzene rings and the aliphatic carbon atoms. The contribution of structures such as (XL) may be increased by the introduction at one end of the molecule, of either an electrophilic or an electron-donor group, so that the energy of the structure may be lowered by providing an atom or atoms which can carry a negative or positive charge more readily than carbon. The absorption system[1] of stilbene and three p-substituted stilbenes are given in Fig. 3. In p-nitrostilbene (XLII) the bathochromic effect is produced by an additional chromophore, the nitro group; and in p-dimethylamino-stilbene (XLIII) a similar effect is produced by an auxochrome, the dimethylamine group. The shift in absorption towards lower frequency is almost identical in the two cases, but the intensity of absorption, as postulated earlier, is increased by the introduction of the auxochrome, while the nitro chromophore has a hypochromic effect. In 4-nitro-4'-dimethylaminostilbene (XLIV) the



(XLIII)



(XLII)



(XLIV)

bathochromic effect is more pronounced than in the case of (XLII) and (XLIII), and is greater than the sum of the effects due to the nitro and the dimethylamino groups; on account of the electron-accepting character of the two oxygen atoms and the electron-donor character of the two nitrogen atoms, the structure (XLIV) makes a large contribution to the optically important resonance of the molecule. These resonance effects influencing light absorption are analogous to those discussed earlier in connection with dipole moments.

Similar effects are apparent from Fig. 3a showing the

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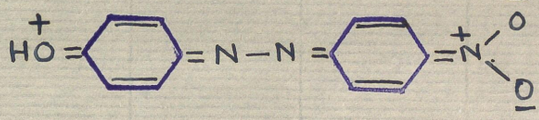
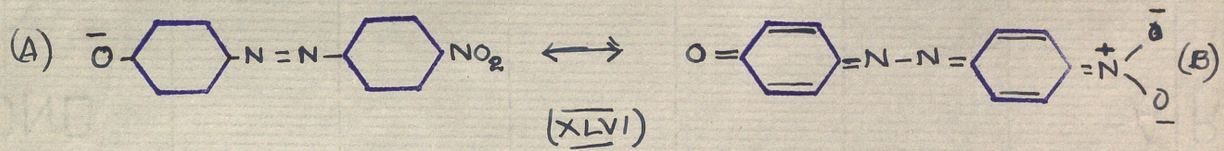
[1] Hertel and Lührmann, Z. physik. Chem., 44, 261 (1939).

the absorption spectra of p-hydroxyazobenzene, 4-nitro-4'-hydroxy-azobenzene, and the last substance in alkaline solution. While for the reasons explained in the case of the stilbene derivative (XLIV), 4-nitro-4'-hydroxyazobenzene (XLV) is deeper in colour than the hydroxy-compound, the same substance in alkaline solution exhibits a large bathochromic shift (Fig. 3a). In the



(XLV)



(XLVI)

resonance structures (XLVIA and B) for the ion, only the movement of a charge is involved and the low energy of the transition is responsible for the deeper colour in comparison with the undissociated compound (XLV).

The influence of alkyl groups on light absorption.- The absorption curves of acetone and hexaethylacetone (Fig. 4) clearly demonstrate the influence of alkyl groups in increasing both the intensity and the wavelength of absorption. The first absorption band of benzene (λ max. 256 mμ; ϵmax. 250) is shifted to wavelength 262 mμ, ϵ300 in toluene. Lewis and Calvin[1] explain the effect as due to induction, which they regard as a

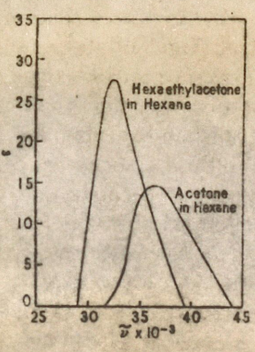


FIG. 4 Absorption curves of acetone and hexaethylacetone

perturbation in existing electronic paths without altering their essential character. Auxochromes with unshared electron pairs provide, through resonance, new electronic paths.

The ability of alkyl substituents in a chromophoric system to

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[1] loc. cit.

increase the absorption is in line with their o:p-directing power as nuclear substituents in the benzene ring. A methyl group in the benzene ring increases the electron density in the o- and p-positions, and the effect is so marked in mesitylene that it can couple with diazotised 2:4-dinitroaniline. It has also been found that toluene has a dipole moment (0.4D), the methyl group being positive with reference to the phenyl and it has been suggested that hyperconjugation[1] may be responsible for the effect. Hyperconjugation is an electronic interaction occurring with covalently saturated groups, especially a methyl group, postulated in substances such as propylene to explain the fact that the ~~height~~ heat of hydrogenation of an olefine is decreased by the presence of alkyl substituents on the unsaturated carbon atoms[1]; and it may be ~~prepared~~ pictured as a resonance effect occurring in propylene between the normal structure (XLVII A) ~~(A)~~ and the less stable

$$H_3C-CH=CH_2 \longleftrightarrow H_3\overset{+}{=}C=CH-\overset{-}{C}H_2$$

(A) (XLVII) (B)

structure (XVII B) ~~(B)~~.

When the size of the alkyl group is increased from methyl to ethyl, etc., the bathochromic shift becomes progressively less. This has been shown in the case of the n-alkylbenzenes (toluene to n-hexylbenzene); the ~~nitr~~ vibrational fine structure of the benzene spectrum disappears in the higher members.[2] ~~(Pestemerxand Gubitzxx Monatsshxxx64, 4~~

Chlorine as an auxochrome.- In the case of the simple C-Cl and C-Br linkages there is ~~a~~ very little absorption in the region of the spectrum down to 200 mμ.

The unshared electrons of the chlorine atom enable small, but significant, contributions to be made by such polar structures as (XXXIV); since however this has to overcome the negative

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[1] Wheland, p. 133; Mulliken, Ricke and Brown, J. Am. Chem. Soc., 63, 41(1941); Bateman and Koch, J.Chem. Soc., 600(1944); 216(1945 J.W.Baker and Hemming, ibid., 191(1942).

[2] Pestemer and Gübitz, Monatsh., 64, 426(1934).

inductive effect, chlorine is usually a very feeble auxochrome. Thus the spectra of 2-chlorophenanthrene and phenanthrene are so similar that structures involving a double bond between the halogen atom and the ring can be making no significant contribution to the activated state of the molecule[1]. Further, on account of the size of the atom, chlorine in the o-position to a chromophore (e.g. in an azo dye) is capable of a steric inhibition of resonance with a consequent decrease in absorption (see also 6hapter ___).

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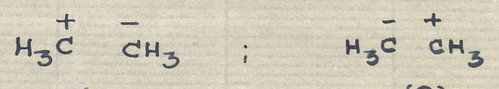
[1] Jones, J. Am. Chem. Soc., 67, 2143(1945).

ELECTRONS AS QUANTISED OSCILLATORS.

Lewis and Calvin[1] in 1939 formulated a comprehensive theory of the colour of organic compounds which has made it possible to calculate and predict the spectra of certain types of coloured molecules, and to make a qualitative correlation of the colour of complex dyes with their resonance structures. The present account is largely based on their treatment, and on the development of their ideas by Brooker, Branch and others.

It is assumed in the Lewis-Calvin theory that electrons in a molecule are acting as oscillators subject to the simple rules of quantisation; that the absorption of light is due to the excitation of electronic oscillations whose extremes are represented by certain polar resonance structures; and that the types of oscillations are indicated by the resonance structures contributing to the ground and excited states of the molecules.

The absorption of ethane, cyclohexane, ethylene, butadiene and cyclopentadiene are given in Fig. 5. For ethane two additional structures (XLVIII A) and (XLVIII B) may be written; their contribution to the



(XLVIII)

actual state of the molecule is small, but it is the polarisability of the bond or bonds in a molecule, which is held to be responsible for the absorption of light. The two lowest curves in Fig. 1 are characteristic of saturated systems; in the curve for cyclohexane there is a shift towards lower frequency on account of the Baeyer strain in the ring. The curve for ethylene is characteristic of a simple double bond, in which resonance occurs to a considerable degree. In the transition between electronic states resulting in light absorption, the ground and excited states are resonance hybrids of the structures (XLIX A, B and C), and less stable structures which are left out of account; the ground

[1] Chem. Rev., 25, 273 (1939).

ground state is represented essentially by (A), while (B) and (C)

$H_2C = CH_2$ (A) $\quad H_2\overset{+}{C}-\overset{-}{C}H_2$ (B) $\quad H_2\overset{-}{C}-\overset{+}{C}H_2$ (C) (XLIX)

make large contributions to the two excited states which arise from

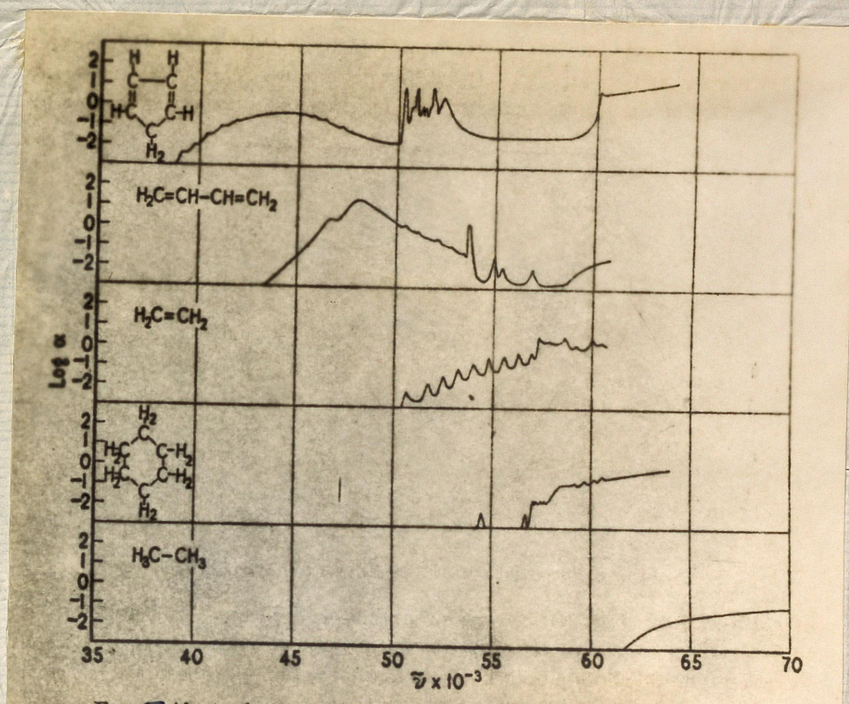


FIG. 5. Absorption curves of cyclopentadiene, 1,3-butadiene, ethylene, cyclohexane, and ethane

the resonance. Butadiene absorbs at lower frequency than ethylene, and the two upper curves in Fig. 5 are characterstic of conjugated systems. The resonance in butadiene is greater than in ethylene on account of contributions from a number of structures such as (L A and B) which do not differ widely in energy. In the spectrum of butadiene and of cyclopentadiene there is a new wide band, which

$\overset{+}{C}H_2-\overset{-}{C}H-CH=CH_2$ (A) $\quad \overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2$ (B) (L)

is not present in ethylene; this is regarded as a "fundamental band" which indicates that each double bond has lost its individuality as an oscillator, the conjugated system having become subject to certain rules governing the whole molecule. With increased conjugation in the system there is a displacement of the fundamental band of absorption to longer wavelengths.

Since it is the polarisability of the double bond in ethylene which is responsible for its chromophoric character, it follows that other double bonded structures in which there is an increased

strain will absorb at lower frequencies or function as "stronger" chromophores than an ethylenic compound. Considering C=N, C=O, N=N and C=S as examples of other types of double bonds, it is of interest to compare the first absorption maxima of stilbene and a series of its analogues:

Compound	First absorption mμ	Visible colour
Stilbene Ph-CH=CH-Ph	295	None
Benzalaniline Ph-CH=N-Ph	330	None
Benzophenone Ph-C(=O)-Ph	330	None
Azobenzene Ph-N=N-Ph	450	Orange
Thiobenzophenone Ph-C(=S)-Ph	620	Blue

It is one of the postulates of the Lewis-Calvin theory that "every displacement from the ideal state makes further displacement easier", i.e. increases the mobility of electrons. The fact that p-nitroaniline has a considerably greater dipole moment than the sum of the moments of nitrobenzene and aniline is an illustration of the principle, and the large contribution from the structure (XXXV), which is responsible for the moment and the increase in electron mobility, is also responsible for a marked increase in light absorption. While aniline and nitrobenzene absorb in the ultraviolet, the absorption band of p-nitroaniline extends into the visible region, and the p-nitroaniline molecule is an auxochromophoric system in which the nitro group is the primary chromophore, the amino group is the auxochrome, and the benzene ring in the quinonoid form provides a conjugated path for the resonance.

The contribution of ionic structures to the resonance of p-nitroaniline becomes greater if the energy required for the charge

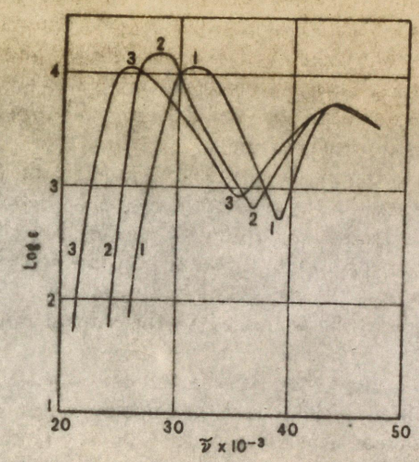
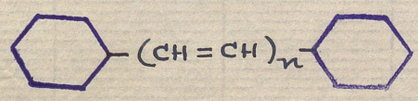


FIG. 6. Absorption curves of *p*-nitroaniline in hexane (curve 1), dioxane (curve 2), and water (curve 3)

separation is decreased, as happens in a solvent of high dielectric constant. This is illustrated in the absorption curves of p-nitroaniline in (1) hexane, (2) ~~dixo~~ dioxane and (3) water (cf. Fig. 6). The dielectric constant of the medium has no influence on absorption when the resonance state of the molecule does not have an average moment and the motions of the electrons are too rapid to be followed by the dipoles of the solvent. However, there is need for much more data to be accumulated on the absorption spectra of organic compounds in solvents of varied character.

Nearly linear oscillators. For molecules which may be considered to be nearly linear in alignment so far as electronic oscillations ~~concerned~~ associated with light absorption are concerned, and in which there is an unbroken chain of alternate single and double bonds, it is possible to derive quantitative relationships between the length of the conjugate chain and the frequency of absorption. Three main types of such linear oscillators have been investigated. In the simplest type, the diphenylpolyenes (~~II~~ LI), it has been shown[1]



(L.I).

[1] Hausser, Kuhn, et al., Z. tech. Physik, 15, 10 (1934); Z. physik. Chem., B29, 363-417 (1935).

that there is a steady decrease in the frequency of the first absorption band with increase in n (Fig. 7); and when the frequencies of the first maxima are plotted against n (adding an arbitrary "colour equivalent" of 1.5 double bonds for each of the end phenyl groups, and adding the actual

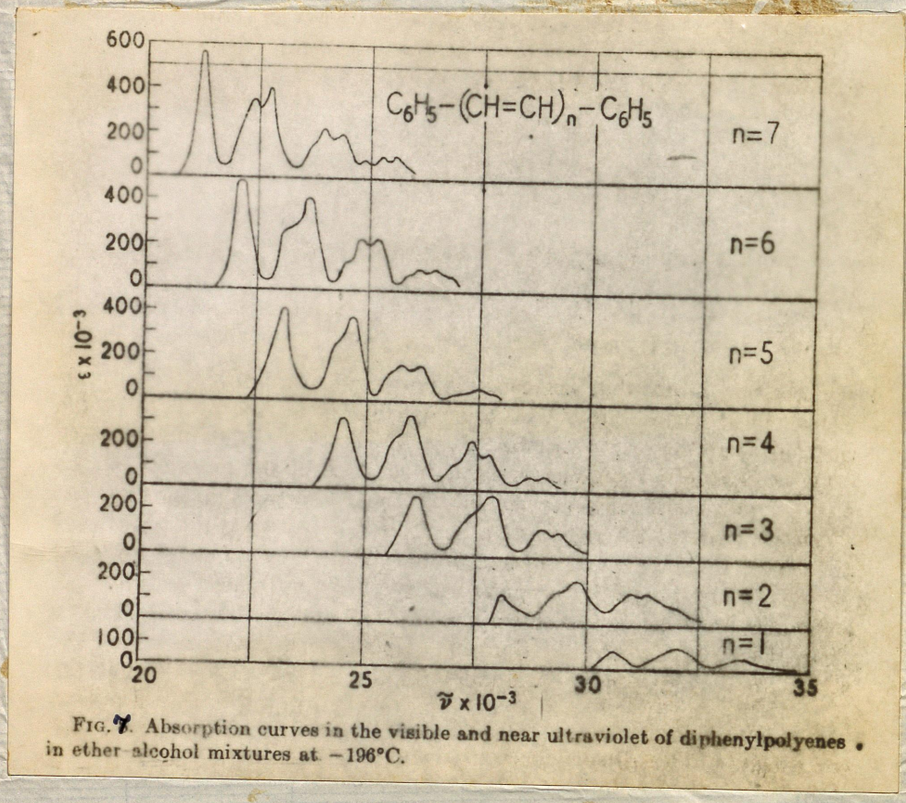


FIG. 7. Absorption curves in the visible and near ultraviolet of diphenylpolyenes in ether-alcohol mixtures at −196°C.

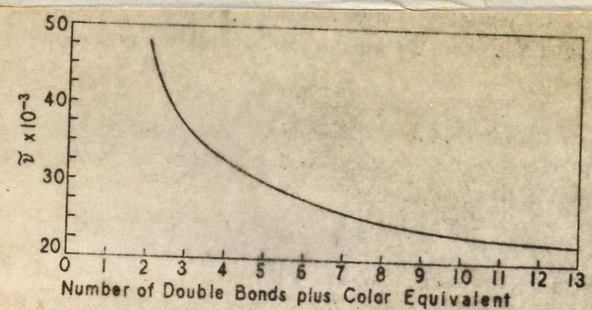


FIG. 8. Plot of frequency of first maximum against the total number of conjugated double bonds for seventy compounds of the polyenic type.

number of double bonds in the end members in other cases, such as alcohols, acids, etc.), all the points approximate to the same curve (Fig. 8) for about 30 compounds. The sharp definition and structure in the curves in Fig. 7, ascribed by Hausser and Kuhn to the atomic vibrations characteristic of the olefines, were obtained by using a solution of ether and alcohol at -196°.

Omitting the terminal groups, the polyene chain may be represented by the major contributing structure (A) and minor polar structures such as (B) and (C), which represent the extreme or

limiting structures. A chain of n-conjugated double bonds may be

$$-C=C-C=C-C=C- \qquad -\overset{+}{C}-C=C-C=C-\overline{C} \qquad -\overline{C}-C=C-C=C-\overset{+}{C}$$

(A) (B) (C)

(I) (II)

considered as a single linear oscillator, or as a system of n unit oscillators moving exactly in phase; it is simpler to do the latter. Assuming that the oscillations are those of a linear harmonic oscillator, the energy levels E_v of the unit oscillator are given by the expression (2), in which v is the vibrational quantum number, h is Planck's constant and ν_0 is the frequency of the light which can change the oscillator from quantum number 0 to 1. The fundamental frequency ν_0 is given by the expression (3), in which k is the coefficient of restoring force and

$$(2) \quad E_v = (v+1/2)h\nu_0 \qquad\qquad \nu_0 = 1/2\pi\sqrt{k/m} \quad (3)$$

m the mass of the effective electrons in each unit; k is a constant for the oscillator which is related to the polarisability α by the equation $k = e^2/\alpha$, in which -e is the effective charge which is displaced. When the system of n unit oscillators, each of which has the same force constant k, is now replaced by a single oscillator, the total mass of the effective electrons is nm, and the characteristic frequency ν_0 for the series of molecules (I–IV) is given by the expression (4), which is merely

$$(4) \quad \nu_0 = 1/2\pi\sqrt{k/nm} \qquad\qquad \lambda = \frac{2\pi c}{\sqrt{k/nm}} \quad (5).$$

equation (2) with m replaced by nm. The wavelengths of the first absorption maxima are then given by equation (5), and if all the constants are replaced by a new constant k^1, we have the equation $\lambda^2 = k^1 n$. From Fig. 4, in which λ^2 is plotted against n from the data in Fig. 7, the linear relationship is fully verified in the case of the diphenylpolyenes. The intercept of the line on the n-axis shows that, if λ^2 is made not merely linear with n, but proportional to it, each phenyl group is equivalent to 2.35 double bonds.

The main contributor to the resonance state of the polylenes (II) is the ~~classical~~ Classical structure (A). It is therefore assumed that

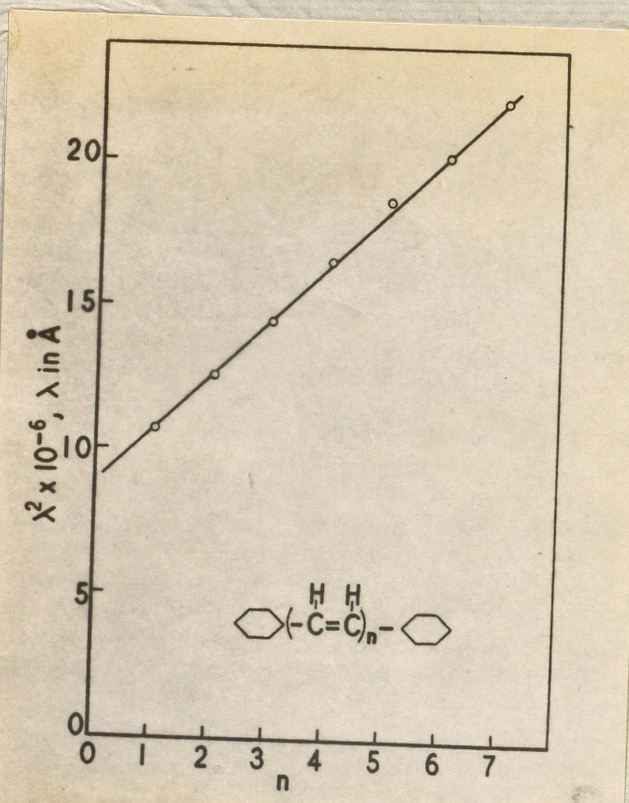
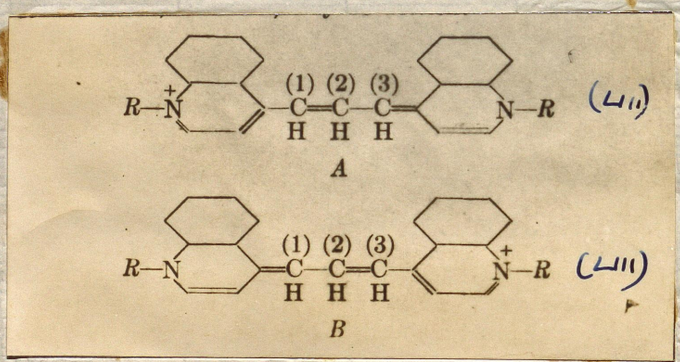


Figure 2. Plot of the square of the wave length of the first absorption band of the diphenylpolyenes against the number of units of the polyenic chain.

that even in the excited states the electrons never get far from the positions indicated in this structure, and the restoring force within a single unit is not appreciably affected by the electrons of the next unit. The ion of a cyanine such as (III) represents



a different type of oscillator. Instead of one main contributing

structure, we have two equivalent low-energy structures (A and B) which contribute equally to the resonance, so that the electron distribution between the carbon atoms 1 and 2, and 2 and 3, is the same. As a result, the electronic cloud is diffuse and more or less uniformly distributed throughout the length of the chain. The restoring force is now dependent mainly on the position of the neighboring electrons, and the oscillation is analogous to the longitudinal vibrations in an elastic string, where the frequency is inversely proportional to the length of the string. For cyanine ions of the general type (III), we should therefore expect the wavelengths of the first absorption maxima to increase linearly with the number of double bonds between the two nitrogen atoms. Hamer's data[1] for a series of carbocyanines are plotted

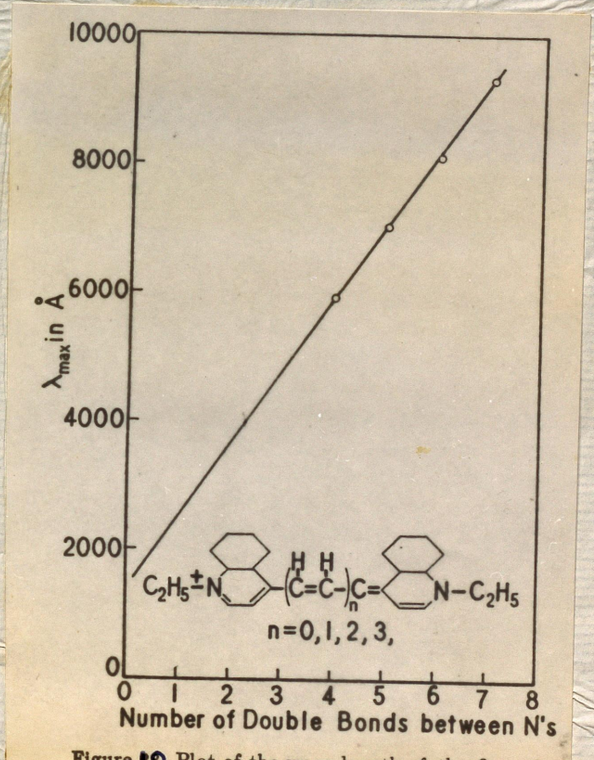


Figure 10 Plot of the wave length of the first absorption band against the number of double bonds between the nitrogen atoms for a series of carbocyanines.

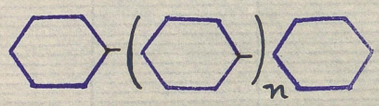
in Fig. 10, and the linear relationship between λmax. and the number of double bonds is obvious.

Quantitative relationships between the structures and spectra of

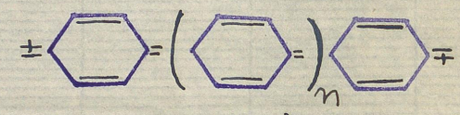
[1] Hamer et al. Proc. Roy. Soc., A154, 703(1936); A163, 138(1937).

numerous symmetrical and unsymmetrical polymethine dyes have been deduced by Brooker[1]. Vinylenic homologous series of other types (e.g. diphenylpolyeneazines) have also been investigated for obtaining empirical equations defining the influence of structure on absorption[2].

A third type of linear oscillator is exemplified by the polyphenyls (~~VIII~~ LV). It follows from the resonance concept of colour that the Kekule structures for benzene are not involved in the light absorption, which is attributed to the minor polar structures



(LIV)



(LV)

such as (~~VIII~~ LV); the weak absorption of benzene is due to the far greater contribution of the Kekule structures, and in derivatives of benzene and other cyclic ~~resonators~~ resonators the absorption increases with an increase in the contribution of the ionic structures. Structures such as (~~VIII~~ LV) for the polyphenyls, which determine the light absorption, can only contribute at the expense of the Kekule resonance. When n is small, the percentage increase in length due to an additional phenylene group produces so great an increase in the polarizability that it counteracts the Kekule resonance, and there is a marked increase in the wavelength of the first absorption maxima. When n is large the importance of these two conflicting effects is in the reverse order; an additional phenylene group produces so small an increase in the polarizability that it is unable to overcome the Kekule resonance of the added group. On account of this difference between the character of the polyphenyls as linear oscillators and of the diphenylpolyenes, k also increases with n in equation (4), and it is to be expected that in the polyphenyls the increase in λmax. with increase in n will become progressively smaller. For a series of p-polyphenyls, Gillam and Hey[3] have found that λmax. varies as follows: diphenyl 2515; terphenyl 2800; quaterphenyl 3000; quinquiphenyl 3100; sexiphenyl 3175A.

Acid-base indicators.- Some of the first applications of the recognition of the ions of dyes such as the triphenylmethanes as resonance hybrids have been in correlating their behaviour as indicators for acids and alkalis with the effect of the hydrogen

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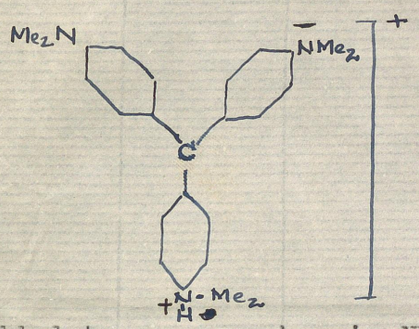
[1] See later.

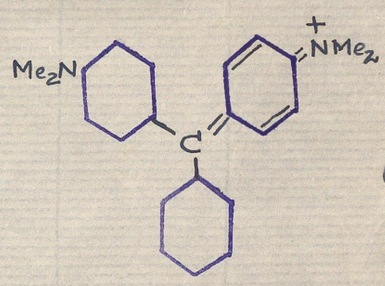
[2] Cf. Ferguson and Branch, J. Am. Chem. Soc., 66, 1475 (1944).

[3] J. Chem. Soc., 1170 (1939).

or hydroxyl ions on the resonance structures. Adams and Rosenstein[1] examined the colour changes of Crystal Violet in acid solution, and showed that the absorption spectra corresponded to successive additions of protons to the cation. Thus the ion (LVII) of Crystal Violet in acid solution, when one proton is

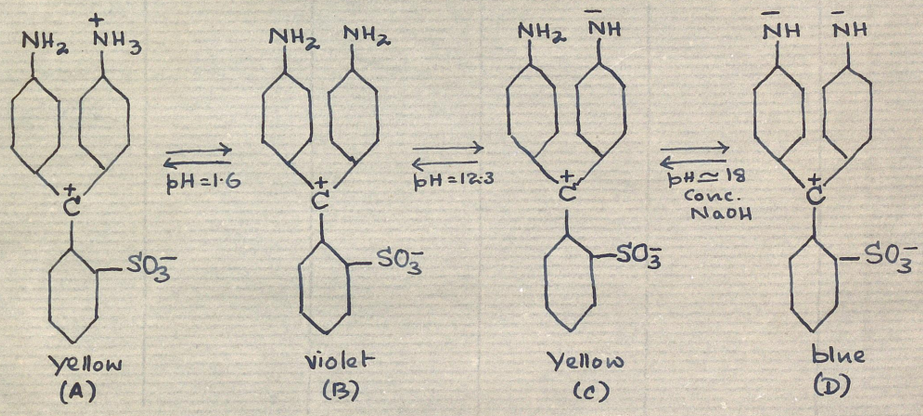
(LVI).



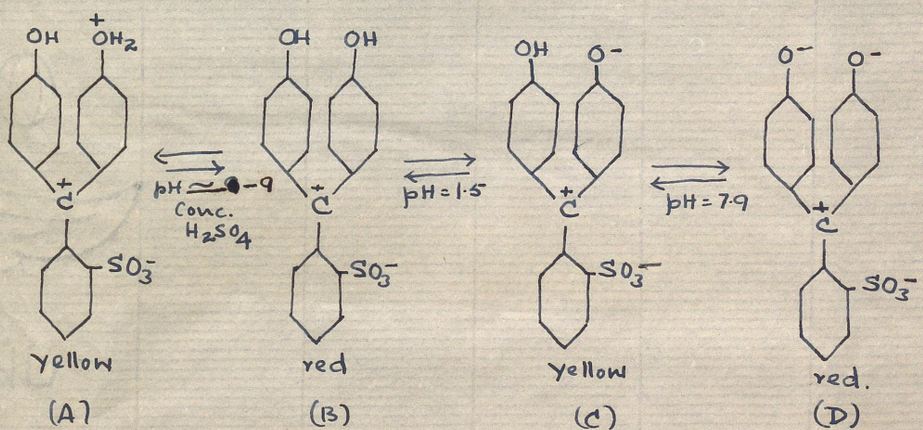


(LVII)

added to an auxochromic NMe_2 group which can therefore no longer participate in the resonance, has an absorption spectrum very similar to that of the cation of Malachite Green (LVII). Schwarzenbach[2] has explained in this manner the colour changes of many indicators. Examples are Anilinesulphonephthalein (LVIII A, B, C and D) and Phenolsulphonephthalein (LVIX A, B, C and D).



(LVIII)
Anilinesulphonephthalein.



(LIX)
phenol sulphonephthalein.

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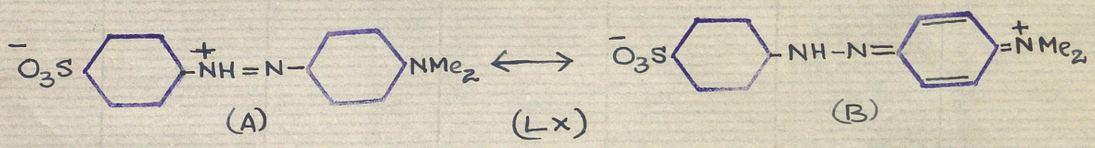
[1] loc. cit.

[2] Schwarzenbach et al., Helv. Chem. Acta, 20, 490,498,627, 654, 1591 (1937).

No space.

Methyl orange in alkaline solution is yellow in colour, being in the azo form. On the addition of acid (pH below 3.1), the colour deepens to red; an azo-nitrogen atom takes on a proton, and the ~~zwitterion~~ ~~then~~ is then a resonance hybrid of the structures (~~VIII~~A) and (~~VIII~~B).



Schwarzenbach[1] has proposed a theory of colour, based on colour changes at varying pH and other properties of dyes. In passing through a pH range of -10 to +17 using solvents other than water, there is usually a periodic change of colour. In the case of dyes with two auxochromic groups, a bathochromic change of colour always follows a hypsochromic one, and vice versa. The larger the number of auxochromic groups, the more complicated is the periodicity. The position of the long wave absorption band is decided by the symmetry of the coloured particle, which affects the resonance energies of the various limiting structures. It is also affected by the length of the resonance chain between the auxochromic groups, and by specific effects due to the

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[1] Z. Elektrochem., 47, 40(1941).

constitution and nature of these groups. The resonance energies of the majority of coloured particles can be estimated from acidity constants.

Insulating groups.- When two or more chromophoric systems are present in a molecule, the effect is roughly additive if the systems are separated by two or more single bonds, i.e. by saturated groups such as $-CH_2-$ and $-CH_2-CH_2-$, which break the conjugation and act as insulators between the two electronic oscillators. This important principle[1] is illustrated in Fig. 11 (see also Fig. 7, Chapter ___). Dyes (LXII) and (LXIII) absorb at

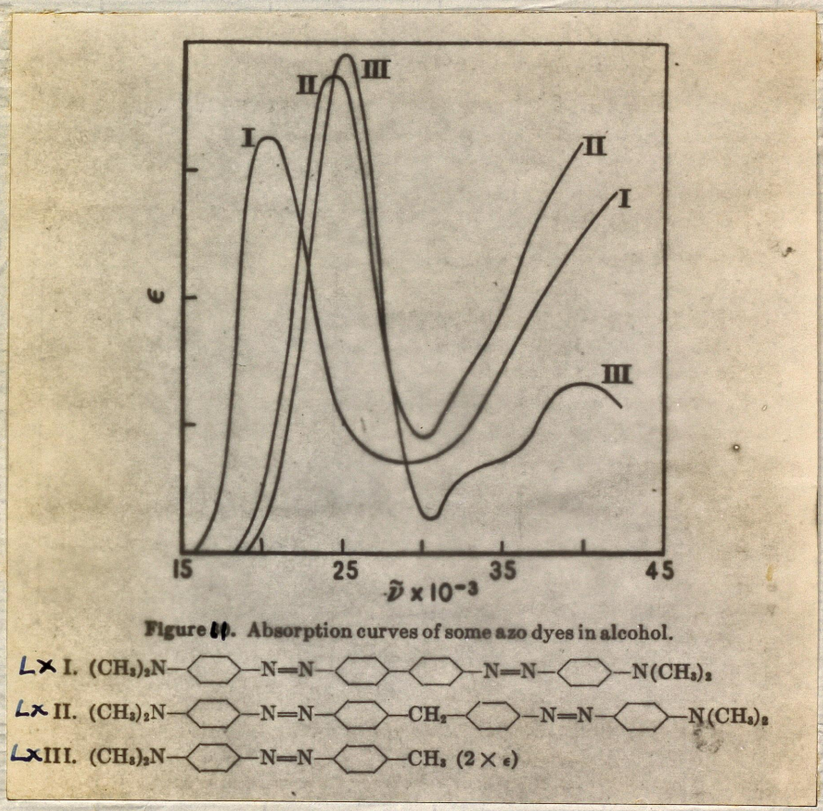

Figure 11. Absorption curves of some azo dyes in alcohol.

LX I. $(CH_3)_2N-C_6H_4-N=N-C_6H_4-C_6H_4-N=N-C_6H_4-N(CH_3)_2$

LX II. $(CH_3)_2N-C_6H_4-N=N-C_6H_4-CH_2-C_6H_4-N=N-C_6H_4-N(CH_3)_2$

LXIII. $(CH_3)_2N-C_6H_4-N=N-C_6H_4-CH_3$ $(2\times\epsilon)$

nearly the same frequency, and the intensity of absorption ($\in$) of the dye (LXII) is about twice the absorption of (LXIII). The dye (LXI) in which the conjugation is unbroken acts as a single oscillator, and it absorbs at a lower frequency than (LXII) and (LXIII).

The absorption curves[2] of dibenzyl, diphenylmethane and triphenylmethane are compared with the curve of for ethylbenzene in Fig. 12 a and b. The union of two or more dye units, by methods other than conjugating them to form a single chromophoric system,

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[1] Piper and Brode, J. Am. Chem. Soc., 57, 135 (1935).

[2] Jones, Chemical Reviews, 32, (1943)

is of very great value in the synthesis of dyes for modifying

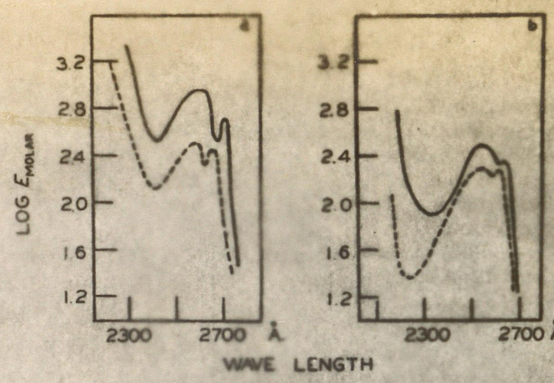

FIG. 13a. Ultraviolet absorption spectra. ——, triphenylmethane in ethanol as solvent (217); ----, diphenylmethane in ethanol as solvent (217).
FIG. 13b. Ultraviolet absorption spectra. ——, dibenzyl in methanol as solvent (154); ----, ethylbenzene in ethanol as solvent (97).

shades by internal compensation in the dye molecule. In dyeing and printing, a self-shade (i.e. a shade produced from a single dye) has advantages over a shade obtained by using a mixture of two or more dyes. Many examples of the preparation of high molecular dyes by linking up smaller dye molecules by means of phosgene, cyanuric chloride, etc., are quoted in later chapters, and it will be useful to have further data on the relative insulating effects of groups such as -O-, -CO-, -NH-, -S-, $-SO_2-$, -NH-CO-NH-, -CO—NH-, m-phenylene, the triazine ring, etc. It is important to remember in this connection that the effect of the insulation between chromophoric units is dependent on their character as well as that of the intervening group. If the chromophoric units which are linked together are highly mobile systems, some electronic interaction can occur even when the two units are not conjugated with each other.

Bonds of "partial oscillations".- In addition to a fundamental absorption band at lower frequency, a conjugated system may sometimes show a "partial bond" (a weak localised band) due to one of the chromophores[1]. An example is diacetyl (curve 1 in Fig. 13) which shows a resolved, fundamental band at about 420 mμ in the visible region, as well as a "partial" band not far from the band

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[1] Lewis and Calvin, loc. cit. See also Kortüm, Z. Elektrochem., 47, 55(1941).

for acetone (curve 3; ~~ε~~ 2) associated with an isolated carbonyl group. Curve 3 in Fig. 13 is for dipropionylethane, which is almost identical with curve 3 representing twice the absorption coefficient of acetone, and confirms the effect of an insulating group, discussed earlier.

The identification of a "partial" band in a conjugated system, which is due to the specific effect of a powerful chromophore, corresponds to the older interpretations of absorption spectra which assigned characteristic frequencies to the presence of particular groups. The appearance of such a partial band does not depend on the insulation of the chromophoric group concerned from the rest of the molecule, so that a fundamental oscillation through the molecule as a whole is prevented. The absorption spectra in the ultraviolet are in general characteristic of individual chromophores. Absorption in the visible region, where the period of the light is greater and the resonance time is shorter on account of the large resonance energies, is associated with conjugated systems acting as single oscillators.

The absorption of three cyanine dyes, studied by Brooker and Smith[1], is shown in Fig. 14 . The formulae of the dye ions (LXIV, LXV and LXVI), only one of the resonance structures being shown in each case, indicate that (LXVI) may be regarded as a composite of (LXIV) and (LXV). The ion (LXVI) has three nitrogen atoms capable of carrying a positive charge; with the charge on nitrogen atom

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[1] J. Am. Chem. Soc., 59, 67(1937)

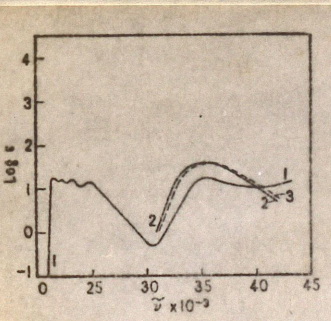
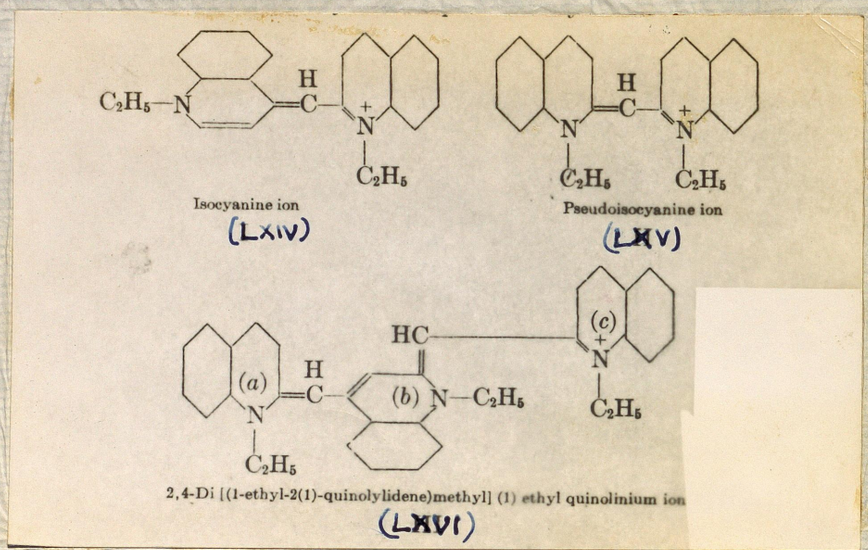


FIG. 13. Effect of insulation of carbonyl groups on the absorption. Curve 1, $CH_3COCOCH_3$ in hexane; curve 2, $C_2H_5COCH_2CH_2COC_2H_5$ in hexane; curve 3, CH_3COCH_3 in hexane (2 × ε).

(a) or (c), an oscillation through the whole molecule can be



pictured, and this fundamental absorption may be justifiably associated with the low frequency band at about 625 mμ in curve 3 representing (LXVI). The high frequency band in curve 3

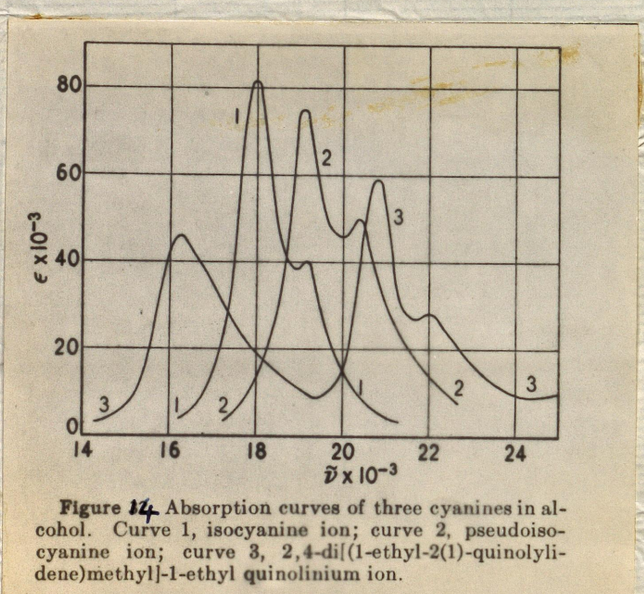


Figure 14. Absorption curves of three cyanines in alcohol. Curve 1, isocyanine ion; curve 2, pseudoisocyanine ion; curve 3, 2,4-di[(1-ethyl-2(1)-quinolylidene)methyl]-1-ethyl quinolinium ion.

is obviously similar to the maxima in curves 1 and 2 for the ions (LXIV) and (LXV) and represents a band of partial oscillation, corresponding to an oscillation in that part of the ion (LXVI) which is similar to the ion (LXIV) or (LXV), or to a merging of the two. The hypsochromic shift in the partial band for (LXVI) in comparison with the corresponding bands for (LXIV) and (LXV) is to be ascribed to the cross conjugation in (LXVI) which weakens the resonance, as explained later.

Oscillations along more than one axis.- In the "nearly linear oscillators", such as the polyenes, the polyphenyls and the cyanines, the large polarizability responsible for colour in the visible region is along one axis, and the major or x- axis will be more or less along the line of maximum extension; but in Malachite Green and other compounds in which the conjugated system extends in two dimensions, we are no longer dealing with even approximately linear oscillators. Two fundamental bands corresponding to the two axes of oscillation can sometimes be identified (x and y bands), the band of lowest frequency being conventionally called the x band. When a planar molecule does not possess a centre of symmetry, x and y bands are to be anticipated, but the location of the y band in the spectrum may be difficult on account of great differences in the intensities of the two bands, if the polarisability or electron mobility in one direction is much larger than in the other.

In the case of a few relatively simple and approximately linear molecules (p-azoxyanisole[1], diphenyloctatetraene and diphenyldodecahexaene[2]) for which x-ray data have indicated the position of the atoms in the crystals, it has been shown that, when the absorption of polarised light is examined, the maximum absorption is observed when the electric vector of the polarised light is roughly along the axis of the molecule.

A molecule having a high degree of polarisability in three directions can exhibit three fundamental bands (x, y and z bands) associated with the three axes, but few examples are available in which z bands have been characterised. The assignment of absorption bands to x and y axes of polarisation in a molecule has generally to be made on the basis of indirect and circumstantial evidence; but proof of the y band has been obtained in a few cases (e.g. Malachite Green) by two methods[2]. The first depends on the production of

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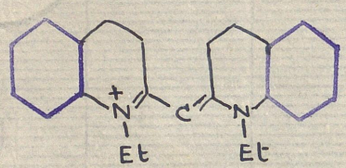
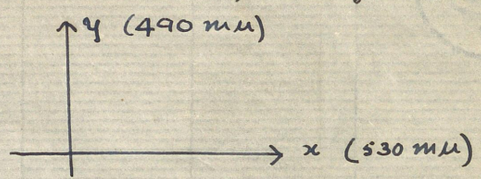
[1] Bernal and Crowfoot, Trans. Faraday Soc., 29, 1032(1933)

[2] Lewis and Bigeleisen, J. Am. Chem. Soc., 65, 2102(1943)

oriented molecules in a rigid solvent, and the second on the use of polarised fluorescence. In one case, pseudoisocyanine (LXVII), Scheibe[1] has been able to characterise x, y, and z bands definitely, and to relate them to the structure and orientation of the molecules. In very dilute aqueous solution, the dye shows

(LXVII)





an x band at 530 mμ and a y band at 490 mμ, but when more concentrated solutions in which pseudoisocyanine forms a fibrillar colloid are examined, a new narrow and very intense band appears at about

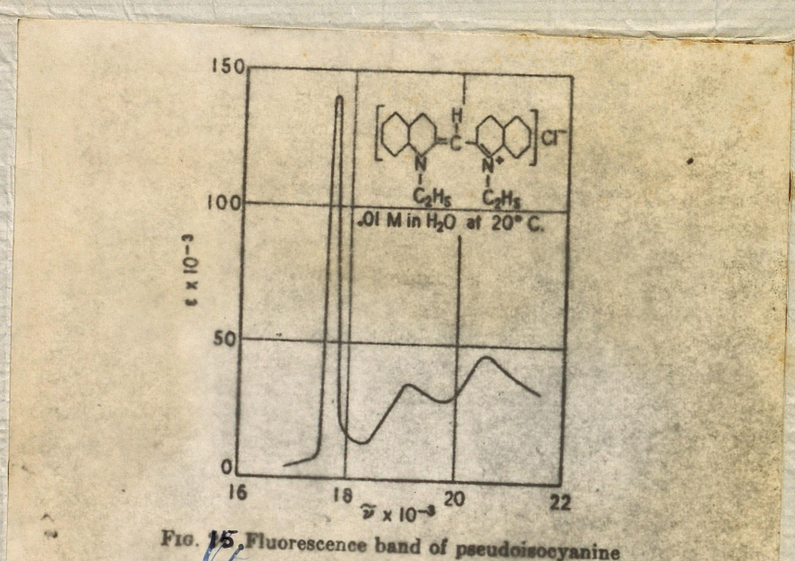


FIG. 15. Fluorescence band of pseudoisocyanine

570 mμ (Fig. 15). This is a z band, which arises from absorption along the length of the long threads of polymerised molecules, formed by the flat molecules lying face to face. There is an intermolecular electronic interaction between the flat molecules which are stacked together in a pile in the fibrils, and this interaction is responsible for the new band polarised linearly with the fibrils. Fig. 16 illustrates the arrangement of the pseudoisocyanine molecules responsible for three dimensional polarisation and the appearance of the x, y and z bands. The formation of ~~aa~~

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[1] Angew. Chem., 52, 631 (1939); see also Jelley, Nature, 139, 631 (1937).

coloured molecular complexes by aromatic compounds is apparently associated with this face to face alignment of the

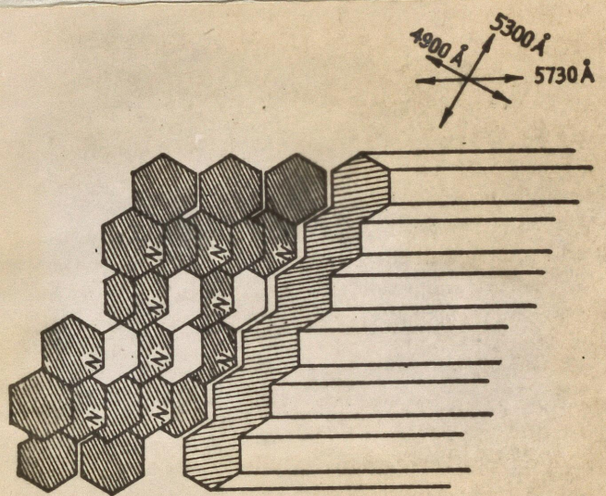

Figure 34. Absorption and structure of the polymer of pseudo-isocyanine.

flat molecules and an intermolecular resonance.

The part played by the π electrons in the long wavelength spectra has been shown in the case of hexamethylbenzene[1], which is a planar molecule. The absorption spectrum has been determined by using polarised light with the electric vector respectively parallel and perpendicular to the plane of the molecule, and the extinction is about a tenth in the latter case. Other examples of the directional properties of light absorption have been reviewed by Morton[2].

The long wave absorption in crystalline anthracene and naphthacene corresponds to light polarised in the molecular plane and along the line of greatest width of the molecule. This is also true of the absorption band of the fluorescein ion at 495 mμ (the x band); the emitted green fluorescence is also polarised along the same line. The ultraviolet absorption band (312.5 mμ) of the fluorescein ion corresponds to light absorption polarised along the short axis of the molecule (the y band); but light absorption by this band emits the same green fluorescence, so that the y oscillation excited by the absorption polarised along the

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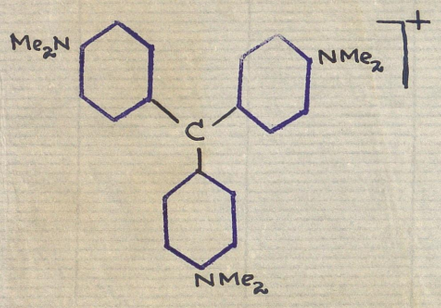
[1] Scheibe, St. Hartwig and Müller, Z. Elektrochem., 49, 372(1943).

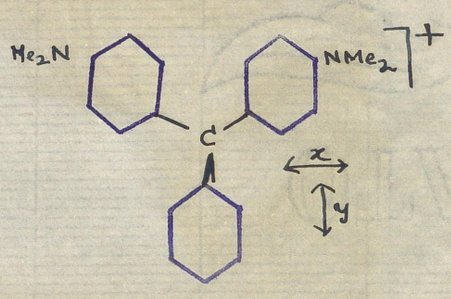
[2] loc. cit.

short axis is partly converted into the x oscillation, the energy of which then emits the green fluorescence.

In the ion of Crystal Violet ⟷ which has a centre of symmetry*, polarisability is the same in all directions of the plane, so that the x and y bands coincide. Malachite Green ⟷ on the other hand has marked dissymetry, and there are two well-



Crystal Violet ion



Malachite Green ion.

defined bands in the visible region (625 mμ and 423 mμ) Fig 17 ; curve 3). The x direction may be reasonably assigned as the direction of oscillation between the N atoms, and the y direction as the one involving the unsubstituted phenyl group. If the dissymmetry in the Malachite Green molecule is accentuated by

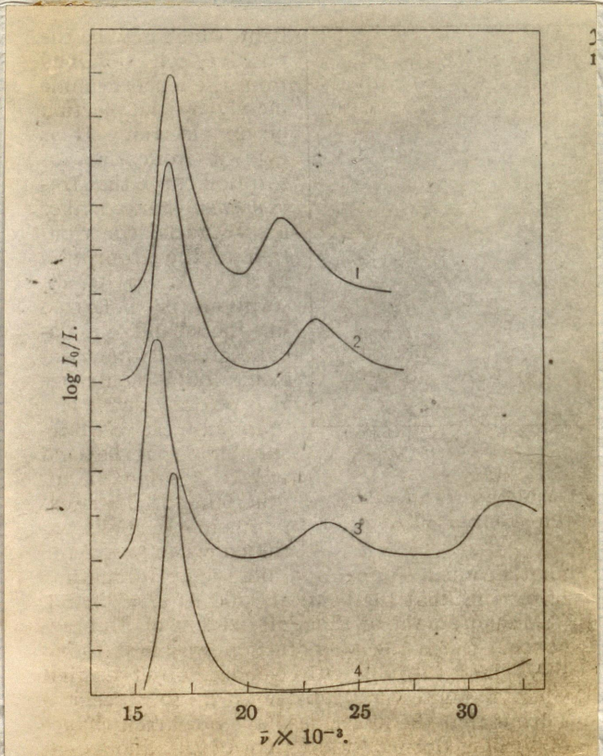


Fig. 2.—*x* and *y* bands of (1) *p*-methoxymalachite green, (2) *p*-methylmalachite green, (3) malachite green (identical with curve for acid green), (4) the ion of Michler's hydrol. All are at room temperature; (1), (2), (3) in ethanol; (4) in glacial acetic acid.

introducing a methoxyl or methyl group in the third phenyl group, the y band is shifted to lower frequency, while the x band

*This would not be true of the B isomer of Crystal Violet found by Lewis, Magel and Lipkin, J. Am. Chem. Soc., 64, 1774 (1942).

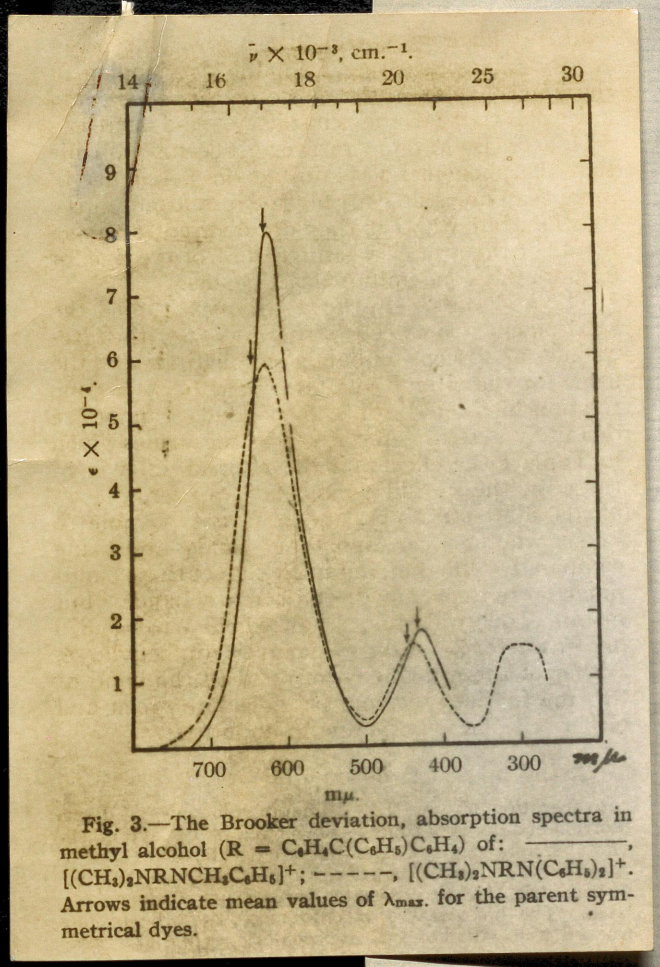
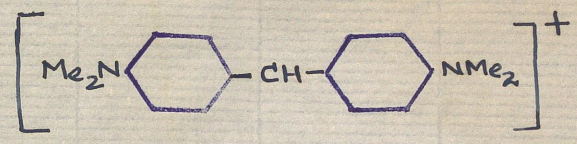


Fig. 3.—The Brooker deviation, absorption spectra in methyl alcohol (R = $C_6H_4C(C_6H_5)C_6H_4$) of: ————, $[(CH_3)_2NRNCH_3C_6H_5]^+$; – – – –, $[(CH_3)_2NRN(C_6H_5)_2]^+$. Arrows indicate mean values of $\lambda_{max.}$ for the parent symmetrical dyes.

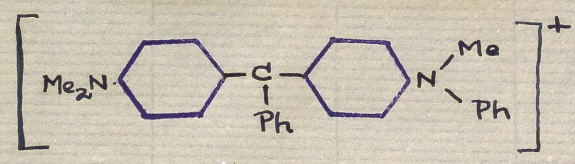
undergoes a slight shift in the opposite direction (Fig. 17 ; curves 1 and 2). Curve 4 in Fig. 17 represents the ion of Michler's hydrol (LXVIII) in which the unsubstituted phenyl group of Malachite



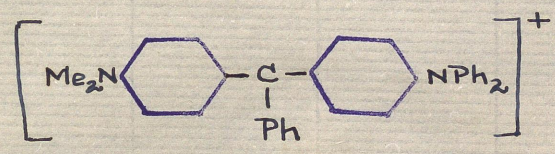
(LXVIII)

Green is replaced by a hydrogen; the scope of ~~os~~ oscillation in the y direction is greatly limited and the second band has become a very weak band in the ultraviolet.[1]

Diaminotriphenylmethane dyes have a spectrum between 800 mμ and 240 mμ consisting of three principal bands, x, y and x^1 (second order) bands . When one or more methyl groups in Malachite Green ~~is~~ are replaced by ~~the~~ phenyl groups, there is a hypsochromic displacement as would be expected from a consideration of the relative basicities of dimethylamine and diphenylamine. However, the values of λmax. for the x or y band of the unsymmetrically substituted analogues (LXIX) and (LXX) deviate very slightly from the calculated values; in Fig. 18 curves 1 and 2 respectively

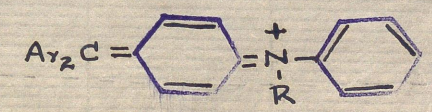


(LXIX)



(LXX)

represent the spectra of (LXIX) and (LXX), and the arrows show the mean of the wavelengths of the symmetrical dyes of which (LXIX) and (LXX) are the structural hybrids[2]. As Brooker has stated, the symmetry of these dyes is not definable in terms of the relative basicities of the nitrogen atoms concerned, and the resonance stabilisation of the relevant ring systems has to be considered. In the quinonoidal ion of a triphenylmethane dye, an N-phenyl group extends the conjugation as indicated in (LXXI) and this



(LXXI)

compensating factor results in the basicity of the N atom being

For footnotes see on the other side.

1 Tolbert, Branch and Berlenbach, J. Am. Chem. Soc., 67, 891 (1945). See also Branch, Tolbert and Lowe, ibid.

reduced to a much smaller extent than in the case of the N-phenylation of aniline.

The relation between the geometry of molecules and their spectral characteristics has been extensively studied in the case of the carotenoid pigments[1]. A natural all-trans carotenoid pigment is partly converted by heat or iodine into a mixture of cis-trans isomers, and the isomerization results in a decrease in the intensities and wavelengths of the absorption maxima in accordance with theory[2]. Among all the stereoisomers of a polyene, the all-trans form, possessing the extended coplanar structure, must have the greatest depth and intensity of colour. However, in a part of the spectral region, a new absorption maximum(the "cis-peak") appears when isomerisation to the cis-arrangement occurs at one or more of the ethylenic bonds, so that the shorter, folded molecule acquires a

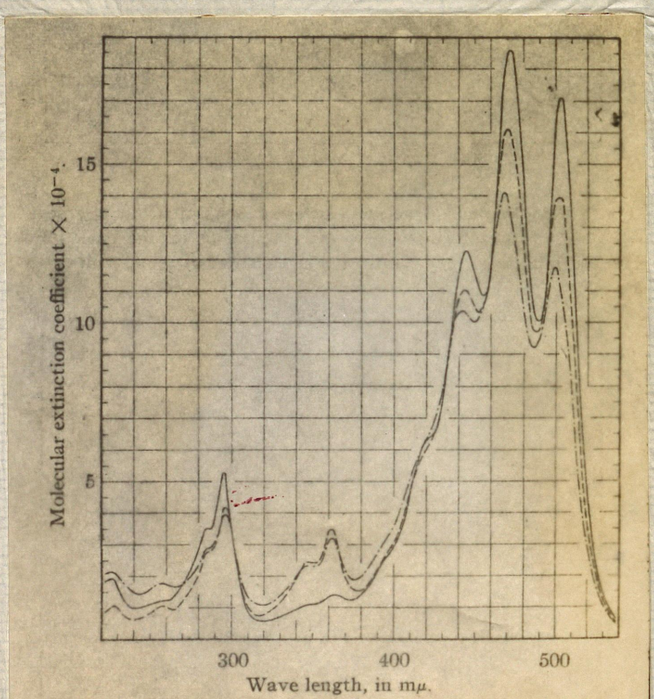


Fig. 3.—Molecular extinction curves of lycopene in hexane: ———, all-*trans* form; – – – –, after refluxing in the dark for forty-five minutes; ——, after iodine catalysis at room temperature.

breadthwise extension. The cis-peak at 360 mu for lycopene (Fig. 19) has maximum intensity in the case of neolycopene A (Fig. 20). Zechmeister and Pauling have proposed a theoretical interpretation of the cis-peak phenomenon, in which the observed absorption spectra of

[1] Zechmeister, Chem. Rev., 34, 267 (1944).

[2] Pauling, Fortschr. Chem. Organ. Naturstoffe, 3, 203 (1939); Mulliken, J. Chem. Phys., 7, 364 (1939); Rev. Modern Phys., 14, 265 (1942).

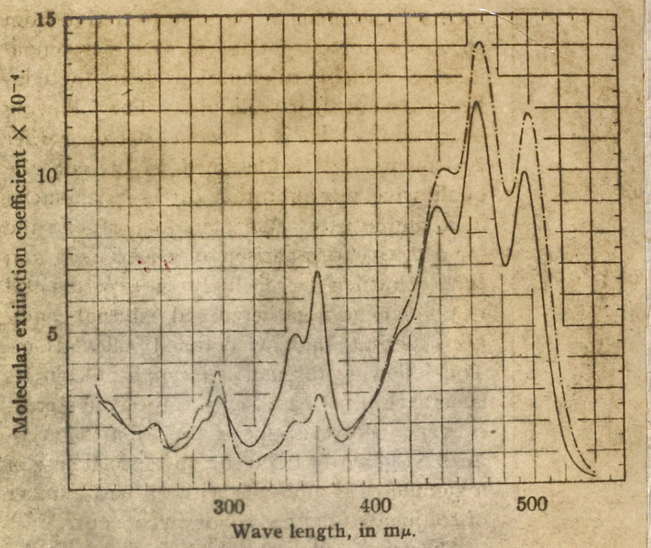


Fig. 6.—Molecular extinction curves of neolycopene A: ———, without iodine; – – –, on iodine catalysis.

the carotenoids are correlated with transitions from the normal electronic state to three excited electronic states (Fig. 21). The transition 0 ⟶ 1 corresponds to the fundamental absorption band

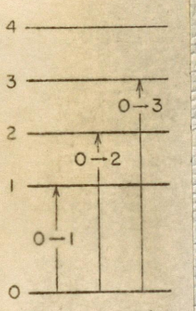


Fig. 9.—Electronic energy levels for a carotenoid molecule, with the transitions indicated corresponding to the three main absorption regions (0 ⟶ 1, fundamental absorption region; 0 ⟶ 2, "*cis*-peak" region or first overtone; 0 ⟶ 3, second overtone).

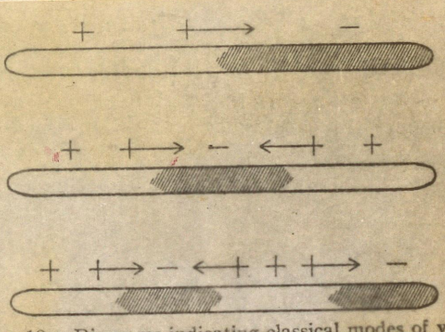


Fig. 10.—Diagrams indicating classical modes of vibration of mobile "unsaturation" electrons of the conjugated system along the chain. The three modes shown correspond to the three main regions of absorption of light by carotenoids (see for example Fig. 6).

(near 470 mu in Fig. 21 for lycopene), 0 ⟶ 2 to the cis-peak and 0 ⟶ 3 to the third band (near 290 mu). The bands are broad, and show a pronounced fine structure. Quantum-mechanical calculations indicate that the three transitions correspond to oscillation of electric charge along the unsaturated chain in the ways shown in Fig. 22 . The simple oscillation from end to end of the chain corresponds to the transition 0 ⟶ 1. The next mode of oscillation of the electrons is from the two ends of the chain to the middle,

and from the middle towards the two ends; the 0 ⟶ 2 oscillation therefore gives rise to no dipole moment, and hence to no absorption band, for the all-trans molecule, or any other molecule with a centre of symmetry. The molecule which is cis at the central double bond, represented diagrammatically in Fig. 23 , has a dipole moment for the transition 0 ⟶ 2 on account of its shape, the moment being

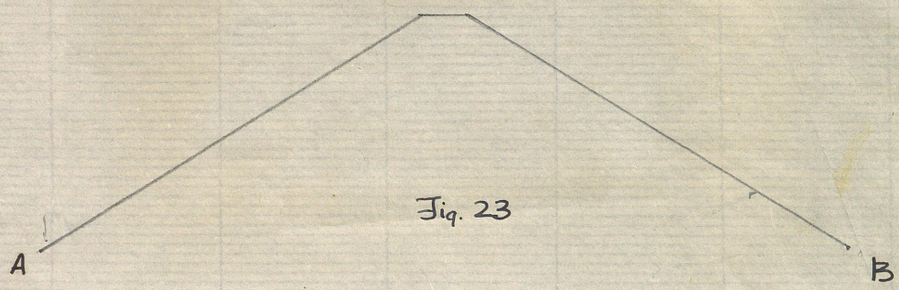
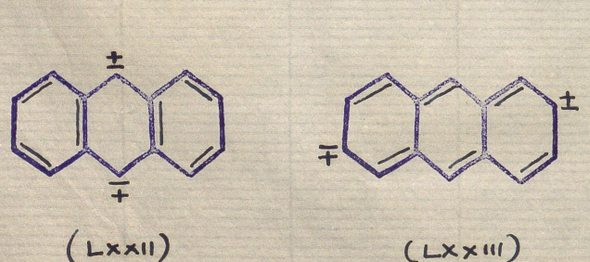


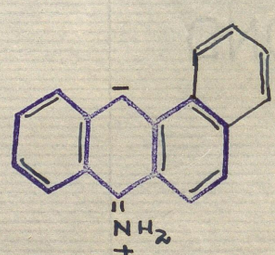
Fig. 23

perpendicular to the line AB. This isomer should show the strongest cis-peak among all the isomers, and is identified among the lycopenes with neolycopene, A. The cis-peaks for other isomers will be of lower intensity, and as a rough approximation, the intensity can be taken to be proportional to the square of the distance between the centre of the conjugated system and the mid-point of the straight line between the two ends.

Chemical evidence of the vectorization of the electronic activations within a molecule and the consequent development of two independent absorption bands has been obtained by Jones[1] in the case of polynuclear aromatic hydrocarbons. In such planar molecules (e.g. chrysene[2]) the absorption is at a maximum when the plane of polarisation of the light is in the plane of the molecule, and at a minimum when the two are normal to each other. It is seen from a consideration of the electronically excited states such as (LXXII)



(LXXII) (LXXIII)

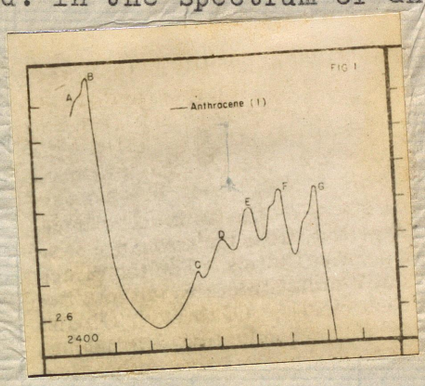


(LXXIV)

[1] J. Am. Chem. Soc., 67, 2127 (1945).

[2] Krishnan and Seshan, Raman Jubilee Vol., Ind. Acad. Sci., 487(1938)

and (LXXIII) for anthracene that a vectorisation of the electrical moment, oriented vertically and horizontally in the plane of the molecule, may be anticipated. In the spectrum of anthracene (Fig. 24) the



short wave group of maxima (A, B) and the series of maxima (C - G) appear to be associated with these two dimensional polarisations, being y and x bands in the Lewis nomenclature. Comparing the spectra of 1:2-benzanthracene and its 10-amino derivative, in which the 10-amino group effects a marked bathochromic shift, together with loss of fine structure, of the x-band, Jones suggests that the x-band is associated with an electrical moment oriented approximately in a vertical direction, since the 10-amino group (cf. LXXIV) should have an auxochromic effect with reference to a vertical polarisation.

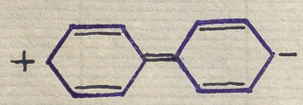
Second order bands.- In the quasi-classical theory of Lewis and Calvin, excitation by light produces an oscillation of the electron cloud in a definite direction along the x or the y axis. This may be regarded as a (quantized) alternating current along the axis. A higher excitation results in a second oscillation of greater amplitude. There are cases of "forbidden" excitations to states which are not in the same class as the ground state (e.g. having a different multiplicity), but Lewis has pointed out that such transitions are not found in the ordinary spectra of dyes. In the absorption curves of various carotenoids there is a band in the ultraviolet which Lewis and Calvin consider to be a second order band (x^1 band). A characteristic band of short wavelength in the spectra of the diphenylpolyenes is likewise regarded as second order absorption[1]. The x^1 bands which, like the first order bands,

[1] See also Heilbron, Jones and Raphael, J.Chem.Soc., 139 (1944).

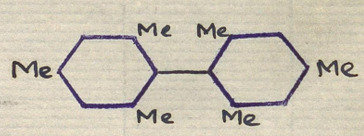
belong to the fundamental oscillation of the molecule as a whole, are ordinarily obscured by the bands of partial oscillation. However, in dyes for which the x-bands are in the red region, definite evidence of x^1 bands has been obtained. Lewis and Bigeleisen[1] have found that the eight dyes in Table II show unambiguous x^1 bands. The x^1 band in the curves for Fluorescein, Rhodamine B and Malachite Green (see Fig. 17, curve 3 for the last curve) was identified and differentiated from the neighbouring y band by the method of fluorescent polarisation. The dyes in Table II are a remarkable series in which ϵ^1/ϵ is always large, and $\bar{\nu}'/\bar{\nu}$ increases almost regularly with increasing wavelength of the band. This is the trend predicted by Lewis and Calvin from their potential diagram for electronic displacements in dye molecules that have left and right symmetry.

Insert Table II →

Steric factors, resonance and colour.- Since the mobility of electrons, which can lead to oscillations through a molecule as a whole and to a consequent increase in light absorption, depends on the extent of the conjugation, steric factors which diminish or inhibit the conjugation will have a corresponding effect on light absorption. This postulate regarding the relation between decrease in light absorption and the steric weakening or inhibition of resonance has been verified in many cases. The absorption of diphenyl is concerned with the contribution made by the structures such as (LXXV)



(LXXV)



(LXXVI)

to the resonance states of the molecule. A planar configuration is necessary for the resonance to be completely effective, and there is evidence to show that in the absence of steric hindrance the molecule tends to be planar. When the two benzene rings are forced into different planes as in dimesityl (LXXVI)[2], the absorption corresponds to that of mesitylene and not to diphenyl. The alteration in the absorption spectrum is more pronounced when the blocking groups

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[2] Pickett, Walter and France, J. Am. Chem. Soc., 58, 2296 (1936)

[1] J. Am. Chem. Soc., 65, 2107 (1943)

Table II

	Solvent	$cm.^{-1}$	$cm.^{-1}$		
1 Fluorescein	Dilute alkali	20400	35100	1.72	0.144
2 Rhodamine B	Dilute alkali	18000	32300	1.80	0.137
3 Crystal violet (A)	Ethanol	16940	32900	1.94	0.258
4 Michler's hydrol	Glacial acetic acid	16670	33300	2.00	0.165
5 Malachite green	Ethanol	16000	31700	1.98	0.197
6.Methylene blue	Ethanol	15200	30700	2.02	0.109
7 Capri blue	Ethanol	15100	32750	2.17	0.153
8 Methylene blue (D^1H^{++})	3M H_2SO_4	13500	29500	2.20	0.110

in the o-positions are larger[1].

From the absorption curves of trans- and cis-stilbene (Fig. 25)[2] it will be observed that the cis-compound absorbs at higher frequency and lower intensity than the trans. For trans-stilbene the molecule

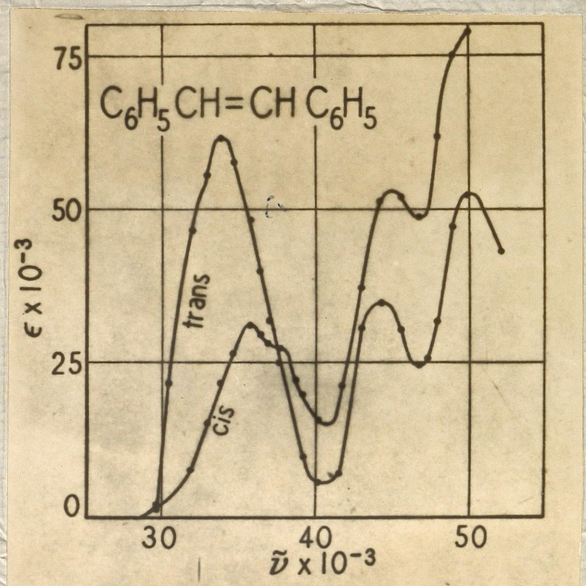

Figure 25. Absorption curves of the *cis* and *trans* forms of stilbene.

is coplanar, and the resonance effect is shown by the position and intensity of the fundamental band. Coplanarity is prevented in cis-stilbene by the interference of the o-hydrogen atoms and as a result of this weakening of the optically important resonance, the light absorption is diminished.

These inter-related factors of resonance, coplanarity and colour are also concerned in the absorption of dyes by cellulose (see Chapter ___).

Cross conjugation and colour.- When the colour of a substance is associated with a resonance along a certain path in the molecule, the frequency of absorption will be increased by any influence which diminishes the optically important resonance, and the frequency will be decreased by any influence which increases such resonance. The triene (LXXVII) absorbs at a much lower frequency than the linear

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[1] Williamson and Rodebush, J. Am. Chem. Soc., 63, 3018(1941).
[2] Smakula and Wasserman, Z. physik. Chem., A155, 353 (1931).

triene (LXXVIII). In (LXXVIII) the opening of the central double bond

$R_2C = CH - \underset{\underset{CH_2}{\|}}{C} - CH = CR_2$ (LXXVII)

$R_2\overset{+}{C} - CH = \underset{\underset{CH_2}{|}}{C} - CH = CR_2$ (LXXVIIC)

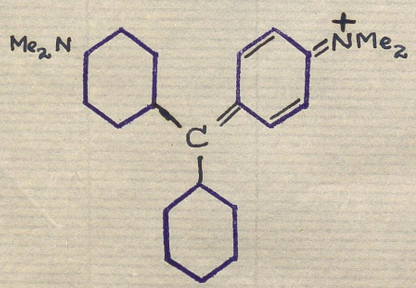
$R_2C = CH - \underset{\underset{CH_2}{|}}{C} = CH - \overset{+}{C}R_2$ (LXXVIIB)

$R_2C = CH - CH = CH - CH = CR_2$ (LXXVIII)

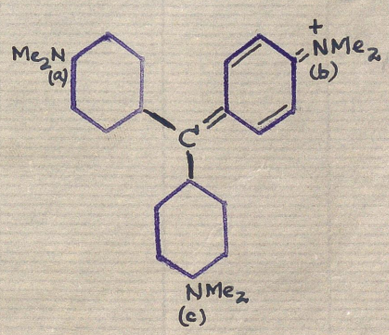
forces a positive or negative charge into the rest of the molecule. The former case is illustrated in (LXXVIIB) and (LXXVIIC), and the increase in the charge, with the oscillation of which the colour is associated, leads to the bathochromic effect.

The hypothesis that colour depends, not on the total resonance in a molecule as represented for instance by the "resonance energy", but on the optically important resonance in which certain ionic structures contribute to the resonance state of the molecule, gives a satisfactory (if merely qualitative) explanation of many observations regarding the depths of colour of related dyes, their colour changes by the addition of acid or alkali, etc.

The deeper colour of Malachite Green (LVII) (λmax. 623 mμ) in comparison with Crystal Violet (LXXIX) (λ max 590 mμ) was inexplicable in terms of the older theories of colour, considering that the latter dye has an extra auxochrome. From the resonance point of view, there are three equivalent contributing structures in the ion of (LXXIX), while there are only two of major importance for (LVII), so that there is greater total resonance in (LXXIX). However, the resonance which is associated with the colour is more effective in the Malachite green ion. If it is assumed that the fundamental band is



(LVII)



(LXXIX)

due to electronic oscillation in one direction, the phase in the oscillations of the Crystal Violet ion in which the positive charge is on the nitrogen atom (c) will not contribute to the oscillations between (a) and (b). It may be stated roughly that two-thirds of a positive charge will be available for the uniaxial oscillation associated with the fundamental band in the case of Crystal Violet, while a whole charge will be available for the corresponding oscillation in Malachite Green; hence the deeper colour of the latter.

DEGENERACY OF LIMITING STRUCTURES IN RELATION TO ABSORPTION.

If a system can be described by more than one state of the same energy (e.g. the two states of the hydrogen molecule), it is said to be "degenerate". The most effective resonance occurs between totally degenerate states, and the degree of degeneracy depends on the number of identical energy states and the energies of the other states which contribute to the resonance.

Deep colours are associated with dyes to which structures having a high degree of degeneracy may be assigned. Conversely, if the degeneracy of the important resonance structures which may be formulated for a dye is diminished by decreasing the symmetry of the molecule, the result is absorption at shorter wavelengths. In symmetrically constituted dyes such as Malachite Greens, the extreme low-energy structures are identical, and the quantum-mechanical degeneracy of the structures is complete. Brooker has studied a series of cyanine dyes for which it is not possible to devise two identical limiting structures, and he[1] has shown that nonidentity of the extreme resonance structures may have a very profound influence on the absorption of a dye.

Vinylene shift.- Like the diphenylpolyenes, there are other types of compounds containing conjugate chains, in which it is possible to increase the length of the chain by adding further vinylene (-CH=CH-) groups. The dyes therefore possess the general form A-(CH=CH)$_n$-B, and as explained in the case of the diphenylpolyenes,

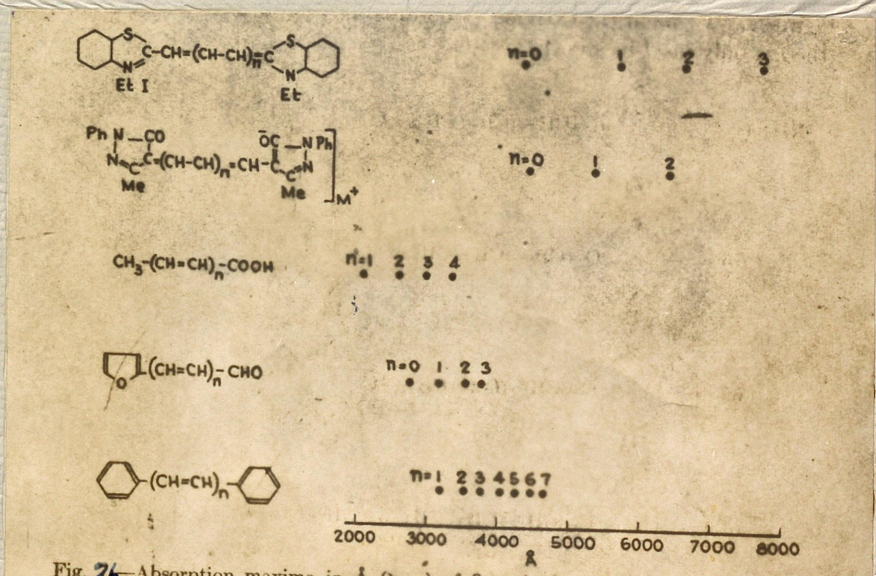


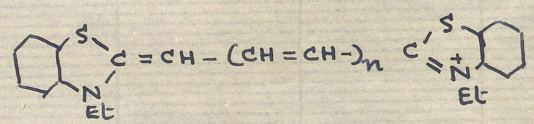
Fig. 26—Absorption maxima in Å (λ_{max}) of five vinylene homologous series. For the cyanine and oxonol dye series occupying the first and second rows, the values are for solutions in methyl alcohol. For the series $CH_3(CH{=}CH)_nCOOH$, the values are for solutions in ethanol [Hausser *et al., Z. physik. Chem.*, **B29, 371** (1935)]. For the series $C_4H_3O(CH{=}CH)_nCHO$, the values are for solutions in ethanol [König, *Ber.*, **58,** 2559 (1925)] and for the series $Ph(CH{=}CH)_nPh$, the values are for benzene solutions [Hausser *et al., Z. physik. Chem.*, **B29,** 384 (1935)].

a bathochromic shift takes place as n is increased. This vinylene bathochromic shift, however, varies in amount from series to series in which A and B are differently constituted. The absorption maxima of five such series[1] are shown in Fig. 26. The first two series (~~I and II~~)

[1] Reviews of Modern Physics, 14, 275(1942); and loc. cit.

represent symmetrical polymethine dyes, in which the successive shifts are large, and the shift per vinylene unit is approximately constant. These two series are non-convergent. In the last three series ~~(III, IV, V)~~, which are described as convergent, the bathochromic shift per vinylene unit is much smaller than in the non-convergent series, and the successive shifts ~~per vinylene~~ tend to diminish as n increases. Convergence of the maxima therefore results in the case of a vinylene series for which the extreme low energy structures are non-degenerate.

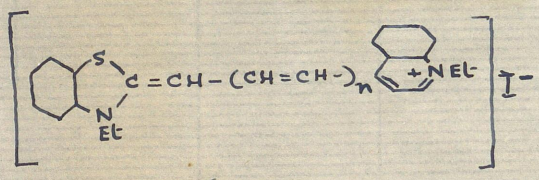
Quantum-mechanical considerations applied to a system of the type of (L×××) have shown that, as the chain is lengthened, the resonance splitting of the identical energy levels of the limiting structures decreases, as represented diagrammatically in Fig. 27.



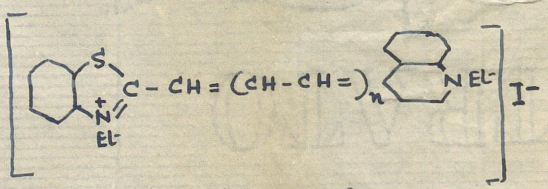
(L×××)

The resonance stabilization therefore diminishes as the series is ascended, clearly demonstrating that the depth of colour is not to be associated with the "strength" of the resonance.

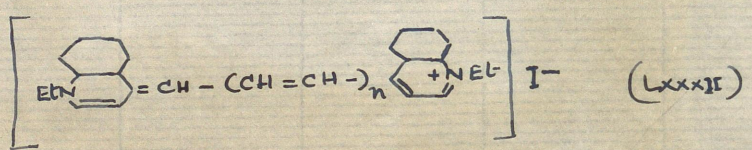
For many unsymmetrical cyanines such as (L×××), λmax. lies very close to the arithmetical mean of the values of λmax. for the



(L×××I A)



(L×××I B).



(L×××II)

two symmetrical dyes (L×××) and (L×××II), of which (L×××I) may be regarded as a structural hybrid. If, however, a nitro group is introduced in the 6-position of the benzthiazole ring in (L×××I), the absorption maxima of the new dyes (L×××III) no longer agree with the calculated mean of the maxima for (L×××II) and (L×××IV), of which (L×××V) is a structural hybrid. There is a considerable deviation in λmax. between

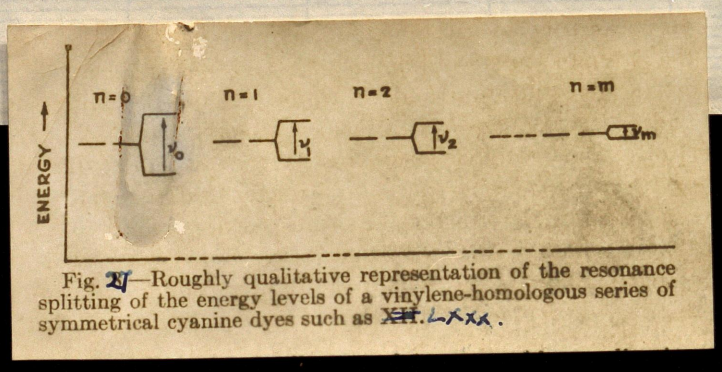
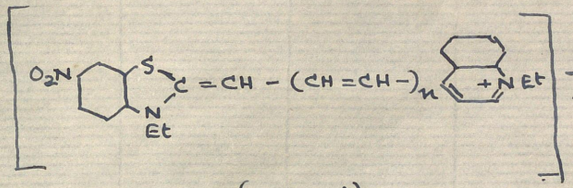
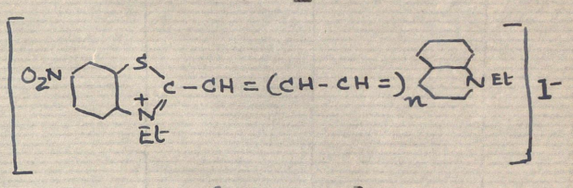


Fig. 27—Roughly qualitative representation of the resonance splitting of the energy levels of a vinylene-homologous series of symmetrical cyanine dyes such as ~~XII~~. L×××.

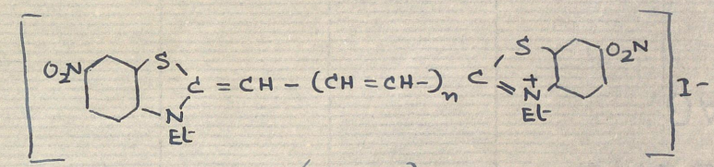
the observed and calculated values. The observed absorption is at shorter wavelength, and the deviation increases with n. When



(LXXXIII A)



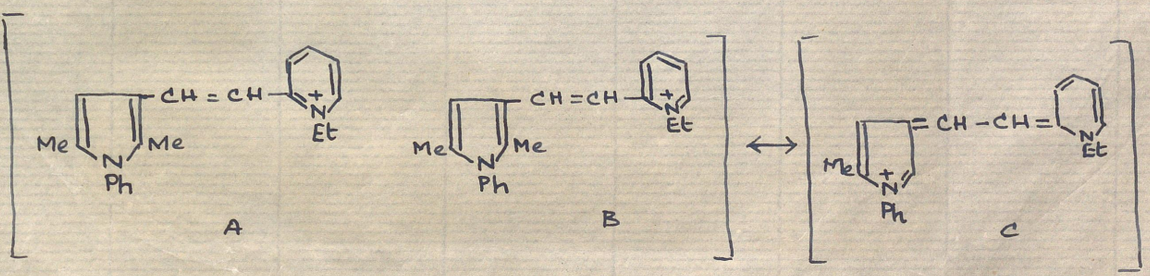
(LXXXIII B).



(LXXXIV).

n = 2, the deviation is so great (675A) that the unsymmetrical dye absorbs at shorter wavelength than either of the parent symmetrical dyes. Brooker has shown that the deviation is due to the unbalance of the basicity of the heterocyclic nuclei in (~~VIII~~ LXXXIII), as a result of the lowering of the basicity of the benzthiazole system by the introduction of the nitro group. The more strongly basic ~~xxx~~ quinoline ring exercises a more powerful attraction on the positive charge, so that structure A for (~~VIII~~ LXXXIII) becomes the dominant structure, and produces a convergent series.

Additional-double-bond stabilization of rings.- The greater attraction of one of the heterocyclic rings for the positive charge in an unsymmetrical cyanine, which determines the "Brooker deviation", is not to be identified with basicity in the usual sense of proton affinity, although they are related. By considering the principal resonance structures of the ion of the unsymmetrical dye, e.g. in the case of (~~X~~ LXXXV A, B and C), it is seen that (A) and (B) comprise a



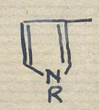
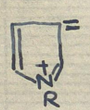
(LXXXV).

closely related set of structures which together contribute to the pyridinium formulation and render it of lower energy than the pyrrolinium structure. The system thus becomes ~~more~~ non-degenerate, and

absorption occurs at markedly shorter wavelength than that calculated.

The extra stabilization of the structures (A) and (B) is essentially due to the benzenoid stabilization of the pyridine ring; in (C) the uncharged pyridine ring has a low resonance stabilization like dihydrobenzene. Brooker refers to the extra stabilization resulting from the entry of an additional double bond into the ring as adbs (additional-double-bond stabilization). In a symmetrical cyanine the adbs of each ring is obviously the same; and unsymmetrical cyanines such as (LXXXI) which show no deviation are those in which the two rings have the same or nearly the same adbs. Increasing divergence in the values of adbs for the ring systems should give increasing deviation. Examining a large number of unsymmetrical cyanines in which one heterocyclic ring was unvaried and the other was one of fifteen different heterocyclic systems, Brooker found that the deviations, which varied from 45 to 855A, were in the order of increasing adbs, as predicted from a study of the resonance characteristics of the nuclei.

The adbs concept is not altogether satisfactory, since for instance in passing from (LXXXVI A) to (LXXXVI B) there is no increase in

(A)   (B).

(LXXXVI)

the number of double bonds within the ring[1]. Brooker has more recently[2] suggested the use of the expression "N^{IV} minus N^{III}" for the difference in resonance stabilization between the rings with 4-covalent and 3-covalent nitrogen.

The effect of replacing one heterocyclic nucleus by another in the cyanines is governed by another generalisation, the sensitivity rule: where a change of structure produces a small effect on the deviation of a symmetrical dye, the same change in structure produces a much greater effect on the deviation of a highly

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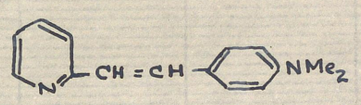
[1] Brooker, private communication

[2] J. Am. Chem. Soc., 67, 1881 (1945).

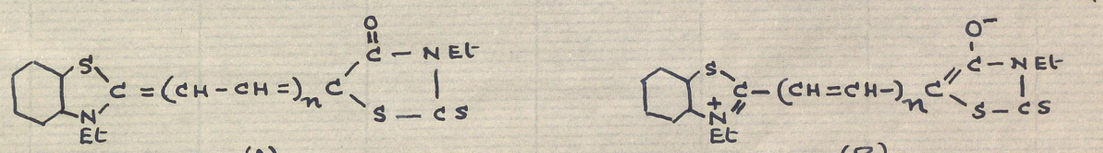
unsymmetrical dye. In other words, the effect on the deviation is greater the less the degeneracy of the extreme structures and the greater the deviation of the compound undergoing the change.

Brooker has shown that the conclusions reached in his study of the unsymmetrical cyanines are applicable to other convergent series, such as the styryl dyes (LXXXVII). The merocyanines (LXXXVIII) comprise by definition a nitrogen heterocycle linked to a moiety



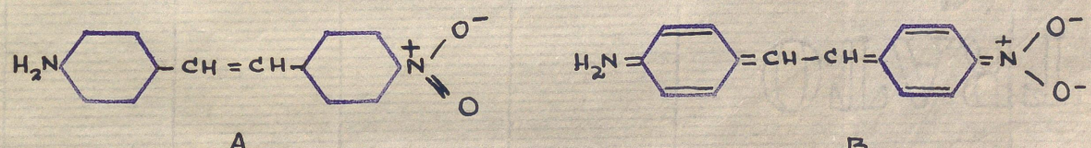
.... (LXXXVII)

which contains a carbonyl group and which may or may not be cyclic. The absorption is accounted for by the resonance (A) ⟷ (B). The structure (B) is a dipole which should normally have considerably higher energy than (A); but both the heterocyclic rings have an additional double bond in the zwitterion structure, and this adbs in the two rings offsets the effect of the dipole to a greater or less extent. It is also interesting to note that, while high adbs of the nitrogen heterocycle corresponds roughly to high basicity, high adbs of the ring containing the C=O group corresponds to high acidity.



(LXXXVIII)

The adbs of rings is a useful consideration for assessing the relative stability of resonance structures, and this treatment of the merocyanines is applicable to other types of dyes involving resonance between uncharged and dipolar structures. Thus in 4-nitro-4'-aminostilbene (LXXXIX) both the benzene rings have higher resonance stabilization in the uncharged structure (A), and the absorption

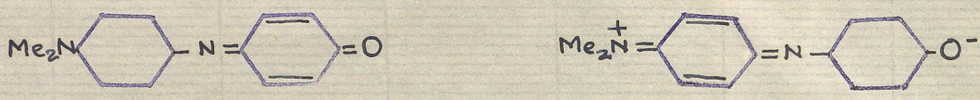


(LXXXIX)

is at relatively short wavelength[1]. In Phenol Blue ⟷ one of

[1] Calvin and Buckles, J. Am. Chem. Soc., 62, 3324(1940); Brooker and Sprague, ibid., 63, 3203 (1941).

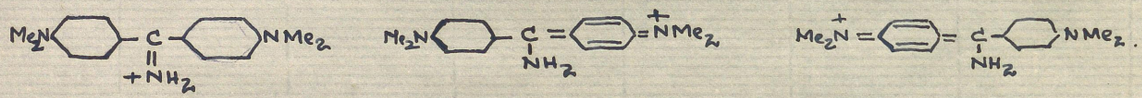
several factors involved in the depth of the colour of this comparatively simple molecule is that the resonance stabilization of the two benzene rings taken together is the same in both the uncharged structure (A) and the polar structure (B)[1].



(A) (B)

Phenol Blue.

The relatively weak colour of Auramine ⟷ is a related problem[2]. The ionic charge may be shared between the 3 nitrogen atoms (⟷ A, B and C), and apart from other considerations[3], it is clear that the structure (⟷ A) will be strongly favoured on account of both the benzene rings being in the benzenoid state, and



(A) (B) (C)

Auramine.

Auramine therefore absorbs at relatively high frequency. When the amino group is acylated, the characteristic positive charge is transferred almost entirely to the dimethylamine group, so that structures B and C are stabilised and the dyes are blue[4].

The influence of a benzene ring in a chromophoric chain is in general to inhibit resonance along the chain, unless the effect is compensated for by other factors. The reactivity of groups and the colour of many organic compounds often become explicable when the relative contributions of the benzenoid and quinonoid structures to the resonance of the molecule are considered.

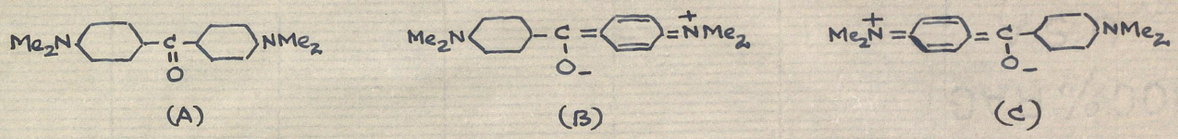
[1] Brooker and Sprague, ibid., 63, 3214 (1941).

[2] Brooker and Sprague, ibid., 3211

[3] Lewis and Calvin, loc. cit.

[4] Taylor and Baker "Sidgwick's Organic Chemistry of Nitrogen", p. 96, Clarendon Press, Oxford, 1937.

One example is the colourless character of Michler's ketone (xc). In the resonance (A, B, C) which would determine the absorption

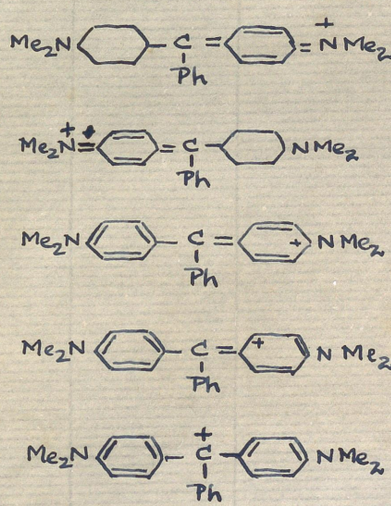


(A) (B) (C)

(xc).

characteristics of the substance, the dominant structure will be A, in which both the rings are benzenoid. There is the further consideration of the energy of charge separation in structures B and C, which will be another factor diminishing their contribution to the resonance state of the molecule.

Depth of colour in relation to the energy difference between extreme and intermediate structures.- As Adams and Rosenstein[1] and Bury surmised, the intense colour of a dye such as Malachite Green is associated with the resonance structures (A) and (B). The dye



..... (A)

..... (B)

..... (C)

..... (D)

..... (E).

Malachite Green.

ion therefore has two identical low energy structures like benzene, with the difference that in the dye the two extreme structures are derived by the movement of a charge from one end of the molecule to the other. Pauling[2], however, has referred to the remote possibility of such a movement of an electron from end to end of a long conjugated chain, and he has suggested a series of intermediate steps, such as

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[1] loc. cit.

[2] Proc. Nat. Acad. Sci., 25, 577(1939).

(C, D and E), involving carbonium ions. These are much less stable than the ammonium ion structures; but by resonance interaction among these various structures, the difference in the energy levels of the ground state and the first excited state is small. The result is the long wave absorption indicated by the green colour; and with the high ~~p~~ probability of the transition due to the large moment associated with it the intensity is also high.

When the absorption characteristics of a molecule are studied by taking intermediate structures into account in addition to the extreme resonance structures, as suggested by Pauling, one reason for the difference in absorption ~~is~~ between closely related dyes becomes apparent[1]. Two symmetrical cyanine dyes (~~XIII~~ XCI) and (~~XIV~~ XCIII) of the same chain length are compared in Fig. 28 The dye (~~XIII~~ XCII) of the upper

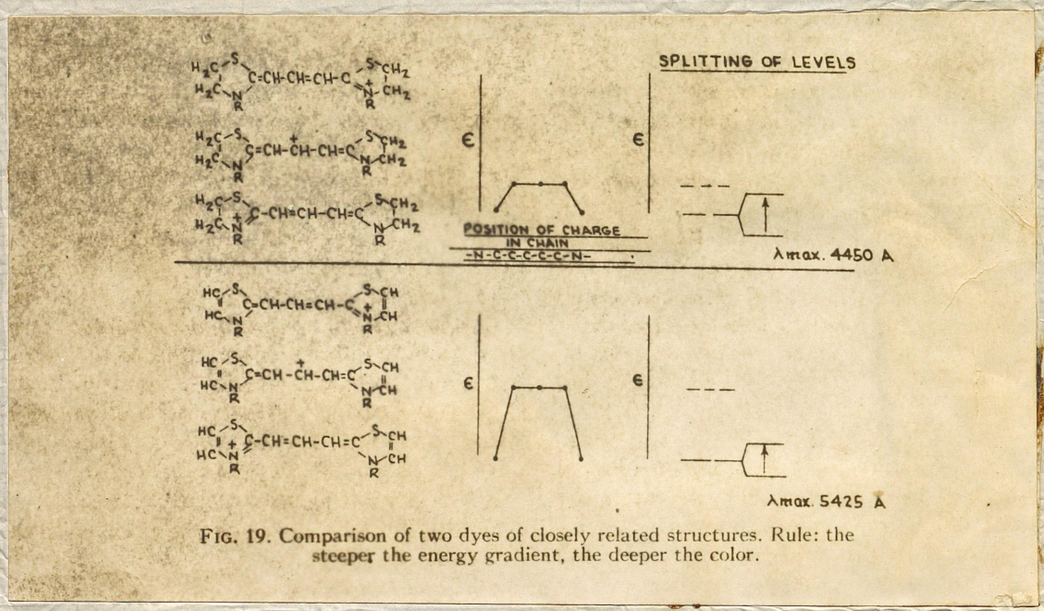

FIG. 19. Comparison of two dyes of closely related structures. Rule: the steeper the energy gradient, the deeper the color.

formulae contains two thiazoline nuclei, and the other (~~XIV~~ XCIII) two thiazole nuclei. In each case, the two limiting structures are formulated, together with one intermediate structure. In (~~XIII~~ XCII) the carbonium structure (B) is not much higher in energy than the ammonium structures (A)and (C); the reduction in the resonance stabilization in the ring when the positive charge is transferred from N to C is not very great. Resonance splitting of the energy levels therefore will be relatively large, corresponding to the

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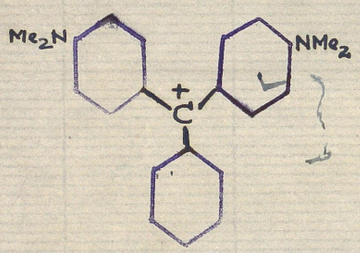
1 Brooker, loc. cit.

absorption of light of shorter wavelength; the observed λ max. is 445 mμ. In (XIV), on the other hand, passage from structure (A) to the carbonium structure (B) involves a considerable reduction in the resonance stabilisation of the ring from which the positive charge is removed. The energy of (B) is therefore higher, relative to the extreme structures (A) and (C), than in the case of the thiazoline dye (XIII). Consequently, the resonance splitting of the energy levels is smaller in (XIV), and the absorption is at longer wavelength (542.5 mμ).

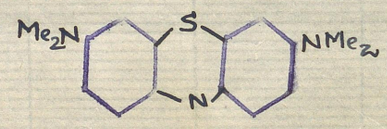
As a rule, among symmetrical dyes of closely related structures, the deeper will be the colour, the steeper the gradient between the energy of the extreme resonance structures and the energy of the intermediate structures.

USE OF QUASI-CLASSICAL METHODS FOR CALCULATING ABSORPTION SPECTRA

The functional nature of the curves obtained by plotting the wavelength of maximum absorption against the number of double bonds in the case of certain polyenic compounds and symmetrical cyanines has been discussed earlier in terms of the Lewis-Calvin quasi-classical theory. The theory has also offered a qualitative solution of many problems concerning the colour of dyes, and in a recent extension of his ideas to a large family of dyes represented by the skeleton formula (XCV), Lewis[1] has succeeded in calculating



Malachite Green (XCIII)



(XCIV)

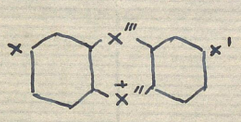
the wavelength of the main absorption band by two rules. In the case of over 70 dyes the difference between the calculated and observed values was less than 3 mu. Where the discrepancies were larger, they were explicable by the amplifications which had to be adopted in obtaining the constants required for the determination.

The rules are that (1) The wavelength is always greater, the greater the fraction of the characteristic positive charge on the auxochromes; and (2) the effect of various groups on wavelength is additive. The second rule is empirical, and both the rules are obviously inapplicable to such large and important groups of dyes as the azo, indigoid, and anthraquinone dyes.

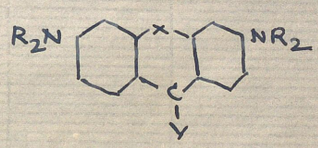
According to the Lewis theory, an excited state produced by the absorption of light is characterised by an oscillation of the electronic cloud along some axis of the molecule, and in Malachite Green (XCIII) the first absorption band (x band) corresponds to

[1] J. Am. Chem. Soc., 67, 770 (1945).

a horizontal oscillation. The characteristic positive charge formally assigned to the central carbon atom in (CXCIII) is distributed by resonance to various parts of the molecule, chiefly to the two NR_2 auxochromes. Since all the molecules in this family have about the same horizontal dimension, it is postulated that the wavelength of the λ band depends solely on the fraction of the characteristic charge on the two auxochromes. Any influence which increases this charge increases the wavelength, and any influence which decreases the charge decreases the wavelength. It can be readily seen that the rule is qualitatively in agreement with available data. Thus when X^{111} is O, S, or NR, there is a shift towards lower values of wavelength, due to the basic character of these groups; they



(XCV)



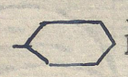
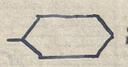
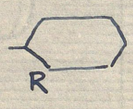
(XCVI)

acquire part of the characteristic charge and leave less available for the auxochromes. A strong positive effect is noticed when at X^{11} we replace CR by N. In the former type (CXCII) represents one of the important resonance structures of the molecule; but in Methylene Blue (CXCIV) will only make a very minor contribution to the resonance on account of the fact that nitrogen has much less tendency than C carbon to act as an acid, and for Methylene Blue λ = 665 mμ. When a proton is added to the central nitrogen in Methylene Blue, any characteristic charge remaining on the nitrogen is driven into the rest of the molecule, so that for Methylene Blue in strong acid λ = 742 mμ.

The observation that any change in X and X^1, or in X^{11} or X^{111} produces the same change in wavelength, regardless of the character of the rest of the molecule (CXCV), has enabled Lewis to obtain additive constants by means of which known absorption maxima could be correlated and new ones calculated. Taking NR_2 as the standard auxochrome, ignoring the minor changes in wavelength due to various alkyl and aralkyl groups, and taking as the standard dye a dye (CXCVI)

of the Malachite Green type (~~XCVI~~; in which X is absent), the following constants have been computed for various structural changes introduced in a dye of the general form (~~XCVI~~).

Table ~~III~~.

Structural change in (~~XCVI~~)	Shift in λ in mμ
Replacement of R by H	-13
Replacement of both NR_2 by O^-	-69
X = O or S	-72
X = NR	-157
Replacement of CY by N	+108
Y = 	+14
Y = 	+ 6
Y =  (R = Me, Cl, etc.)	+11

Although according to chemical evidence O^- is more basic than NH_2, the two prove to be about the same as auxochromes in this series of dyes. When the p-position in the unsubstituted phenyl group of Malachite Green (~~XCIII~~) is occupied by $\overset{+}{N}H_3$ or $\overset{+}{N}R_3$, the coulombic effect is to drive a part of the characteristic charge towards the NR_2 groups, and there is an increase in wavelength. When the p-position is occupied by SO_3^-, the coulombic effect is in the opposite direction, but it is more than offset by the conjugation of the acid group, which tends to drive part of the characteristic charge towards the NR_2 groups. This effect, however, is less than in the case of the NO_2 group. An o-substituent in the unsubstituted phenyl group of Malachite Green has an interesting steric effect; it forces the phenyl group away from the nearly coplanar configuration and diminishes its part in the general resonance, so that the positive charge on the NR_2 groups is increased with a consequent increase in wavelength.

The only class of dyes in which Lewis found a marked discrepancy between the observed and calculated value of wavelength was the acridine type (~~XCVI~~; X = N; Y = H). This is also the only

class in the whole family of dyes of the general formula (~~I~~ XIV) in which there is a large part of the characteristic positive charge on both X^{II} and X^{III}. It is therefore likely that in the acridine dyes the electronic oscillation of lowest energy, corresponding to the x band, is not the horizontal but the vertical one. The calculated values would then be not for the (vertical) x* band, but for the (horizontal) y band. In fact, for Acridine Yellow (3:6-Diamino-2:7-dimethylacridine hydrochloride), Formanek found a second band at 417 mu in close agreement with the value of 411 mu calculated by Lewis.

QUANTUM MECHANICAL TREATMENTS

While the resonance concept has enabled us to understand certain broad relationships between the structure of molecules and their absorption spectra, a more quantitative approach has also been attempted in the case of a limited series of compounds.

Absorption spectra of benzene and polynuclear aromatic compounds.- A study of the spectra of aromatic hydrocarbons and their derivatives is of obvious importance in dyestuff chemistry, since all dyes are derived from aromatic hydrocarbons. During the last few years data on the spectra of a large number of polynuclear aromatic compounds have been accumulated[1], and although the complexity of the compounds generally precludes quantitative treatment, the absorption spectra of some aromatic hydrocarbons have been calculated from quantum-mechanical principles.

Both the molecular orbital (L.C.A.O.) and the resonance(or valence-bond; V.B.) methods have been used in the treatment of the benzene molecule. In the first method, the orbitals of the so-called π electrons (the electrons of the "aromatic sextet") are considered and calculations made of the energies of a few of the lowest orbitals constructed by linear combinations of six equal atomic p orbitals with nodes coplanar with the ring. The second method utilises the concept of resonance between valence-bond structures, the energy levels being calculated[2] in terms of a parameter α derived by comparing the heats of hydrogenation of benzene and of cyclohexadiene(dihydrobenzene). The energy of a structure is lowered by $-\alpha$(α being negative) when two electrons on neighboring atoms form a covalent bond, and it is raised by $-\frac{\alpha}{2}$ if they are not paired. The energy of a single Kekule structure is therefore lowered by $-3\alpha/2$, i.e. 1.5α, compared to a structure containing only single bonds. By resonance the identical energy levels of the two degenerate Kekule

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[1] For a review of the ultraviolet absorption spectra of aromatic hydrocarbons, see Jones, Chem. Reviews, 32, 1 (1943).

[2] Sklar, J.Chem.Phys., 5, 670(1937); 7, 984(1939); 10,135, 521(1942); Rev. Mod. Physics, 14, 232 (1942); Forster, Z. Elektrochem., 45, 548 (1939).

structures split into a lower energy level(the ground state) and a higher energy level (the first excited state) which are calculated by a complicated mathematical process, and the difference of which is 2.4α*. The frequency of the first absorption maximum of benzene should then be $\frac{2.4\alpha}{h}$; taking α as 49 kcals per mole, the wavelength of the band comes to 245 mμ, in good agreement with the observed value of 255 mμ. Similar quantum-mechanical calculations have been made for several polynuclear aromatic hydrocarbons by a consideration of the number and relative contributions of the various canonical structures to the resonance states of the molecule. The calculated and observed wavelengths of the first absorption maximum for some aromatic hydrocarbons are stated in Table IV.

Table IV

Hydrocarbon	Wavelength of first absorption maximum in mu	
	Calc.	Obs.
Benzene	245	255
Diphenyl	257	251.5
Naphthalene	295	275
Anthracene	365	370
Phenanthrene	300	295
Pyrene	345	330
Naphthacene	450	460
Pentacene	545	580

While there is a general agreement between the observed and calculated values in spite of the approximations that have to be used in the mathematical process, it must be noted that the treatment is based entirely on covalent structures and does not consider polarised structures. The significance of this in the case of dye molecules

*The difference between this figure and the value of -1.5α for the lowering of energy in a single Kekule structure is -0.9α, and this is the "resonance energy". When the three Dewar structures, which make a small contribution to the resonance of benzene, are taken into account, the resonance energy is slightly larger.

will be apparent from the earlier discussion. The absorption bands associated with the excited states involving ionic structures are not calculable by this treatment, and the calculations therefore do not necessarily apply to the first absorption maxima. They may be assumed, however, to indicate that absorption will commence at a wavelength at least as great as the calculated value.

The absorption spectra of numerous hydrocarbons have been measured[1], and on account of their being characteristic of the particular system of fused aromatic rings, they have been utilised for the identification of the hydrocarbons, in connection for e.g. with their carcinogenic properties. It is clear from Table IV that the wavelength of the absorption increases as the number of benzene rings is increased. This observation provides a simple device for increasing the depth of colour in dye molecules; among the azo dyes for instance it is well known that naphthalene derivatives are deeper coloured than the corresponding benzene analogues. The bathochromic displacement is greater in the linear hydrocarbons than in the angular isomers.

Clar[2] has found that for a series of linear benzenoid hydrocarbons the position of the absorption maxima of the lowest frequency (ν_p) is stated by equation (6), in which R_p is a numerical constant and n is the number of benzene rings.

$$\sqrt{\frac{R_p}{\nu_p}} = n \qquad \text{(6)}$$

The relationship may be compared with Moseley's rule for atomic spectra. The reactivity (e.g. towards oxygen in the presence of light, maleic anhydride, etc.) of the linear condensed ring systems also increases as the number of the rings increases.

Aromatic heterocyclics.- Although heterocyclic systems are present in numerous dyes, information regarding their spectra is meagre. Braude[3] has tabulated the available data (Table V).

[1] Cf. Jones, loc. cit.; J. Am. Chem. Soc., 67, 2021, 2127 (1945).
[2] Ber., 73, 81, 104, 596(1940); 76, 257, 458(1943).
[3] loc. cit.; see this review for the sources of the data.

Table V

ABSORPTION CHARACTERISTICS OF HETEROCYCLIC SYSTEMS

	λmax. mμ	ϵmax.	λmax. mμ	ϵmax.
Pyrrole	~210	15,000	240	300
Furan	~200	10,000	250f	1
Thiophen	-	-	235	4,500
Iminazole	< 210	> 5,000		
Thiazole	-	-	240	4,000
Indole	215	25,000	265f	6,300
Thionaphthen	225	30,000	260f	10,000
Carbazole	-	-	242 291	24,000 19,000
Diphenylene oxide	-	-	250f 280f	20,000 16,000
Pyridine	195	7,500	250f	2,000
Pyrimidine	-	-	245f	3,000
Quinoline			275f 311f	4,500 6,300
isoQuinoline			262f 318f	2,300 3,200
1:2:3-Benztriazole			276f	4,500
Acridine	250	160,000	360f	1,000
Phenazine	250	120,000	370	1,600

Note: 'f' refers to a band showing fine structure.

ABSORPTION CHARACTERISTICS OF HETEROCYCLIC SYSTEMS.

Heterocyclic systems in which a nitrogen atom has replaced a methine group are similar in their absorption spectra to the hydrocarbon. The intensities are somewhat greater for the nitrogen heterocyclics, but the difference is not marked. The larger polarisability of the azomethine in comparison with the ethylene linkage, indicated for instance by the bathochromic shift in passing from stilbene to benzalaniline, thus plays a minor role in the cyclic resonators.

Shifrin[1] has applied the valence-bond treatment to pyridine, quinoline, acridine and phenazine on the assumption that a nitrogen atom in a heterocyclic molecule is analogous to a CH group, contributing one π-electron. Maccoll[2] has questioned this treatment of nitrogen atoms as equivalent to CH groups from a study of the gaseous absorption spectra of benzene, pyridine and pyrimidine in which there is a displacement towards lower frequencies by the progressive replacement of CH by N.

Quantum-mechanical treatment of the absorption of unsymmetrical cyanines.- Brooker's data have been submitted to quantum-mechanical treatment by Sklar[3], who has devised an equation in agreement with the generalisations found empirically.

It has been explained earlier that, in the absorption spectrum of a molecule, the frequency of the fundamental band (the longest wavelength band) is proportional to the energy of the transition from the ground state to the first excited state. If $\underline{e}_1$ and $\underline{e}_2$ are the energy levels of the extreme structures of an unsymmetrical cyanine, the non-degeneracy is represented by $\underline{e}_1 - \underline{e}_2$. If the transition energies of the two related symmetrical cyanines are $\alpha - N_1$ and $\alpha - N_2$, the calculated mean is $(\alpha - N_1 + \alpha - N_2)/2$

[1] Compt. rend. Acad. Sci. U.R.S.S., 29, 27(1940)

[2] J. Chem. Soc., 670(1946).

[3] J. Chem. Phys., 10, 521(1942); Herzfeld and Sklar, Rev. Modern Phys. 14, 294(1942).

Using a number of approximations, the transition energy of the unsymmetrical cyanine, ΔE_N corresponding to the observed absorption, is given by the equation(7):

$$2\Delta E_N = \left[(\underline{e}_1 - \underline{e}_2)^2 + (\alpha\sigma N_1)^2\right]^{1/2} + \left[(\underline{e}_1 - \underline{e}_2)^2 + (\alpha\sigma N_2)^2\right]^{1/2} \quad -(7)$$

The Brooker deviation, expressed as frequency, should then be proportional to the difference between ΔE_N and $(\alpha\sigma N_1 + \alpha\sigma N_2)/2$. The equation indicates three relationships all in agreement with the experimental findings. (1) The term $(\underline{e}_1 - \underline{e}_2)^2$ is positive, and the observed frequency of absorption should always be higher than the calculated frequency; i.e. the deviation should always be towards shorter wavelengths. (2) The term $(\underline{e}_1 - \underline{e}_2)^2$ will increase as the non-degeneracy of the extreme structures increases; the deviation should therefore increase with increasing asymmetry of the molecule. (3) In a vinylene homologous series of unsymmetrical cyanines such as (LXXXIII), $(\underline{e}_1 - \underline{e}_2)$ may be regarded as constant for all values of $\underline{n}$; but the terms $\alpha\sigma N_1$ and $\alpha\sigma N_2$ diminish with $\underline{n}$, and therefore the deviation should increase as the chain length increases. (4) The equation also affords

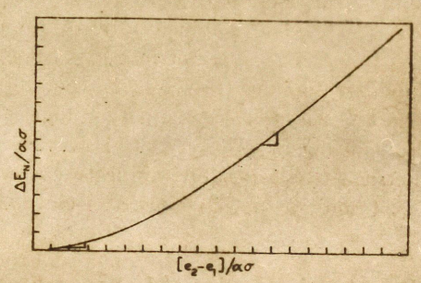

Fig. 15.—Dependence of the transition energy, ΔE_N, on the energy difference, $e_1 - e_2$. Each scale division represents one-tenth. The abscissae run from 0 to 1.9, the ordinates from 1.0 to 2.2 [Herzfeld and Sklar (22)].

an explanation of the "sensitivity rule". This follows from the fact that the resonance interactions $\alpha\sigma$ and the energy difference $\underline{e}_1 - \underline{e}_2$ enter into the transition energy as the square root of the sum of squares. When the difference $\underline{e}_1 - \underline{e}_2$ is small compared with the α terms, a given increase in $\underline{e}_1 - \underline{e}_2$ affects ΔE_N much less than

the same increase if $\underline{e}_1 - \underline{e}_2$ is of the same order of magnitude as $\alpha\sigma$ or larger.

The relationship is also illustrated in Fig. 29 taken from Harzfeld and Sklar's paper[1], in which the transition energy is plotted against $\underline{e}_1 + \underline{e}_2$ for fixed values of $\alpha\sigma N_1$ and $\alpha\sigma N_2$ (these were taken to be equal in drawing the figure). It is clear that, because of the quadratic relationship, the effect on the transition energy of increasing $\underline{e}_1 - \underline{e}_2$ by an amount $\Delta\underline{e}$ is very much less when $\underline{e}_1 - \underline{e}_2$ is zero or small, than when it is already appreciable.

Quantum mechanical calculations for idealised systems. - Quantum mechanical calculations have been made by Forster[2] for two models. One was an odd-membered conjugated chain of CH groups with auxochrome groups such as NH_2 or OH at both ends, represented by the cyanines. The other was similar but with a branched chain in the middle, represented by $(CPh_3)^+$, and its mono-, di- and tri-substitution derivatives. For both models absorption was displaced towards longer wavelength with increasing length of chain and strength of auxochrome group in agreement with known properties of coloured compounds. A theoretical substitution rule is deduced, stating that the absorption range of an unsubstituted ion breaks into two regions, one of shorter and the other of longer wavelength, when the first auxochromic group is substituted. When the second auxochromic group is substituted both regions are shifted to longer wavelengths, and when the third is substituted, the two regions merge into one of intermediate wavelength. The models appeared to be suitable as a starting point for calculations on more complicated systems.

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[1] loc. cit.

[2] Z.Physik. Chem., B47, 245 (1940) ; Z.Elektrochem., 47, 52 (1941)

INTENSITIES OF ABSORPTION BANDS

The problem of the intensities of absorption bands in relation to the structure of the absorbing molecule is even more complex than the frequency relationships, and there has been much greater success in correlating absorption frequencies with structural changes. There is no doubt, however, that the intensities of the absorption bands, as well as their wavelengths, are associated with the resonance states of the molecule, but the quantitative relationships are still largely obscure.

In butadiene the intensity per double bond is greater than in ethylene, and there is in general an increase in intensity as the length of the conjugate chain increases. High intensity has been related theoretically to the effect of structures (such as XCVII) with large dipole moments[1], which make the major contributions to the first excited state. The intensity of an absorption band is proportional to the square of the corresponding dipole moment, and hence essentially to the square of the length of the system.

The intensity of absorption is greater per benzene ring in diphenyl than in benzene, and it increases in the order benzene < naphthalene < anthracene, etc.

An ionic charge, which occupies different positions in the important resonance structures which can be formulated for a system as in the cations of basic dyes such as Malachite Green, Crystal Violet and Methylene Blue, has been shown to be associated with intense absorption. Pauling[2] has deduced theoretically that this intensity of absorption is due to the marked difference in the distribution of charge in the various structures.

Rodebush[3] and others have shown that when there is a steric inhibition of resonance in diphenyls by ortho-substitution, the

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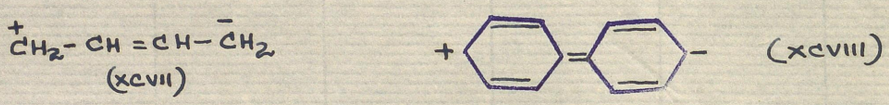
[1] Mulliken, J. Chem. Phys., 7, 121(1939); Mulliken and Rieke, Reports on Progress in Physics, 8, 231(1941).

[2] Gilman's Organic Chemistry, II, 2nd ed., Chapter 26, Wiley, New York, 1943.

[3] loc. cit.

effect on the absorption spectra is that the decrease in the intensity is much more pronounced than the change in the wavelength of maximum absorption. Mulliken[1] has explained this observation. The first absorption band of diphenyl, which is of high intensity, is probably due to a transition to an excited state that results from resonance, principally if not entirely, among ionic structures such as (xcviii). The first absorption ~~of~~



band, which is of low intensity, is due to a transition to an excited state that mainly results from resonance between the Kekule structures. In the nonplanar diphenyls, ionic structures such as (xcvii) are less stable than in diphenyl itself. The absorption is displaced towards shorter wavelengths; however, since the benzene rings are no longer effectively conjugated with each other, they now give rise to their normal absorption which, as in benzene occurs at about the same wavelength as in diphenyl, but is of considerably lower intensity.

Chako[2] and Förster[3] have attempted to calculate the intensity and width of absorption bands from theoretical considerations. In terms of the classical theory of the light absorption process, Chako arrived at a relationship between the half-width of an absorption band (the distance between the points in the curve at which $\epsilon = 1/2\ \epsilon_{max.}$), the frequency ($\nu_j$), the "oscillator strength" (f_j), and a quantity (γ_j) which is a measure of the damping responsible for the width of the band. In classical theory f_j is the number of electrons in a molecule which produce the band of absorption, and in quantum theory it represents the probability

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[1] Quoted by Wheland, The Theory of Resonance, p. 161.

[2] J. Chem. Phys., 2, 644(1934).

[3] Z. Elektrochem., 45, 551 (1939).

of the transition. Since absorption bands in the visible and ultraviolet region are weak in comparison with those in the far ultraviolet with which the refractive index is associated, it followed from the theory of dispersion, e being the charge ∅ and m the mass of an electron

$$2n^2k = \frac{e^2}{\pi m} N' \frac{f_j \gamma_j \nu}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2 \nu^2} \qquad \text{—— (8)}$$

With $\epsilon = 4\pi nk$ and $N' = N\mu$ (μ = molecules/c.c.)

$$\epsilon = \frac{2e^2}{cm} \frac{N}{n} \frac{f_j \gamma_j \nu^2}{(\nu_j^2 - \nu^2)^2 + \gamma_j^2 \nu^2} \qquad \text{—— (9)}$$

In the case of a narrow band,

$$\int \epsilon \, d\nu = \frac{\pi e^2}{cm\nu_j^2} \cdot \frac{N}{n} \cdot f_j \text{ which is independent of } \gamma \qquad \text{—(10)}$$

It then follows that

$$\epsilon_{max} = \frac{2e^2 N}{cm\nu} \cdot \frac{f_j}{\nu^2} \cdot \frac{1}{\gamma_j} \quad (\nu = \nu_j) \qquad \text{—(11)}$$

$$\text{Or} \qquad \gamma_j \cdot \epsilon_{max} = \frac{2}{\pi} \int \epsilon \, d\nu. \qquad \text{—— (12)}$$

If γ is independent of ν throughout the band, the half-width is $\Delta\nu = 2\gamma$. These equations apply to the gaseous state, and the intensity being measured in solution, a correction has to be applied to the measured intensity for obtaining the value for the gaseous state. Chako concluded that the influence of the solvent could not be accounted for by taking into account the Lorentz-Lorenz forces acting on the absorbing molecule due to the polarisation of surrounding molecules. Mulliken and Rieke[1] have suggested that, in the absence of data on the ratio between the intensities in solution and in the vapour state, the refrantive index of the solvent may be assumed to be 1, and no correction applied. From equation (4), and assuming that one electron per molecule is involved in the absorption and that the half-width

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[1] Rep. Prog. Physics, 8, 231 (1941).

is ∽ 2000 cm^{-1}, ϵ max works out to ~10^5. This is the upper limit of observed values for absorption in the visible and near ultraviolet, as well as the values indicated by quantum-mechanical calculations. For most substances ϵ max. is considerably smaller than this value.

Mulliken[1] has considered the quantum-mechanical aspects of absorption, using the molecular orbital method. Most absorption bands in the visible or near ultraviolet may be characterised by transitions from a normal or homopolar state ($\underline{N}$) to an ionic excited state ($\underline{V}_1$). In molecular orbital terms, the transitions arise from the transfer of a π-electron from a bonding molecular orbital to a nonbonding one. The intensity of absorption is mainly associated with the longest wavelength transition ($\underline{N}$ —— $\underline{V}_1$), although the degree of this concentration is dependent on molecular character. Examining the absorption spectra of the carotenoids from this point of view, Mulliken has concluded that "the more elongated the molecule, the more the intensity should be confined to the long wavelength and the more intense should be the colour". In the case of some of the simpler molecules, he has made quantum-mechanical calculations of the intensity of the absorption bands.

Sklar[2] has calculated the intensities of the long wavelength transitions in substituted benzenes by the antisymmetrical molecular orbital method. The inductive and resonance effects of substituent groups in the benzene ring and their relation to the auxochromic properties of the groups have been discussed earlier. Intensity changes are mainly due to resonance or electron migration effects. Thus the amino group in aniline, by virtue of its unshared pair of electrons, produces a marked increase in the intensity of the forbidden transition of benzene at 260 mu.

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[1] J. Chem. Phys., 7, 14, 121, 339, 570 (1939).

[2] Ibid., 7, 984(1939); 10, 135 (1942).

When the amino group is converted into the anilinium anion, it no longer possesses the unshared electron pair, and its spectrum is nearly identical with that of benzene. Sklar's treatment has shown that a large auxochromic or intensification effect is produced by a group which has an unshared electron pair, a shortened bond linking it with the nucleus, and a low ionisation potential.

Ultimately it may be possible to calculate from quantum-mechanical principles the energy differences between ground and excited states of complicated dye molecules. Meanwhile, the continued search for empirical relationships between structure and spectra is useful, especially if they can be stated quantitatively as in the case of the groups of dyes examined by Lewis and by Brooker. The quantum-mechanical treatment of simple molecules and a consideration of the resonance states of complex dyes are two opposite methods of approach which have been pursued in recent years, and a complete theory of the colour of organic molecules is gradually taking shape.