

Wavelength Formulas and Configuration Interaction in Brooker Dyes and Chain Molecules*

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The zero-order wavelength of absorption, λ_I , of a conjugated chain of N bonds with all bonds equal is

$$\lambda_I = N\lambda_c + \lambda_L + \lambda_R, \quad (1)$$

where λ_c is a universal constant, about 500 Å per bond, and λ_L , λ_R are end-group corrections. The corresponding energy, E_I , is modified in second order by configurational mixing of the ground state with a certain excited state, to give within experimental error the observed transition energy

$$E = [E_I^2 + (b_L - b_R)^2]^{1/2}. \quad (15)$$

The derivation is a simplified adaptation of the ideas of Brooker, Herzfeld, and Sklar. The end-group basicities, b_L and b_R , or stabilizations of alternative resonance structures, locate the electron

density maxima in the chain and determine the bond density alternations and bond length alternations that probably produce the mixing. They are additive and consistent for over 50 end groups and can be derived theoretically in many cases. Their dependence on chain length and solvent is shown. Substituent groups have two parameters, λ , b , as in aromatic ultraviolet spectra.

The changes in transition band widths, vibrational structure, and intensity in changing solvents are accounted for. The strong convergence of polyene series spectra and the nonharmonic spacing of their higher states is attributed to their large b -values, about 20 kK. The corresponding mixing of states is related to the probable character of the excited state wave functions and to the probable strong alternation of polyene bond lengths even in long chains.

I. INTRODUCTION

The Second-Order Perturbation

CONSIDER the problem of making a purely theoretical prediction of the low transitions in the spectrum of an arbitrary planar conjugated organic molecule. At present, it could probably be done most simply in three steps. First, a "zero-order" calculation of the spectrum of the isoconjugate "parent" hydrocarbon molecule with all bonds equivalent. This is the problem familiarly solved by the simple LCAO or free-electron molecular-orbital method, usually with a secular equation, or by the resonance method in cases where the bond order is fairly constant.

Then a "first-order" perturbation step, of computing the effects of each substituent or keto- or aza-replacement on the parent molecule. In the strong allowed transitions of dyes, such substitution effects are also now well understood. The red shifts or blue shifts, approximately linear and additive, can be computed from the donor or acceptor character of the substituent which determines the size and sign of the perturbation, and from the electron density at the position of substitution associated with its starred or unstarred location in the parent molecule. These shifts will be discussed again in Sec. VIII.

Finally, it is important in predicting the strong allowed transition of many molecules to add a "second-order" perturbation step. Such a perturbation is apparently responsible for the quadratic blue shifts or "Brooker deviations" when a chemical asymmetry in either direction is introduced into a symmetrical cyanine dye so as to produce a local asymmetry of electron

density around each atom and an alternation of single and double bond lengths.

The purpose of the present paper is to examine quantitatively the nature of such second-order shifts and their general implications for the theory of molecular spectra. The conjugated chain molecules are the best material for study since, on the one hand, they should be especially simple theoretically and, on the other hand, they show very large shifts of this kind, with the deviation from the zero-energy molecular-orbital prediction in long polyenes and unsymmetrical dyes reaching values up to 20 kilokaysers (kK; 10^3 cm^{-1}).

Brooker Results

The central phenomena to be explained are those described by Brooker and co-workers,¹⁻¹¹ who made systematic studies of the spectra of several large families of chain dyes in various solvents and showed how to

¹ Brooker, Sprague, Smyth, and Lewis, *J. Am. Chem. Soc.* **62**, 1116 (1940). I.

² Brooker, White, Keyes, Smyth, and Oesper, *J. Am. Chem. Soc.* **63**, 3192 (1941). II.

³ L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.* **63**, 3203 (1941). III.

⁴ L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.* **63**, 3214 (1941). IV.

⁵ Brooker, Keyes, and Williams, *J. Am. Chem. Soc.* **64**, 199 (1942). V.

⁶ L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.* **67**, 1869 (1945). VI.

⁷ Brooker, Sklar, Cressman, Keyes, Smith, Sprague, Van Lare, Van Zandt, White, and Williams, *J. Am. Chem. Soc.* **67**, 1875 (1945). VII.

⁸ Brooker, Sprague, and Cressman, *J. Am. Chem. Soc.* **67**, 1889 (1945). VIII.

⁹ Brooker, White, and Sprague, *J. Am. Chem. Soc.* **73**, 1087 (1951). IX.

¹⁰ Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Cressman, and Dent, *J. Am. Chem. Soc.* **73**, 5332 (1951). X.

¹¹ Brooker, Keyes, and Heseltine, *J. Am. Chem. Soc.* **73**, 5350 (1951). XI.

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interpret the spectral differences qualitatively and semi-quantitatively on the basis of resonance theory.^{12,13,13a} The following general empirical conclusions were reached.

(a) The first absorption wavelength of any long symmetrical odd-atom dye increases by 1000 ± 50 Å for every additional vinyl group in the chain, successive increases being "nonconvergent."

(b) The wavelength of absorption of an unsymmetrical dye or chain molecule must be computed in first approximation as the "isoenergetic wavelength," λ_I , given by the arithmetic mean of the wavelengths of its symmetrical "parent" dyes.

(c) This absorption is shifted to shorter wavelengths by $\Delta\lambda$, the Brooker deviation, involving quadratically the difference in energy of two resonance structures, which is determined by the difference in basicity of the two end groups of the dye.

(d) The Brooker deviation becomes very large where one structure is dominant, as in the polyenes, with the result that the spectra of a vinylogous series of this type lie at much higher energies than the cyanines and "converge" with increasing chain length, probably to a finite limiting wavelength of absorption.

Conclusion (a) had been noted by Lewis and Calvin,¹⁴ (b) had been reached by Beilenson, Fisher, and Hamer,¹⁵ and conclusions (c) and (d) were also given by Schwarzenbach,¹⁶ but they were not so thoroughly documented as in the Brooker studies.

Previous Theories and Formulas

Numerous empirical and theoretical formulas have been proposed to describe these phenomena.

Hausser and co-workers¹⁷ showed that the first absorption wavelength, λ , of polyenic series varied approximately as $L^{\frac{1}{2}}$, where L is the chain length. Lewis and Calvin¹⁴ treated conjugated chain molecules as classical oscillators and identified the first strong electronic transitions as the "fundamental" frequencies and the higher transitions as harmonics or second-order bands. With this analogy, they accounted for conclusion (a), the linear dependence of λ on L in the symmetrical cyanines. They also tried to justify the $L^{\frac{1}{2}}$ formula by making the radical assumption that for polyenes all the absorption electrons can be treated together as a single

harmonic oscillator. This is unsatisfactory; for the assumption, if it works at all, ought to be even better for the *p*-polyphenyls, whereas their spectra actually converge much too rapidly and fit no such formula; and in addition, the higher polyenes themselves¹⁸ deviate from the $L^{\frac{1}{2}}$ formula, showing a convergence which the formula does not show. Revisions and improvements in this rather crude classical approach have been made by W. Kuhn (interacting oscillators),¹⁹ Fieser,²⁰ and Porter.^{20a,21}

Förster²² described the ground and first excited states of dyes as different mixtures of two interacting resonance structures. He showed how the energy should depend (quadratically) on the mixture; and he was able to predict correctly the possibility of making strongly dipolar dyes, like the Brooker merocyanines, having anomalous solvent-behavior. Pauling²³ pointed out that intermediate structures were also needed, and Herzfeld²⁴ and Sklar^{25,26} wrote the HLSP secular equation for this case. Under certain assumptions, they derived the working formula favored by Brooker^{12,13} which will be discussed later. It is qualitatively correct in that it shows features (c) and (d) and a modified version of (b) although it does not seem to have been actually tested quantitatively on any spectra. Simpson²⁷ has written similar formulas containing more complicated parameters.

The molecular orbital treatment of the Brooker results has had more difficulties, perhaps because it separates the zero-order and the second-order or bond length effects more sharply. Mulliken^{28,29} showed that the simple LCAO method with all bonds equal makes λ proportional to L for all very long chains, polyenes included. Herzfeld and Sklar emphasized this difficulty. Bayliss³⁰⁻³³ first applied the free-electron molecular orbital method to polyenes but, on finding λ nearly proportional to L , he first treated L as an adjustable parameter and later varied the shape of his potential function to obtain a fit. Kuhn³⁴⁻³⁶ pointed out that the zero-order theories should only be applied to the cya-

¹⁸ R. Kuhn, *J. Chem. Soc.* 1938, 605.

¹⁹ W. Kuhn, *Helv. Chim. Acta* 31, 1780 (1948).

²⁰ L. F. Fieser, *J. Org. Chem.* 15, 930 (1950).

^{20a} K. Shibata, *Bull. Chem. Soc. Japan* 25, 378 (1952).

²¹ J. W. Porter, *Arch. Biochem. and Biophys.* 45, 291 (1953).

²² Th. Förster, *Z. Elektrochem.* 45, 548 (1939).

²³ L. Pauling, *Proc. Natl. Acad. Sci.* 25, 577 (1939).

²⁴ K. F. Herzfeld, *J. Chem. Phys.* 10, 508 (1942).

²⁵ A. L. Sklar, *J. Chem. Phys.* 10, 521 (1942).

²⁶ K. F. Herzfeld and A. L. Sklar, *Revs. Modern Phys.* 14, 294 (1942).

²⁷ W. T. Simpson, *J. Am. Chem. Soc.* 73, 5359 (1951).

²⁸ R. S. Mulliken, *J. Chem. Phys.* 7, 121 (1939).

²⁹ R. S. Mulliken, *J. Chem. Phys.* 7, 364 (1939).

³⁰ N. S. Bayliss, *J. Chem. Phys.* 16, 287 (1948).

³¹ N. S. Bayliss, *Aust. J. Sci. Res.* 3A, 109 (1950).

³² N. S. Bayliss and J. C. Riviere, *Australian J. Sci. Research* 4A, 344 (1951).

³³ N. S. Bayliss, *Quart. Revs. (London)* 6, 319 (1952).

³⁴ H. Kuhn, *Chimia* 2, 1 (1948).

³⁵ H. Kuhn, *Helv. Chim. Acta* 31, 1441 (1948).

³⁶ H. Kuhn, *J. Chem. Phys.* 17, 1198 (1949).

¹² L. G. S. Brooker, *Revs. Modern Phys.* 14, 275 (1942).

¹³ L. G. S. Brooker, *Advances in Nuclear Chemistry and Theoretical Organic Chemistry*, R. E. Burk and O. Grummitt, editors. (Interscience Publishers, Inc., New York, 1945), Chap. 4.

^{13a} L. G. S. Brooker and W. T. Simpson, *Ann. Rev. Phys. Chem.* 2, 121 (1951).

¹⁴ G. N. Lewis and M. Calvin, *Chem. Revs.* 25, 273 (1939).

¹⁵ Beilenson, Fisher, and Hamer, *Proc. Roy. Soc. (London)* A163, 138 (1937).

¹⁶ G. Schwarzenbach, *Z. O. Elektrochem.* 47, 40 (1941). For an interesting example of confusion between the first- and second-order perturbations, see the audience discussion on p. 52.

¹⁷ Hausser, Kuhn, and Smakula, *Z. physik. Chem.* B29, 384 (1935); Hausser, Kuhn, Smakula, and Hoffer, *Z. physik. Chem.* B29, 371 (1935).

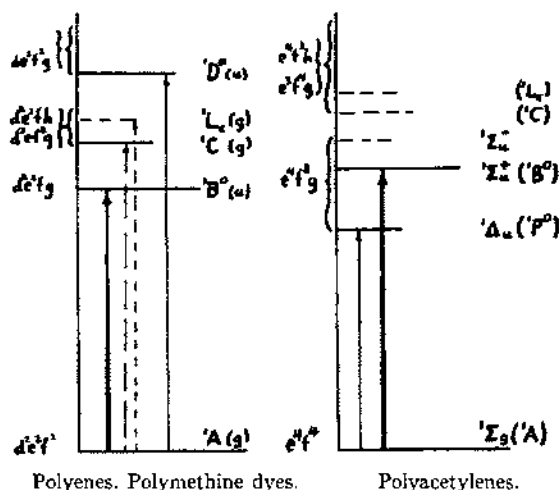


FIG. 1. Low singlet states and transitions of chain molecules.

nines, (as Simpson had applied them^{36a}), and that the polyene case could be remedied so as to fit conclusion (d) by considering the alternation of electron density and effective nuclear potential in the alternate single and double bonds of the chain. This periodicity introduces a Brillouin gap and spreads apart the orbitals involved in the first transition, shifting it to shorter wavelengths according to the strength of the alternation parameter. (The shift is formally linear but practically quadratic, for reasons to be discussed later.) But Bayliss and Rivière³² objected that such alternations are expected to get smaller with increasing chain length, as described by Lennard-Jones.³⁷ In long chains, such a decrease would destroy the short-wavelength shift and the convergence in the Kuhn treatment; so that convergence must be explained in some other way, or it must be assumed that the Lennard-Jones theoretical prediction is wrong in practice. Pitzer^{37a} gives a good brief account of the Kuhn treatment and mentions this dilemma.

Dewar³⁸ put such alternating bond strengths into an LCAO-type treatment and got a convergent two-parameter formula fitting all the polyene spectra, the convergence however depending again on violation of the Lennard-Jones result. Several more elaborate variations on the free-electron theme have also been tried in efforts to fit one or another group of chain spectra.³⁹⁻⁴³

^{36a} W. T. Simpson, *J. Chem. Phys.* **16**, 1124 (1948).

³⁷ J. E. Lennard-Jones, *Proc. Roy. Soc. (London)* **158**, 280 (1937).

^{37a} K. S. Pitzer, *Quantum Chemistry* (Prentice-Hall, Inc., New York, 1953), pp. 265-273.

³⁸ M. J. S. Dewar, *J. Chem. Soc.* **1952**, 3544.

³⁹ Fukui, Nagata, and Yonezawa, *J. Chem. Phys.* **21**, 186 (1953).

⁴⁰ G. Araki and T. Murai, *Progr. Theoret. Phys. (Japan)* **8**, 639 (1952).

⁴¹ G. Araki, "Symposium on molecular physics," Nikko, Japan (1953), p. 35.

⁴² G. Araki and H. Araki, *Progr. Theoret. Phys. (Japan)* **11**, 20 (1954).

⁴³ G. Araki and S. Huzinaga, *J. Chem. Phys.* **22**, 1141 (1954).

The first objectives here will be to set down explicitly a zero-order first-order formula, Eq. (1), that represents conclusions (a) and (b) and by-passes all secular equations; and then to try to justify for both chain dyes and polyenes a second-order working formula, Eq. (15), that accounts for conclusions (c) and (d) and seems to surpass even the Herzfeld-Sklar formula in its generality, quantitative success, and simplicity.

II. CLASSIFICATION AND NOMENCLATURE

The classification and nomenclature of the singlet energy states and transitions of closed-shell chain molecules is shown in Fig. 1. The main interest here is in the strong allowed even-odd ${}^1A \rightarrow {}^1B^o$ transitions. The notation is a standard one devised for the electronic spectra of large molecules.^{44,45} It is extended here by using the designation ${}^1A \rightarrow {}^1P^o$ for the weak long-wavelength ${}^1\Sigma_g \rightarrow {}^1\Delta_u$ (symmetry notation) transitions of polyacetylenes,^{46,47} so as to keep a uniform Roman symbolism.

The ${}^1A \rightarrow {}^1L_c$ transitions in Fig. 1 represent a further extension. In polyenes, they are the counterparts of the lowest even-even ${}^1A \rightarrow {}^1C$ transitions (forbidden in an all-*trans* system), but differ from the latter in that the one-electron transition moments cancel to a still higher order because of one-electron-configuration interaction. They probably exist in polymethines also but without such complete cancellation of moments. States of these types have been described recently by Moffitt,⁴⁸ Dewar and Longuet-Higgins,⁴⁹ and Pariser ("minns" states),⁵⁰ and will play an important role in the later interpretation.

III. DYE FORMULAS

(A) Formulas for the Isoenergetic Wavelength

Before trying to determine the second-order shift in a dye, any first-order shift must be eliminated, by locating the isoenergetic wavelength, λ_I , to which the second-order shift is to be referred.

Consider a polymethine chain of N carbons with end groups or nuclei L and R as in Fig. 2. Conclusions (a) and (b) imply that if all bonds were equal, the position of the first absorption peak, or λ_I , would be given by the equation,

$$\lambda_I = N\lambda_C + \lambda_L + \lambda_R. \quad (1)$$

⁴⁴ J. R. Platt, *J. Opt. Soc. Am.* **43**, 252 (1953).

⁴⁵ J. R. Platt, "Electronic structure and excitation of polyenes and porphyrins," Gatlinburg Conference on Photosynthesis, 1951 in *Radiation Biology*, Alexander Hollaender, editor (McGraw-Hill Book Company, Inc., New York, 1956), Vol. III, Chap. 2, pp. 71-123.

⁴⁶ J. R. Platt (unpublished).

⁴⁷ M. Beer, Abstracts of The Ohio State University Conference on Molecular Spectra and Structure, Columbus, Ohio, (June 1954); M. Beer and H. C. Longuet-Higgins (to be published).

⁴⁸ W. Moffitt, *J. Chem. Phys.* **22**, 1820 (1954).

⁴⁹ M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **A67**, 795 (1954).

⁵⁰ R. Pariser, *J. Chem. Phys.* **24**, 250 (1956).

(A slightly different form is given by Pitzer.^{37a} The chain constant, λ_c , is a characteristic wavelength increase per methine carbon atom, or per C—C bond, evidently almost exactly 500 Å per bond. Substantially the same empirical value comes out of the analysis of polyene spectra in Sec. IV, and the absolute value can also be derived theoretically as shown below, so it may be regarded as a kind of universal constant of conjugated organic spectra.

In Eq. (1), λ_L and λ_R are characteristic wavelength contributions from the nuclei. The arbitrary cut between the chain and the end groups is conveniently located in the chain bonds adjacent to these groups. The λ values for various groups are given in Table I. They have been determined by applying Eq. (1) to the Brooker data for the symmetrical odd-atom dyes and inserting the proper values of N and λ_c .^{50a}

For an unsymmetrical dye, LR , conclusion (b) is equivalent to adding the two Eqs. (1) for the two symmetrical parent dyes, LL and RR , of the proper chain lengths, to give a first-order mean-wavelength equation

$$\lambda_L(LR) = \frac{1}{2}[\lambda_L(LL) + \lambda_L(RR)]. \quad (2)$$

This interpolation formula is of course more accurate than the absolute formula in Eq. (1). It is noteworthy that the use of a mean wavelength gave empirically more consistent results in the subsequent Brooker analysis than the use of a mean frequency or energy.

The λ_L values of ionic dyes were found to be almost independent of the other ion present. They do not seem to need correction for Coulomb effects owing to the net charge on the dye, and they are surprisingly independent of the dielectric constant or refractive index of the solvent. The increase of 100 or 200 Å in λ_L in solvents of high refractive index is easy to measure and allow for, and is small compared to some of the larger Brooker deviations. Probably if dye spectra could be obtained in the vapor state, the effects of the total charge and of the ionic partner would be more apparent.

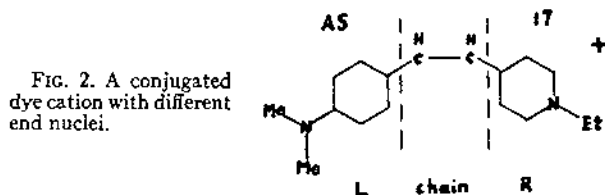
Theoretical Value of the Chain Constant

In the free-electron molecular-orbital theory the predicted energy to lift an electron from the highest filled (f) orbital to the lowest unfilled (g) orbital is

$$E_f = \frac{h^2}{8md^2} \frac{N+1}{N^2} = 204 \frac{N+1}{N^2} \text{ kK} \quad (3)$$

for a chain of N atoms (even) with N pi-electrons each of mass m . The numerical value applies to an all-*trans* zig-zag polymethine chain with the usual C—C spacing, $d = (\cos 30^\circ)(1.40 \text{ Å})$, as projected on the x -axis. For odd-atom chains with $N+1$ or $N-1$ electrons (even), the numerator changes accordingly, but in the limit,

^{50a} Shibata, reference 20a, gives a short table of λ values, which he calls "color factors."



E_f always varies inversely with N and the absorption wavelength therefore varies directly with N :

$$\lambda_f \rightarrow \frac{8md^2c}{h} N = N(490 \text{ Å}), \quad (4)$$

the numerical coefficient being the reciprocal of the one in Eq. (3). Evidently, the asymptotic result for long chains should approach the same chain constant regardless of what end groups are attached.

The general result, that λ_f is proportional to the length L (or N) of the system, would also be expected by the correspondence principle, using the Lewis and Calvin analogy with a classical dipole antenna. This is a most powerful and general argument, in cases where the second-order effects can be ignored.

For each methine group, the free-electron prediction of the "universal chain constant" is then^{37a}

$$\lambda_c(\text{theoret.}) = 490 \text{ Å}. \quad (5)$$

Since the orbital excitation should correspond to the mean of a singlet and a triplet, the strong singlet transition would be expected to fit a value of λ_c perhaps as much as 10% smaller than given by Eq. (5). Even with this correction, the numerical prediction is satisfyingly close to the empirical Brooker value, considering the simplicity of the assumptions. It is this agreement that is fundamental to the general success of the free-electron method.

Use of the zig-zag chain length, with $d = 1.40 \text{ Å}$, would increase the λ_c of Eqs. (4) and (5) to 650 Å, too large for a good fit with the cyanine data. The unknown singlet-triplet split and this alternative assumption for d are the only uncertain elements in the absolute free-electron orbital calculation of λ_c , so that it is fixed by this theory between about 450 and 650 Å.

(The LCAO molecular orbital theory gives in place of Eq. (3),

$$E_f = 4\beta \sin \frac{\pi}{2(N+1)} \cong \frac{2\pi\beta}{N+1}; \quad (6)$$

so that λ_f approaches

$$\lambda_f = hcN/2\pi\beta, \quad (7)$$

and

$$\lambda_c(\text{theoret.}) = hc/2\pi\beta, \quad (8)$$

but β , the bond integral, must be determined from the spectra. Its value of 32 kK, obtained earlier from short

TABLE I—Continued.

[illegible]

* Treating thiazole rings as pyridine rings, with —S— assumed equivalent to a vinyl group.

Alternant-orbital coefficients on the oxygen atom instead of nitrogen: co/cr .

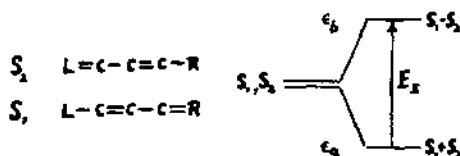


Fig. 3. Interaction of equivalent resonance structures to give ground and excited states.

polyene spectra,⁵¹ agrees exactly with the value given by inserting the observed cyanine λ_C in Eq. (8). For a zig-zag λ_C of 650 Å, the value of β would come down to 24 kK, curiously close to the observed value for ring systems.⁵¹

(B) Formulas for Asymmetric Dyes

The second-order working formulas for the dyes will be derived first from an oversimplified form of the Förster-Herzfeld-Sklar arguments. Suppose that a dye at the isoenergetic point has two resonance structures, S_1 and S_2 , of equal energy. The other possible intermediate structures are neglected here. They are redundant in the spectroscopic specification of structures⁵²⁻⁵⁴ as well as in the density interpretation to be given in Sec. VI. Figure 3 suggests how, in these terms, the structures may formally interact to give the ground and excited states, separated by the interaction energy, E_I . The problem of evaluating this interaction is avoided by equating it to the energy at the isoenergetic wavelength,

$$E_I = hc/\lambda_I. \quad (9)$$

The assumed relation between the structures can be expressed by setting up a secular equation for the interaction between the wave functions Ψ_1 of the structure S_1 and Ψ_2 of the structure S_2 ,

$$\begin{vmatrix} \Psi_1 & \Psi_2 \\ \Psi_1 \left| \begin{array}{cc} \epsilon & \frac{1}{2}E_I \\ \frac{1}{2}E_I & \epsilon \end{array} \right| & 0, \end{vmatrix} \quad (10)$$

contrived to give two values of ϵ ,

$$\epsilon_{a,b} = \pm \frac{1}{2}E_I, \quad (11)$$

with the desired transition energy

$$E = \epsilon_b - \epsilon_a = E_I. \quad (12)$$

Equations (10) to (12) are simply other ways of writing E_I . But now lower or stabilize one resonance structure, say S_1 , by an amount $\frac{1}{2}b$, and raise the other by the same amount so they are no longer degenerate. The secular equation then becomes

$$\begin{vmatrix} \Psi_1 & \Psi_2 \\ \Psi_1 \left| \begin{array}{cc} \epsilon + \frac{1}{2}b & \frac{1}{2}E_I \\ \frac{1}{2}E_I & \epsilon - \frac{1}{2}b \end{array} \right| & 0, \end{vmatrix} \quad (13)$$

with two values of ϵ ,

$$\epsilon_{a,b} = \pm \frac{1}{2}[E_I^2 + b^2]^{\frac{1}{2}}, \quad (14)$$

and a transition energy,

$$E = [E_I^2 + b^2]^{\frac{1}{2}}. \quad (15a)$$

The quantity b is the difference of energies of structures S_1 and S_2 and can be written

$$b = b_{12} = b_2 - b_1. \quad (16)$$

The Herzfeld-Sklar formula for E differs from Eq. (15a) only in that it has *two* terms of the same square-root type, with the E_I being replaced in them by the E_I 's of the two symmetrical parent dye ions, LL and RR . However, this leads to a mean-energy equation for $E_I(LR)$ when $b=0$, rather than the mean wavelength Eq. (2) which fits conclusions (a) and (b). And although the Herzfeld-Sklar equation, because it is so similar to Eq. (15a), could probably be used as the basis for the subsequent empirical development here with little change of accuracy, it is certainly more practical to choose the latter simpler form.

The b_{12} -value of Eq. (16) can be written in still another way. Each nucleus L can be assigned a value b_L for its contribution to the difference in energy of the structures, and each nucleus R a value b_R , so that

$$b = b_{12} = b_{LR} = b_L - b_R, \quad (17)$$

for the typical case of basic nuclei in an odd-methine cyanine dye, where the two nuclei stabilize opposite structures. If they stabilize the same structures, the same formal equation may still be used if changes of sign in b_L and b_R are allowed. Equation (17) leads to the working form of Eq. (15), the mathematical formulation of conclusion (c):

$$E = [E_I^2 + (b_L - b_R)^2]^{\frac{1}{2}}. \quad (15b)$$

A similar equation was given by Nagakura^{54a} but he did not carry it on to quantitative numerical analysis like that described here. The principal empirical result of the present study is the finding that for a given polymethine chain and a given solvent, the b_L -value of each nucleus determined from Eq. (15b) and the Brooker data is indeed constant within experimental

⁵¹ J. R. Platt, J. Chem. Phys. 18, 1168 (1950).

⁵² W. T. Simpson, J. Am. Chem. Soc. 75, 597 (1953).

⁵³ W. T. Simpson and C. W. Looney, J. Am. Chem. Soc. 76, 6285 (1954).

⁵⁴ C. W. Looney and W. T. Simpson, J. Am. Chem. Soc. 76, 6293 (1954). The present structures, S_1 , S_2 , are of the type called "structures₂" by these authors, defined from the spectroscopic states themselves in Eqs. (10) to (15) so as not to require intermediate structures. The translation of this treatment into the language of molecular states in Sec. VI is the transformation to the "Heisenberg representation" described by these authors. The present analysis seems to bear at many points on the questions discussed by Simpson as to the relation between "structures₂" and ordinary valence-bond "structures," and state wave functions.

^{54a} S. Nagakura, Repts. Radiation Chem. Research Inst., Tokyo Univ. 2, 25 (1949). (In Japanese.)

error regardless of what nucleus is on the other end of the dye.

The test of constancy is whether the values satisfy a "combination principle"; just as the test of the existence and reliability of energy levels determined from the difference energies given by the lines in atomic spectra is whether the energies satisfy the Ritz combination principle. Here the principle would be represented by relations of the forms

$$b_{AB} + b_{BC} = b_{AC} \quad \text{and} \quad b_{AC} - b_{BC} = b_{AD} - b_{BD}, \quad (18)$$

for asymmetric dyes containing arbitrary nuclei A , B , C , and D .

The rest of Sec. III will be devoted to details of how the numerical b -values in the dyes were determined and tested and how they vary. Section IV will treat similarly the large b -values encountered in polyenes and similar chain systems. This paves the way for an attempt in Sec. V to predict b -values and to justify conclusion (c) relating them to chemical basicity.

(C) b -Values of Dye Nuclei

Numerical Determination

The b_{LR} 's were determined from the observed values of E and the calculated values of E_I by rearranging Eq. (15) to the form

$$b_{LR} = [E^2 - E_I^2]^{\frac{1}{2}}, \quad (19)$$

or to the following form which involves wavelengths directly and is convenient for sliderule use,

$$b_{LR} = \frac{[\Delta\lambda \cdot \Sigma\lambda]^{\frac{1}{2}}}{\lambda_I \lambda} \times 10^5 \text{ kK-Å}, \quad (20)$$

where $\Sigma\lambda$ is $\lambda_I + \lambda$ and $\Delta\lambda$ is $\lambda_I - \lambda$, the Brooker deviation.

Because of the square-root relation to $\Delta\lambda$, the accuracy of b varies inversely with b . Values less than 2 kK are therefore quite uncertain. Negative deviations give formally imaginary values for b , but they are generally small and can be set equal to zero on the assumption that they are due to uncertainty in locating the band maxima. Large values of b become quite accurate. For values over 5 kK, even a 40-Å uncertainty in location of the peak wavelength in the visible region gives an uncertainty in b which is in the range of ± 0.2 kK.

Equation (20) can be put in the approximate form

$$b_{LR} = [2\Delta\lambda/\lambda_I^3]^{\frac{1}{2}}, \quad (21)$$

when $\Delta\lambda$ is small. But when it is more than about 200 Å, the b -values determined from Eq. (21) are significantly worse in satisfying the combination-principle relations than those determined from Eq. (20). The square-root dependence on $\Delta\lambda$ explains and is equivalent to Brooker's "sensitivity rule." This rule states that the

change of Brooker deviation produced by a given small change in basicity is greater the greater the initial deviation. The Herzfeld-Sklar formula gives a similar dependence on $\Delta\lambda$ and has been discussed in connection with this rule.^{18,26}

The power law in the denominator of Eq. (21) is the reason why, with constant b , the Brooker deviation in the numerator must get so large for long chains—of the order of 2000 Å and more. Correspondingly, it is the reason why the deviations are fairly unimportant—of the order of 100 Å or less—for nonchain aromatic systems absorbing only in the ultraviolet.

The most convenient way to get a consistent set of b -values for the Brooker dye nuclei is as follows. For a set of dyes with the same R -group on one end, plot on a strip of paper all the b_{LR} 's as determined empirically from Eq. (20), indicating the uncertainties. On another strip plot to the same scale the b_{LR} 's for dyes with another constant end group R' but with some of the same L -groups as before. Slide the strips along each other until the two sets of b 's for the same L -groups coincide best. The consistency or lack of it—which represents the accuracy with which the combination Eqs. (18) are satisfied—is then obvious at a glance. If the number of common L -groups is large, this procedure determines $b_R - b_{R'}$, the relative displacement of the origins of the two strips, especially accurately.

The ambiguity of sign in the b_{LR} 's is quickly resolved by this procedure if the R - and R' -groups differ enough. It is convenient if one of them is extremely basic or extremely acidic so that all the b 's on its strip are likely to have the same sign.

The b -values determined in this way for the nuclei of the Brooker dyes are given in Table I relative to nucleus 1 of paper X¹⁰ as reference nucleus. They are adopted values representing a weighted average of all the available Brooker data for each nucleus.

Test of Additivity

Table II shows how well the combination-principle relations hold among the b -values of 15 fairly typical nuclei in all the 46 unsymmetrical dye combinations of these nuclei which were studied. Along the edges of Table II are given the adopted b_L -values from Table I for the L -nuclei of the rows and the adopted b_R -values for the R -nuclei of the columns. In each square of Table II are the observed values of λ_{LR} and $\Delta\lambda_{LR}$ and the empirical b_{LR} determined directly from these two quantities. In the lower right-hand corner of each square is the correction necessary to bring the computed value of $b_L - b_R$, determined from the adopted values for the row and column, into agreement with this empirical b_{LR} .

It will be seen that the absolute errors in the computed $b_L - b_R$ are indeed largest near the diagonal of Table II, where the value itself is smallest. The errors get very small in the upper right and lower left corners

of the table. Throughout the table, they correspond to fairly constant uncertainties of about ± 30 Å in wavelength determination. This may be near the experimental variance in λ or λ_I judging by the accuracy of repetition of λ data in different experiments in the Brooker series.

In Table II, nucleus 24 is particularly bad. It is among the half-dozen least consistent nuclei in the MeOH column of Table I. (The large uncertainties indicated in the other columns of Table I are mostly interconnected uncertainties which could be cleared up quickly with data on a few more dyes with large b -values.)

It is noteworthy that even in the extreme corners of Table II, where there are Brooker deviations of over 1000 Å—representing changes of 20% in the transition energy from the isoenergetic energy—and where such a simplified theory might be expected to begin to break down, there still seems to be no systematic decrease in the accuracy of the combination relations.

For most of the nuclei treated here, therefore, the λ_I values and b -values of Table I, when used with Eqs. (1), (9), and (15), relate the dye absorption peaks accurately and permit computation of their positions within the experimental uncertainty. This procedure may be empirically useful regardless of how well we can justify it theoretically.

Effect of Increasing Chain Length

The b -values for pentamethine dyes in Table I are spread consistently farther apart than for trimethine dyes. In Fig. 4 these differences are plotted for several nuclei. (The designations of nuclei in the figures are taken from paper X¹⁰ of Brooker and co-workers, with some extensions of the notation as indicated in column 8 of Table I.) The increased spread of the pentamethine b -values may be a reflection of a general increase in basicity differences with chain length. (Also see Simpson.²⁷) The acid nucleus 23, 3-ethyl-rhodamine, does not seem to share in the spread very much. More data are needed to reduce the uncertainties before the spread can be profitably discussed in much detail.

(D) Solvent Effects

b -Values as Indicators of Solvent Properties

The extensive data given in the Brooker papers X¹⁰ and XI¹¹ on dyes in pyridine-water solvent mixtures have been converted to b_{LR} -values and plotted in Fig. 5. In several cases, unfortunately, the λ_I values could not be directly computed from the data given and had to be estimated in special ways; as by making reasonable small corrections for solvent shifts; or by assuming λ_I to lie some small but reasonable distance from the longest λ observed for a given dye, where the intensity behavior indicated this λ was approaching the isoenergetic wavelength. The larger b 's in any case are in-

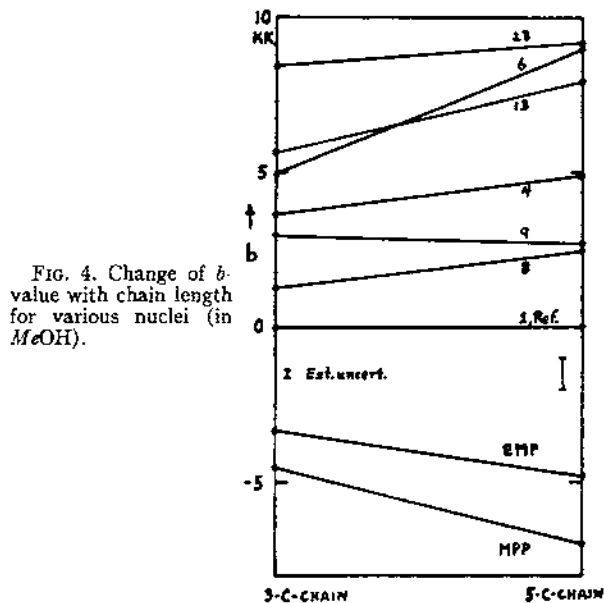


FIG. 4. Change of b -value with chain length for various nuclei (in MeOH).

sensitive to the exact value of λ_I . The λ_I could be estimated especially well for those dyes of paper XI that pass with changing solvent completely through the isoenergetic point where λ reaches a maximum and turns back. This point must correspond to $b_{LR}=0$ for that particular solvent mixture and so must correspond to λ_I . These dye lines cross the axis in Fig. 5.

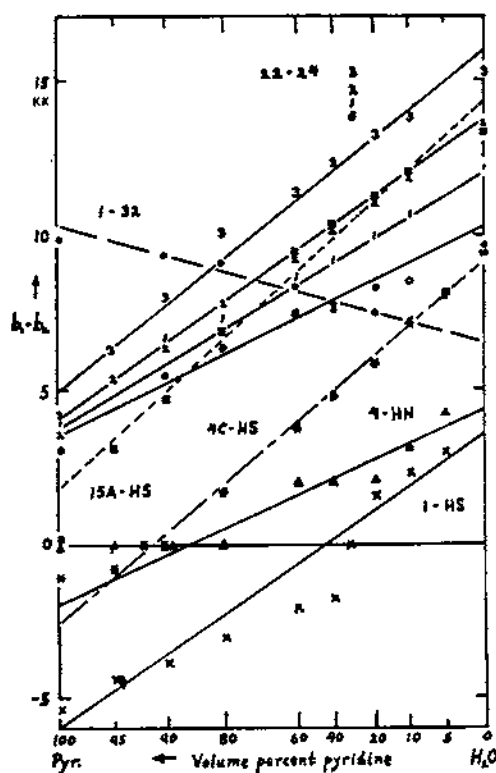


FIG. 5. Changes of b -value for various dyes in pyridine-water mixtures.

Because of these less direct procedures in the variable-solvent calculations, the errors in Fig. 5 are probably larger than most of the uncertainties in Table I, and are of course especially large near $b_{LR}=0$. Within these errors, however, it appears that each solvent mixture shifts the b_{LR} for every dye by the same fraction of the way between $b_{LR}(\text{pyridine})$ and $b_{LR}(\text{water})$.

It is this fraction which is the abscissa in Fig. 5. It was determined by a successive approximation procedure. First the b_{LR} -values for 10% and for 90% pyridine (avoiding the less reliable data at 100% pyridine) were plotted on two vertical lines or "solvent lines"; and the values for the same dye were connected by straight slanted lines or "dye lines." The b_{LR} -values for each other solvent mixture were then plotted on a strip of paper which was held vertical and moved horizontally until the values gave the best general fit with their proper dye lines. When all the vertical solvent lines had been located in this way, the dye lines were redrawn to give the best fit to the whole set of b_{LR} -values for that dye, taking into account the changing reliability with changing b -value. The vertical solvent lines were then readjusted in turn to give the best fit for the b 's on each vertical line to these new dye lines; and so on, the dye lines and solvent lines converging rapidly to their limiting positions. It was taken into account in weighting the points during the adjustment that the vinylogous series of the four dyes having nuclei 22 and 24 should form a smooth sequence. Figure 5 shows the final dye lines and the final position of the solvent verticals.

Within the experimental uncertainty it is seen that the same choice of location of the solvent verticals will make all the dye lines straight simultaneously. Algebraically, this means that

$$b_{LR}(m) = b_{LR}(0) + k_{LR}x(m), \quad (22)$$

where $b(0)$ and k are constants of each dye, and x is a universal function of the mixture m . If this relation is general, there must be a similar relation for the b_L - and b_R -values of individual nuclei.

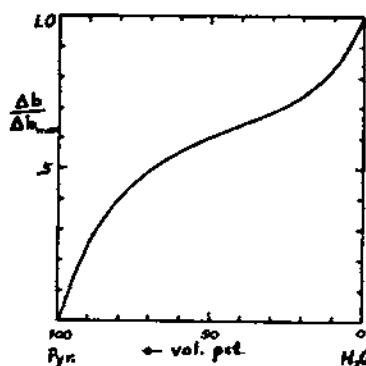


FIG. 6. Average relative change in b -value of thirteen dyes versus pyridine-water solvent ratio.

The abscissa, x , in Fig. 5 is plotted as the ordinate in Fig. 6 against the volume percentage mixture, m , of the solvents. This figure is a more general way of representing the several curves of Fig. 11 of the Brooker paper X. It is striking that the first few percent of the minority component produces an especially steep slope at both ends of the curve. Possibly, this is owing to the tenacious attraction of the two ends of the dye, each for its own preferred component of the mixture as the percentage of that component approaches zero. A comparison of this curve with a dielectric constant curve, and studies at temperatures other than room temperature, and studies of other solvent mixtures would tell us much about the nature of the dye-solvent interaction. They might also provide a convenient tool for study of solvents in general, using the dye as a kind of tracer. It may well be that some of the deviations of the points in Fig. 5 from the straight lines are significant and might become even larger for dyes with grossly different types of end nuclei; so that different dyes would give sensibly different curves in Fig. 6. This question needs to be checked; it would be convenient if there were no such effect, but extremely interesting if there were.

Red Shifts, Blue Shifts, and Relative Dipole Moment

To go back to Fig. 5, the dye lines which cross the axis must pass through a point, on the resonance theory interpretation, where the two structures S_1 and S_2 of Fig. 3 are of equal energy. These particular dyes are highly polar, so that although one of the structures is uncharged, the other structure has a negative charge at one end and a positive charge at the other. As Brooker and co-workers pointed out, the polar solvent, water, undoubtedly stabilizes the second of these structures, the one with the dipolar charges. To the left of the isoenergetic point in Fig. 5, the dipolar form must therefore predominate in the excited state of the molecule; to the right, it must predominate in the ground state; and at the isoenergetic crossover point both the ground and the excited state must have the same dipolar contribution.

The behavior of the spectra on each side of this point then illustrates particularly well a more general physical picture that has been emphasized by McConnell⁵⁵ and especially by Bayliss and McRae.⁵⁶ If the dipole moment is greater in the excited state than in the ground state, the differential heat of solution in going to a more polar solvent will likewise be greater in the excited state. This is true even for a Franck-Condon "vertical" transition. In the more polar solvent, it follows that the absorption must shift to the red.

This is the situation to the left of the isoenergetic

⁵⁵ H. McConnell, J. Chem. Phys. 20, 700 (1952), and unpublished.

⁵⁶ N. S. Bayliss and E. G. McRae, J. Phys. Chem. 58, 1002 (1954).

crossover point on any dye line in Fig. 5; and in this region, a change to a more polar solvent decreases the absolute value of b and does increase the wavelength of absorption.

If the dipole moment is less in the excited state, the differential heat of solution for this state in going to a more polar solvent is less than for the ground state, and there is a blue shift. And this is the situation to the right of any isoenergetic point in Fig. 5, where the more polar solvent increases the absolute value of b and produces absorption at shorter wavelengths.

Solvent Effects on b -Values of Individual Nuclei

Some of the more accurate b -value lines for particular nuclei in the pyridine-water mixtures have been drawn in Fig. 7.

An attempt has also been made to locate the $MeOH$ and $MeNO_2$ sets of b -values on this diagram at the pyridine-water mixture ratios to which these solvents seem most nearly equivalent. It may be, of course, that these solvents are not equivalent to the same mixture for all dyes. Some of the discrepancies do seem to be near or outside the limit of experimental uncertainty. However, only three groups, nuclei 22, 32, and 24, give a really sensitive test of this question. If more weight were given to the b -values for nucleus 24, the $MeOH$ line would move closer to equivalence with the 50-50 pyridine-water mixture, where Brooker and co-workers seemed to imply it should be.

In any case, the sequence of solvents on Fig. 7 is *not* the sequence of refractive indices, since the $MeNO_2$ vertical line lies between the $MeOH$ and the H_2O verticals; it seems closer to the sequence of static dielectric constants. This is what might have been expected if the change of b -value in a more polar solvent is due mainly to the static stabilization of ground-state charge distribution; and if the Franck-Condon principle holds both the solute and solvent atoms approximately fixed in their ground-state arrangement during the act of light absorption.

The stabilization may also involve hydrogen bonding or specific complex formation. Bayliss and McRae⁵⁷ have given absorption curves for the merocyanine dye with nuclei 22 and 24 in a series of solvents and found blue shifts increasing in the sequence, chloroform, nitrobenzene, pyridine, acetone, ethanol, formamide, and water. This sequence, conforming neither to that of refractive indices nor dielectric constants, suggested that hydrogen bonding to the solvent molecules is very important, giving perhaps a local polar character not measured by the gross dielectric constant. The question of solute-solvent interaction mechanisms and their

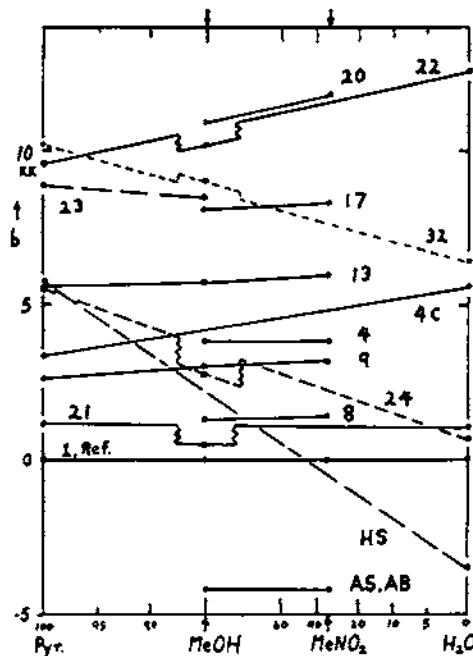


FIG. 7. Change of b -value with solvent for acid and basic nuclei.

effect on light absorption is a lively current subject⁵⁸⁻⁶⁰ but will not be discussed further here.

In Fig. 7, the lines for acid nuclei, which are drawn dashed, all slope downward toward the right, while the lines for the basic nuclei, which are drawn solid, all slope upward. This shows that the reference group, nucleus 1, is fairly neutral. The aminostyryl nucleus AS (or AB) might have been a better choice for the reference group if data had been available on it in pyridine and water.

The Brooker explanation of these slopes could be translated into the present language somewhat as follows. The value of b in Fig. 7 is in every case the energy of the structure with two pi-electrons on the critical heteroatom minus the energy of the structure with only one. In acid nuclei, the two-electron structure is the charged one, charged negatively. A polar solvent like water stabilizes charged structures by reducing the Coulomb energy of charge separation. As a result, the b -value of acid groups falls in water. In basic nuclei, the one-electron structure is the charged one, charged positively. In water, which stabilizes this structure, the value of b then rises.

IV. FORMULAS FOR POLYENES AND CHAINS WITH LARGE b -VALUES

Convergence

Equation (15) is also the mathematical formulation of conclusion (d). In a vinylogous series where the b -

⁵⁷ N. S. Bayliss and E. G. McRae, *J. Am. Chem. Soc.* 74, 5803 (1952).

⁵⁸ S. Nagakura, *J. Am. Chem. Soc.* 76, 1003, 3070 (1954).

⁵⁹ Y. Ooshika, *J. Phys. Soc. Japan* 9, 594 (1954).

⁶⁰ G. J. Brealey and M. Kasha, *J. Chem. Phys.* (to be published).

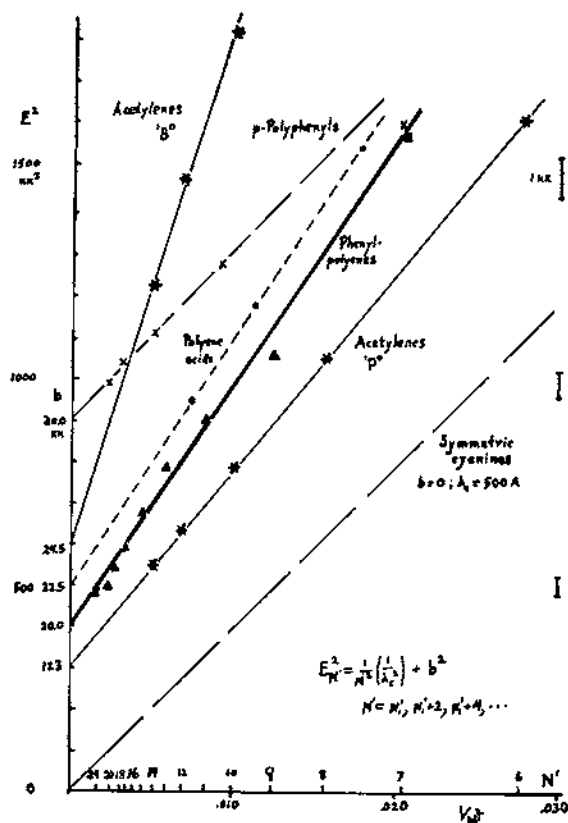


FIG. 8. Graphical determination of b and λ_C for homologous series.

value is constant or increases with increasing chain length, λ_I will increase in proportion to the length and E_I will decrease correspondingly toward zero, but the energy E will converge to the limiting value of b_{LR} .²⁶

$$E_{lim} = b_{lim}; \quad \lambda_{lim} = 1/b_{lim} \times 10^5 \text{ kK-Å.} \quad (23)$$

The convergence is most marked for large values of b_{LR} , which occur in systems where one ground-state structure is strongly stabilized compared to any other. These include the even-atom polyene,^{5,12,13,16} polyacetylene and polyphenyl chains and some of their fairly nonpolar derivatives. If convergence is described quantitatively by Eq. (15), it will provide a way of determining large b -values. These are hard to measure by the methods of Sec. III³ because of the difficulty of preparing the symmetrical ionic dyes needed for computing λ_I .

For a convergent series where two members are known, differing in length by ΔN carbon atoms, but with unknown isoenergetic wavelengths λ_{I1} and λ_{I2} , Eq. (1) gives a relation between these wavelengths,

$$\lambda_{I2} = \lambda_{I1} + \Delta N \lambda_C; \quad (24)$$

and if the standard chain constant is assumed, this equation combined with Eq. (15) and the two observed absorption wavelengths suffices to determine two unknowns, such as λ_{I1} and b .

If there are more members of the series, the additional data can be used to make an independent determination of some additional unknown, for example, λ_C itself.

Figure 8 shows how the best values of λ_{I1} , λ_C , and b could be determined by a graphical method for series having many members. The series plotted are the polyenes and diphenyl polyenes^{17,18,38} and polyene acids,¹⁷ the *p*-polyphenyls,⁶¹ and the dimethyl polyacetylenes.⁶² Equation (15) is rewritten in the form

$$E^2 = (1/\lambda_I^2) + b^2. \quad (25)$$

(The wavelength unit is taken as 10μ to make the numerator of the fraction unity when the energies are in kilokaysers.) For vinylogous series, it is convenient to introduce a new variable, N' , the "effective number of carbon bonds in the chain length," such that

$$\lambda_I = N' \lambda_C. \quad (26)$$

Here N' is not necessarily an integer, but must change by two units for every added vinyl group. Equation (23) becomes

$$E_N^2 = (1/N'^2) [1/\lambda_C^2] + b^2; \\ N' = N_1', N_1' + 2, N_1' + 4, \dots \quad (27)$$

The problem of finding N_1' , λ_C , and b is like the textbook problem of finding the quantum defect, the Rydberg constant, and the series limit for a Rydberg series, which has a similar kind of denominator and convergence limit.

The graphical procedure is to plot E_N^2 against $1/N'^2$ for the successive series members, using a trial value of N_1' and changing N' by two units for each vinyl addition. In general, the series will lie on a curved line, but the line can be straightened by adjusting N_1' to its best value. The slope of the straight line is then $1/\lambda_C^2$ and the intercept on the E^2 axis is b^2 .^{62a}

Unfortunately, the curvature is not very sensitive to N_1' , and real changes of b with length may be disguised as changes of N_1' and λ_C by this procedure. It is probably better therefore to set N_1' to a physically reasonable value corresponding closely to the geometric length of the conjugated chain. This leaves two unknowns to be determined, and it reduces the dependence of the apparent b -values and λ_C values on small experimental errors that may critically affect the line-straightening procedure. In Fig. 8, the values of N_1' were fixed by adopting the following standard geometrical approximations. A simple conjugated chain of N carbons, whether polyene or polyacetylene, was taken as having a length of N bonds; plus an end correction of 0.5 bond at each end, which gives the best fit to the LCAO and

⁶¹ A. E. Gillam and D. H. Hey, *J. Chem. Soc.* 1939, 1170.

⁶² Cook, Jones, and Whiting, *J. Chem. Soc.* 1952, 2883. These authors justify the L^2 relation for their series, but the present Eq. (27) seems to fit even better.

^{62a} Shibata's equations, reference 20a, are like Eq. (27) with N' raised only to the first power. As a result his graphs are not linear.

TABLE III. Convergence values of b and λ_C from series (Fig. 8).

Series	Transition	λ_C	b
Symmetrical cyanine dyes	${}^1A-{}^1B^0$	500 ± 20 Å	0.0 kK
$C \equiv C(-C \equiv C)_n - C \equiv C$ and $Ph(-C \equiv C)_n - Ph$	${}^1A-{}^1B^0$	410 ± 50	20.0 ± 3
(Higher members)—		(350)	(17.5)
$Me(-C \equiv C)_n - COOH$	${}^1A-{}^1B^0$	410	22.5
$Ph(-Ph)_n - Ph(para)$	${}^1A-{}^1B^0$	490	30.0
			(24 corr. for zero order)
$Me-C \equiv C(-C \equiv C)_n - C \equiv C-Me$	${}^1A-{}^1B^0({}^1\Sigma_u^+)$	290	24.5
	(L -band)		
	${}^1A-{}^1P^0({}^1\Delta_u)$	460	17.3
	(A -band)		

free-electron formulations. A phenyl group was given an effective length of 3.5 bonds with no end correction. The $-COOH$ group was given an effective length of 2.0 bonds; and a terminal $-CH_3$ group an effective length of 0.5 bond.

b Values and λ_C Values

With these assumptions, values of b and λ_C were obtained from each of the series of Fig. 8 and are given in Table III. The uncertainties in the b -values associated with the curve-fitting process are of the order of ± 3 kK, since an extrapolation is involved. The uncertainties in λ_C are due largely to the uncertainty in the choice of N_1' . A change of N_1' by 1.0 bond would change the apparent b -values in the several series in Fig. 8 by only about 5% or 1 kK, but would change the apparent value of λ_C by 20%. In the diphenyl polyenes there seems to be a change in b -value along the series from a polyphenyl-like value in the low members to a polyene-like value in the high members³⁸; and this will also affect the apparent value of λ_C .

Within this uncertainty of about 20%, the two polyene series of Fig. 8 and Table III give λ_C almost equal to both the symmetrical cyanine dye value and the theoretical value derived in Sec. III.

The discussion to be given later will suggest that the largest possible b -value for any vinylogous series should be equal to the value, about 20 kK, for the polyenes themselves. The polyene acids of Fig. 8 seem to have a somewhat higher b -value than this, but the series is short and uncertain.

For the acetylenes, the two states ${}^1P^0$ and ${}^1B^0$ belong to the same f_g excited configuration, but are separated by electron interaction (see Fig. 1). The λ_C values for these two series should therefore lie above and below the λ_C value for the single f_g ${}^1B^0$ series of the polyenes, and Fig. 8 shows that this is the case. It might have been expected that the stronger alternation of bond lengths in the polyacetylenes would lead to larger b -values in both series than in the polyenes, but here also one value is above the polyenes and one below. This may be a reminder that the b -values are differences in the energy of two structures. An acetylene is a polyene in the y -conjugation electrons superimposed on a

polyene in the z -conjugation electrons; and the difference in energy of two y -structures—such as the energy to go from the acetylenic structure to the y -allenic structure—may be almost independent of the distortion of both energies resulting from the fixed z -conjugation.

The diphenyl polyacetylenes⁶³ have been omitted from Fig. 8 because they show an even greater change of character along the series than the diphenylpolyenes. Only when the chains are very long do the spectra approach the acetylenic wavelengths and intensities and character of states as given in Fig. 1. This change undoubtedly occurs because the phenyl groups destroy the longitudinal cylindrical symmetry of the acetylene groups that gave rise to the orbital degeneracy and the special distinction between the ${}^1P^0$ (${}^1\Delta_u$) and the ${}^1B^0$ (${}^1\Sigma_u^+$) states in Fig. 1. Such changes of character will be a major problem in describing the spectra of mixed series of this kind.

The p -polyphenyl series have been included in Fig. 8 for comparison, but Eq. (27) should really not be applied to them (although Eq. (25) may be), since the zero-order free-electron predictions themselves converge to a finite limiting energy of about 17 kK for the infinite chain.⁶⁴ This is due to the structural periodicity that is present whether the bonds alternate or not. The observed intercept in Fig. 8 is 30 kK for the infinite chain; if these values are put in Eq. (15), they give a b -value of about 24 kK to be attributed to the bond alternation, not much greater than the polyene value.

The m -polyphenyls absorb at an energy near 39 kK almost independent of their chain length. Their zero-order free-electron predicted energies are about 32 kK,⁶⁴ theoretically independent of chain length,³⁸ and the b -value from the bond alternation is therefore roughly 22 kK. Dewar calls these molecules "cross-conjugated," implying that even though they have a continuously connected system of pi-electrons they do not form a truly conjugated chain.

Classical oscillator theory encounters similar gross displacements and convergences of the resonant fre-

⁶³ Armitage, Entwistle, Jones, and Whiting, J. Chem. Soc. 1954, 147.

⁶⁴ T. Nakajima, Sci. Rept. Tohoku Univ. 5A, 98 (1953).

quency in antennas with periodic structures. Possibly the analogy to the polyphenyls deserves closer examination.

Comparison of Deviation and Convergence Methods

The convergence method alone is not accurate enough for making an independent determination of the smaller b -values unless the series is very long, with spectra far into the infrared. Only one of Brooker's series seems to be long enough and to have large enough b -values to test the agreement of "convergence" and "deviation" methods of determination. This is the series in Fig. 5 with nuclei 22 and 24 on chains 0 to 4 vinyls long, but it is this very series which shows the greatest change of b -value with length, from about 10 kK for the first member in water to 15 kK in the fourth. On a plot like that of Fig. 8, if a geometrically reasonable value of 7.0 bonds is adopted for the N_1' of these dyes and if λ_C is assumed normal, the b -values vary from 0 to 14 kK. But the best straight line through the points gives a much higher apparent value of λ_C and a b -value of 16 to 18 kK; actually this b -value may represent a limiting value as the series is made longer. Possibly, in the light of Fig. 5, changes of b -values with length are peculiar to strongly dipolar dyes, where the polarizability of the chain affects the energy; and may not occur for neutral systems such as the polyenes. More data are needed on these questions.

The repeated appearance of b -values in the range from 17 to 24 kK for various even-atom chains and for this extreme dye suggests that this energy may also be

a "universal constant" representing a general natural limit for bond density alternation in conjugated chains, not merely in polyenes alone.

V. A THEORY OF b -VALUES IN DYES

Charge Density on Heteroatoms

The b -values in Eq. (13) have the form of H_{11} and H_{22} integrals, that is, integrals of the perturbation of the end groups over the squared wave functions Ψ_1 or Ψ_2 . Following Longuet-Higgins,⁶⁶ the b -value of a dye end group containing one heteroatom, say N , might therefore be related to the product of the local excess charge density, q_N , of Ψ_1 (or Ψ_2) on the heteroatom, times the perturbed Coulomb potential of that atom.

The excess charge density in the ground state, Ψ_A , of an odd-atom alternant hydrocarbon negative ion (closed-shell) is the square of the Longuet-Higgins alternant-orbital coefficient, c_r , at each atom, r . (The same expression gives the defect in charge density for the positive ion.) These orbitals are written out in Fig. 9 for several dyes. Each one is defined by the following unique and simple properties: c_r vanishes at alternate carbon atoms (called the "unstarred" atoms); and the sum of c 's over the neighbor of each such atom (called the "starred" atoms) vanishes also. Starting with an arbitrary coefficient at one starred atom, the coefficients can be written down quickly for successive alternate atoms throughout the system; the sum of the squares of the c 's can be normalized to unity to remove the arbitrariness.

The charge distribution in some odd-ring systems can also be estimated. For example, a thiazole nucleus can be treated approximately as a pyridine nucleus, replacing the $-S-$ atom by a vinyl group to make a 6-ring system.^{66,67}

In Fig. 9, the c -values for heteroatoms, c_N or c_a , are shown in boxes. The chain amino group is taken as a reference group, R , most closely approximated in the Brooker dyes by dimethyl amine (DMA); except for alkyl corrections, its c_N -value would be unchanged in the $-NHPh$ group (PA), the $-NMePh$ group (PMA), and the N -ethyl-indole-(2) group (nucleus 8). The last column of Table I gives theoretical values of $c_N(L)/c_N(R)$ for the 6-ring amines and the thiazoles; and it gives $c_0(L)/c_N(R)$ for the two oxy-acids, nuclei HS and HN. The other systems in Table I have odd rings or many substituents and are too difficult for plausible computations even with the present approximations.

Dewar and Longuet-Higgins⁶⁸ have shown that the alternant-orbital coefficient at any atom indicates the number of Kekulé structures in the usual resonance formulation that leave a charge on that (starred) atom.

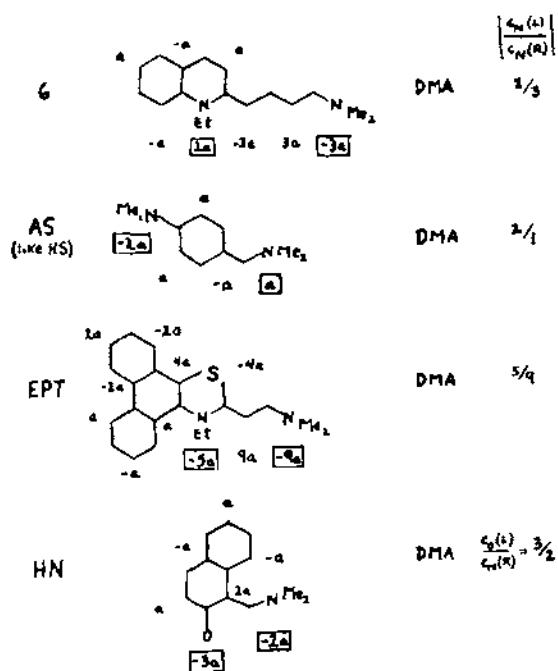


Fig. 9. Alternant-orbital coefficients in alternant and pseudo-alternant dyes.

⁶⁶ H. C. Longuet-Higgins, J. Chem. Phys. 18, 265, 275 (1950).

⁶⁷ T. Nakajima, Sci. Rept. Tohoku Univ. 37, 257 (1953).

⁶⁸ H. C. Longuet-Higgins, Trans. Faraday Soc. 45, 173 (1949).

⁶⁹ M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A214, 482 (1952).

This result can be easily checked in Fig. 9. This method of getting charge distributions must therefore be in perfect qualitative agreement with the resonance arguments which Brooker and co-workers used in accounting for basicities and b -values. The alternant-orbital method makes these arguments quantitative and is quicker and easier than the attempt to write down explicitly all the structures.

In Table I the relation of the c -values to basicity or acidity stands out clearly. The 2-oxy-naphthalene-(1) nucleus HN is less acidic than the 4-oxy-benzene-(1) nucleus HS which occurs in the hydroxystyryl dyes because the latter has a relatively larger $c_0(L)$ and $q_0(L)$ and therefore can accept more excess electronic charge on the oxygen atom. Similarly, the dimethylaminostyryl nucleus AS is a very weak base because its $c_N(L)$ and $q_N(L)$ are relatively large and the nitrogen atom can donate very little of its original unit excess electronic charge. It is easy to see in this way that the theoretical ratios in the last column of Table I get smaller with increasing basicity and decreasing acidity and with increasing b -value, within each type of nuclear group.

Charge Distribution for Structures and States

Equation (13) implies that the two structures S_1 and S_2 can be assigned orthogonal total molecular wave functions Ψ_1 and Ψ_2 . For a simple chain system, such as one of the 4-electron systems of Fig. 10, an electron density distribution (free-electron model) closely resembling that of Ψ_1 around each atom can be created by making the end group on the right a vinyl group. This forces the last electron—which would have been an excess electron in a 3-carbon system—over to the right. It brings the excess charge on the left to zero. It gives the bond to the left of the center "chain carbon" the character and electron density and bond length of a full polyene double bond, while the bond to the right of this chain carbon gets the character and density and length of a polyene single bond. The b_{LR} -value must then equal the full polyene value, say b_P , since the bond alternation presumably has the maximum amplitude it can have without acetylene groups present.

The electron density distribution of Ψ_2 is exactly opposite, since it is now the end group on the left which behaves like a vinyl group. The b_{LR} -value for this case is $-b_P$; for it is again a polyene, but now the opposite arrangement of bonds about the central carbon is stabilized.

Considering the Dewar-Longuet-Higgins result in connection with Figs. 9 and 10, it is evident that the alternant-orbital excess electronic charge on the heteroatom in the usual type of L -group, $c_N(L)^2$ or $q_N(L)$, is associated with only one structure in the chain, Ψ_2 , while that in an R -group, $c_N(R)^2$ or $q_N(R)$, is associated with the other chain structure, Ψ_1 . By assuming that all the excess charge goes on the heteroatoms in pro-

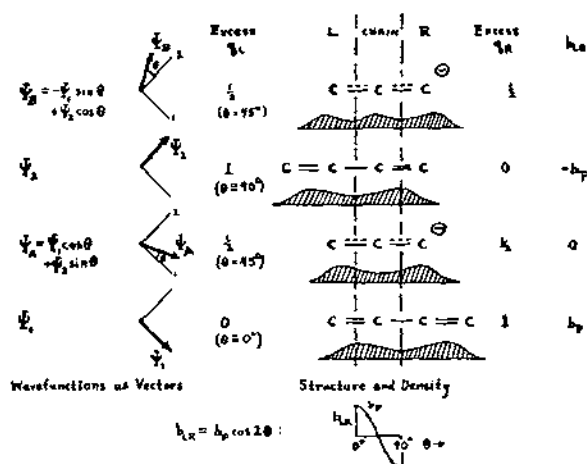


FIG. 10. Structure vectors, state vectors, and charge densities in four-electron systems.

portion to these theoretical densities; and that the b -values, like H_{11} -integrals, are proportional to the plus charges at least when the heteroatoms are the same; and that the maximum b -value is that of the polyenes, where only one structure dominates, and the "excess charge" on one end is unity; the following relation between b -values and alternant-orbital theoretical charge densities becomes plausible:

$$\frac{b_2 - b_1}{b_P} = \frac{b_R - b_L}{b_P} = \frac{q_N(L; \Psi_2) - q_N(R; \Psi_1)}{q_N(L; \Psi_1) + q_N(R; \Psi_1)} \quad (28)$$

or

$$b_L = b_P \left[\frac{c_N(R)^2 - c_N(L)^2}{c_N(R)^2 + c_N(L)^2} \right]_{\text{theoret.}} + b_R \quad (29)$$

Test of Theory

Figure 11 is a test of the linear relation in Eq. (29). It shows the empirical b_L -values for nuclei in trimethine and pentamethine dyes plotted against the theoretical quantity in brackets, which can be obtained from the numbers in the last column of Table I. The b -values are the observed values in water as given in Table I, except for the bases, which had to be extrapolated from the $MeOH$ data. This extrapolation is a small correction and was made systematically, in general accord with Fig. 7, by adding 10% to the b -values in $MeOH$. It is important to compare the theory against data taken in a medium such as water in order to reduce the Coulomb effects which are neglected in the alternant orbital calculation.

The solid straight line fits the points for the ten different trimethine 6-ring nitrogen bases within 1 kK. The oxy-acids in water, shown by circles in Fig. 11, lie near this line but off it, presumably because of the difference in the perturbation potential for the oxygen atom. The thiazole line, fitting six nuclei and shown with short dashes, is displaced to the right, undoubtedly

because of the systematic theoretical error in treating $-S-$ as a vinyl group. The pentamethine points for two thiazoles and for three aza-bases are in accord with an increase in the slope of the lines by about 40%, which would be expected from the chain length effects of Fig. 4; these effects are not taken into account in the assumptions underlying Eqs. (28) and (29). The long dashed line is drawn to give about the same fit for the pentamethine aza-bases as the long solid line gives for the same trimethine bases.

The slopes of the two long lines in Fig. 11 are 12 kK and 17 kK. It is reassuring to see that these slopes are of roughly the right magnitude to be identified with the polyene coefficient, b_P , in Eq. (29), for which values of 17.5 to 20 kK were obtained from convergence data. Perhaps the slopes for longer chains would tend to move still closer to this convergence value of b_P ; but no very critical agreement should be expected when the theoretical treatment is based on so many approximations.

In summary, it appears that the absorption wavelengths of many chain systems should be predictable to fair accuracy from the structural formula alone, by estimating λ_1 from the geometrical length and b from the alternant-orbital coefficients. With the help of some empirical corrections, this might be made into an easy predictive method of great accuracy and chemical usefulness.

The appearance of two parameters for each end group is reminiscent of the situation in aromatic ultra-violet spectra, where two parameters are required to describe the wavelength and intensity changes produced by a substituent.⁶⁹⁻⁷⁴ One of these, dominant in aza-substitution, is determined by the electron donor or acceptor character of the substituent^{69,71} and produces configuration interaction between two particular states, giving quadratic energy and intensity changes; in all these respects like the second-order b -values here. The other, dominant in vinyl substitution,⁷¹ is a first-order red-shift parameter that increases with decreasing ionization potential of the substituent, that is, with increasing wavelength of the first strong absorption; but it does not change intensities or produce significant configuration interaction; and it is in these respects like the λ values here. These two effects have been called inductive and conjugative, respectively,^{73,74} although they have not always been connected to donor-acceptor and ionization properties or to first- and second-order shifts of state energies in the way stated here.

It seems likely that every chemical perturbation of electronic spectra may be expressible in terms of two such parameters. No doubt it is the double complication of this situation that has hampered the general

quantitative analysis and prediction of spectral wavelength shifts and intensities. The success of the present two-parameter analysis of chains suggests the possibility of extension later to nonchain systems and of expansion into a unified treatment which might include the substituted aromatics as a special case.

VI. STATES, DENSITIES, AND INTERACTIONS

(A) Density Maxima and Minima

Up to this point it has been convenient to describe the b -values and the second-order effects in terms of resonance structures and their interactions. It is now time to examine their physical significance more directly in terms of the interaction between molecular states and the electron-density and bond-length alternations which are probably responsible for them.

The free-electron density distribution in chains oscillates strongly in the ground state.⁷⁵ Some of the chemical and spectroscopic implications of this fact⁷⁶ have been summarized and extended to excited states by Bayliss.³³ Figure 12 shows his ground and excited state curves for 6-electron systems: they are the simple sums of squares of the sine-function amplitudes of the occupied orbitals.

The density maxima are almost exactly two bond lengths apart, and the oscillation can be described by a single sine function of this period with varying amplitude.⁴⁶ In the ground state of odd-atom alternant systems, this two-bond density periodicity is implied by the alternant-orbital formulation for the total density. In even-atom alternant systems, it is a necessary consequence of the Coulson-Rushbrooke LCAO

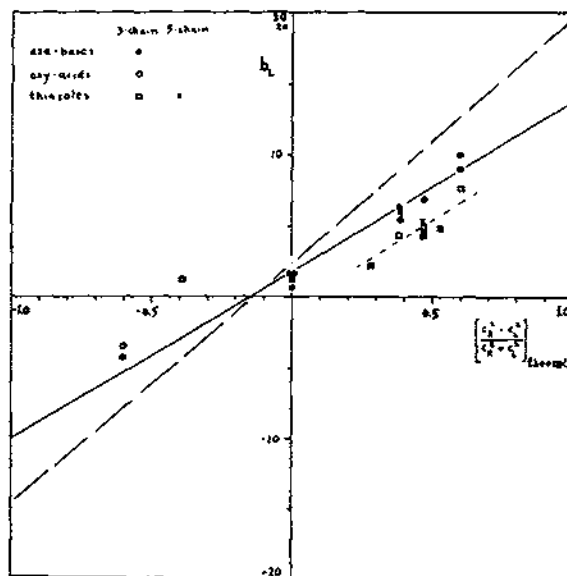


Fig. 11. Comparison of experimental and theoretical b -values.

⁶⁹ A. L. Sklar, J. Chem. Phys. 10, 135 (1942); Revs. Modern Phys. 14, 232 (1942).

⁷⁰ Th. Förster, Z. Naturforsch. 2a, 149 (1947).

⁷¹ J. R. Platt, J. Chem. Phys. 19, 263 (1951), and unpublished.

⁷² H. Sponer, J. Chem. Phys. 22, 234 (1954).

⁷³ F. A. Matsen, J. Am. Chem. Soc. 72, 5243 (1950).

⁷⁴ C. A. Coulson, Proc. Phys. Soc. (London) A65, 933 (1952).

⁷⁵ J. R. Platt, J. Chem. Phys. 17, 489 (1949).

⁷⁶ H. Kuhn, Chimia (Switz.) 4, 203 (1950).

theorem of equal charge density at every atom and its free-electron counterpart⁷⁷; for the bonds must then have alternate maxima and minima; and this theorem has now been shown to apply to all excited states as well.^{48,49}

The density maxima for the even-atom system occur at the positions of the classical double bonds, and for the odd-atom system at the positions of excess charge (starred) in the classical resonance formulation. This matching of the two-bond periodicity of the Kekulé structures to the electron density periodicity may be the secret of their success. In fact, we can think of each structure, S , as a symbolic representation of an electron density distribution, just as the Bohr orbit is a symbolic representation of an atomic electron density distribution.⁴⁶ Simpson⁵² has remarked similarly that a structure symbolizes the square of a wave function rather than the wave function itself.

It is instructive to apply electrical alternating-current notation to the description of these alternating maxima and minima. Let structure S_1 be symbolized by the square of the real part of a complex function F_1 with wavelength $4d$ and density maxima $2d$ apart. Near the center of a chain, where end effects can be neglected,

$$F_1 = a \exp(i\pi x/2d). \quad (30)$$

Structure S_2 is moved a distance d or 90° in phase:

$$F_2 = a \exp[i\pi(x+d)/2d] = iF_1. \quad (31)$$

Every arbitrary state with the same periodicity of density can be represented similarly, with a particular phase displacement, θ , and linear displacement, l , of the density maxima:

$$\begin{aligned} F_A &= a \exp[i\pi(x+l)/2d] = a \exp[(i\pi x/2d) + i\theta] \\ &= F_1 \cos\theta + F_2 \sin\theta. \end{aligned} \quad (32)$$

An orthogonal state, with reversed maxima and minima, somewhat like the excited state ${}^1B^0$ near the center of the chain in Fig. 12, is represented by

$$\begin{aligned} F_B &= a \exp[i\pi(x+l+d)/2d] \\ &= a \exp[i\pi x/2d + i(\pi + \theta)] = iF_A \\ &= -F_1 \sin\theta + F_2 \cos\theta. \end{aligned} \quad (33)$$

These F 's (real part) resemble closely the alternant-orbital wave functions in odd-atom systems and the "frontier" orbitals⁷⁸ that largely determine the density maxima and minima in even-atom systems; but it may be better to think of F not as a strict wave function but as a useful representation of the gross spatial oscillation of the true total state wave function, Ψ . Thus F_1 , F_2 , F_A , F_B may be described strictly by vectors in the complex plane, like those in Fig. 10, and this description may then have some approximate

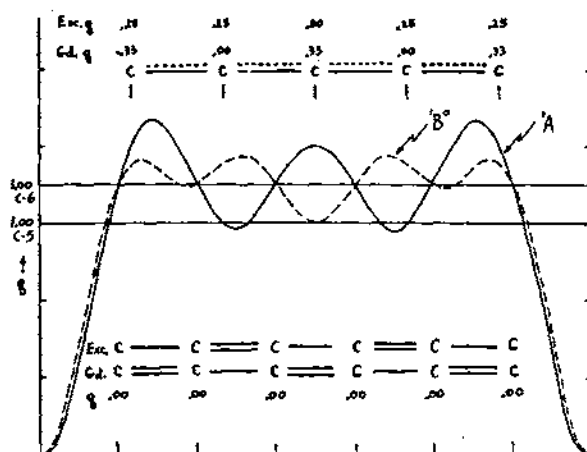


Fig. 12. Total electron densities in ground and excited states of six-electron chains. After Bayliss.³⁸

validity and usefulness for state wave functions Ψ_1 , Ψ_2 , Ψ_A , Ψ_B .

Since F_A and F_B are linear combinations of F_1 and F_2 , density maxima can be located without reference to "intermediate structures." As one end of a chain is more or less basic, it pulls the density maxima of ground and excited states more or less to one side, changing their location with respect to the atoms in the chain and changing the asymmetry and degree of alternation in the chain bonds around each atom. The secular equation (13) could then be thought of not as an interaction equation between structure wave functions Ψ , but as the equation between functions F for determining the best values of θ and l , the location of the density maxima that will minimize the energy in the ground state.

Much of the discussion hereafter will be in the more familiar Ψ language of structures and states but it should be kept in mind that, at least in dealing with density-alternation interactions, this may be a formalism whose physical significance is rather in the transformations of the corresponding F -functions and the displacement of density maxima.

(B) State Formulation for Dyes

Rotation of the Secular Equation

For the dyes, the structure vectors, Ψ_1 and Ψ_2 , which are the basis for Eqs. (10) and (13), may be rotated by 45° so that the zero-order wave functions become true stationary state wave functions possibly of a real molecule, such as a symmetrical or isoenergetic dye with $b=0$. These wave functions are Ψ_{A0} and Ψ_{B0} of Fig. 10, the second subscript being added to indicate that θ is fixed at 45° .

$$\Psi_{A0} = 2^{-1/2} (\Psi_1 + \Psi_2) \quad (g\text{-function, even parity}), \quad (34)$$

$$\Psi_{B0} = 2^{-1/2} (-\Psi_1 + \Psi_2) \quad (u\text{-function, odd parity}). \quad (35)$$

⁷⁷ K. Ruedenberg and C. W. Scherr, J. Chem. Phys. 21, 1565 (1953).

⁷⁸ Fukui, Yonezawa, and Shingu, J. Chem. Phys. 20, 722 (1952).

Equation (10) is then rotated to the diagonal form, as in the procedure of Simpson and Looney,⁵²⁻⁵⁴

$$\begin{vmatrix} \Psi_{A0} & \Psi_{B0} \\ \Psi_{A0} \left| \epsilon + \frac{1}{2} E_I \right. & 0 \\ \Psi_{B0} \left| 0 & \epsilon - \frac{1}{2} E_I \right. \end{vmatrix} = 0, \quad (36)$$

and the interaction energy between structures has become an energy difference between states—largely a difference in kinetic energy, judging by the success of the free-electron zero-order predictions. Equation (36) of course still has the solutions and transition energies given by Eqs. (11) and (12).

Equation (13) is similarly rotated to

$$\begin{vmatrix} \Psi_{A0} & \Psi_{B0} \\ \Psi_{A0} \left| \epsilon + \frac{1}{2} E_I \right. & \frac{1}{2} b \\ \Psi_{B0} \left| \frac{1}{2} b & \epsilon - \frac{1}{2} E_I \right. \end{vmatrix} = 0, \quad (37)$$

and the difference in stability between the two structures which formerly appeared on the diagonal now appears as an off-diagonal element or interaction energy between the states. Equation (37) still has the solutions given by Eqs. (14) and (15).

Alternative Derivation of b -Values

The antisymmetric perturbation by the end groups is just the kind to produce an off-diagonal matrix element, $b_{LR} = b_L - b_R$, between an odd and even state. Assuming it is due to the appearance of bond alternation (which is antisymmetric), it can be computed, provided the first-order displacement of the density maxima can be determined. For if the bond alternation is defined as the difference in either center density or average density between adjacent bonds, it should have a sinusoidal oscillation as θ or t increases, so that

$$b_L - b_R = b_{LR} = b_P \cos 2\theta = b_P \cos \pi t/d, \quad (38)$$

with a periodicity of two bond lengths in t ; t and θ are taken as zero when the density maxima are in the centers of bonds.

This t or θ can in turn be estimated as follows by using the alternant-orbital densities to give a first approximation for the charge distribution in state Ψ_A . On the left end of the chains in Fig. 10, the Ψ_A amplitude for the excess electron is just the contribution from the function Ψ_2 alone [see Eq. (32)]:

$$\Psi_A(L) = \sin \theta, \quad (39a)$$

since the amplitude for Ψ_1 vanishes at that end. Similarly, on the right end the Ψ_A amplitude is only the contribution from Ψ_1 ,

$$\Psi_A(R) = \cos \theta. \quad (39b)$$

The charge at the two ends due to the excess electron is then given by

$$q_A(L) = \sin^2 \theta; \quad q_A(R) = \cos^2 \theta. \quad (40)$$

[Equation (33) suggests that the orthogonal state, Ψ_B , should have the excess charge distributions at the two ends approximately interchanged.]

Comparing Eqs. (39) with the theoretical alternant-orbital amplitudes, c , and charge densities, q , at the ends of the chain, gives

$$\frac{\sin \theta}{\cos \theta} = \frac{c(L)}{c(R)}. \quad (41)$$

This ratio is the theoretical ratio of the contributions of structures S_2 and S_1 in the chain. If the assumption is made as before that with complex end groups, all the charge goes on the heteroatoms, it is $c_N(L)$ and $c_N(R)$ that determine the ratio of the contributions. The trigonometric quantity needed in Eq. (38) is $\cos 2\theta$, which can then be written

$$\begin{aligned} \cos 2\theta &= \cos^2 \theta - \sin^2 \theta = \frac{\cos^2 \theta - \sin^2 \theta}{\cos^2 \theta + \sin^2 \theta} \\ &= \left[\frac{c_N(R)^2 - c_N(L)^2}{c_N(R)^2 + c_N(L)^2} \right]_{\text{theoret.}} \quad (42) \end{aligned}$$

Inserting this result in Eq. (38) leads again to Eq. (29) for the theoretical b -values, but now with a different interpretation. Probably the essential element in the success of that equation, at least to the degree shown by Fig. 11, is that the charge densities on the heteroatoms are related to the locations of the density maxima in the bonds; and perhaps any monotonic relationship will give a fairly successful prediction of b -values.

(C) State Formulation for Polyenes

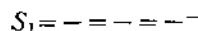
Need for Additional Structures and States

A polyene may also be treated as a symmetric odd-atom dye in which one end attracts electrons very strongly, as it would if it were a methyl group. It can be supposed that the alternant orbital is so strongly changed by this perturbation that the location of the density maxima for computing b must be assumed to be displaced one-half bond from the symmetric dye maxima, so that b becomes b_P . (It can be displaced back by putting the polyene in sulfuric acid,¹⁴ making it a dye with an even number of pi-electrons in an odd-atom conjugated chain.) This is an extreme way to approach polyenes but it does not violate any physical principle.

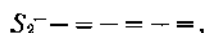
On the other hand, if the attempt is made to write a secular equation based on two zero-order *polyene* state wave functions, Ψ_{AP} (even) and Ψ_{BP} (odd), of a symmetric even-atom chain with equal bond lengths, this

equation *cannot* be perturbed by bond alternation so as to lead to Eq. (15). For the alternating electron densities now form a symmetric perturbation which cannot mix an even ground state with an odd excited state.

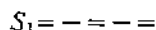
This difficulty in the simple resonance formulation was pointed out early by Mulliken.²⁸ His conclusions may be stated in the present language and amplified. On approaching the polyenes, the two resonance structures used for the dyes,



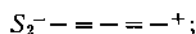
and



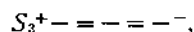
approach



and



and it is evident that a third structure,



which had been at much higher energies in the dyes, must now be given equal consideration with S_2 . (The minus signs in the dye structures indicate the excess-electron location and not necessarily the total charge.)

Translating this into state language, S_1 is the principal structure in the symmetric ground state. Now S_2 and S_3 can form a symmetric and an antisymmetric excited combination. (A structure S_4 with a long bond between the end atoms can also contribute to this symmetric combination.) From the ground state, a spectroscopic jump will go to the antisymmetric one of these, giving the ${}^1A - {}^1B^0$ strong allowed even-odd transition. The symmetric perturbing potential, although it cannot mix the ground state energetically with this antisymmetric state, *can* mix it with the other, symmetric, state formed from the excited structures. The allowed transition is to one excited state; the mixture is with the other.²⁸

For polyenes, this means the secular Eq. (37) must become

$$\begin{vmatrix} \Psi_{AP}(\text{sym}) & \Psi_{BP^0}(\text{asy}) & \Psi_{exc}(\text{sym}) \\ \Psi_{AP}(\text{sym}) & \epsilon + \frac{1}{2}E_I & 0 & \frac{1}{2}b \\ \Psi_{BP^0}(\text{asy}) & 0 & \epsilon - \frac{1}{2}E_I & 0 \\ \Psi_{exc}(\text{sym}) & \frac{1}{2}b & 0 & \epsilon - \frac{1}{2}E_I \end{vmatrix} = 0, \quad (43)$$

assuming the two excited combinations are at the same energy. The solutions are

$$\epsilon_{a,b,c} = \frac{1}{2}E_I, \quad \pm \frac{1}{2}[E_I^2 + b^2]^{\frac{1}{2}}, \quad (44)$$

and the ${}^1A - {}^1B^0$ transition energy is

$$E = \frac{1}{2}E_I + \frac{1}{2}[E_I^2 + b^2]^{\frac{1}{2}}. \quad (45)$$

The counterpart of Eq. (19) becomes

$$b = 2[E^2 - EE_I]^{\frac{1}{2}}, \quad (46)$$

and of Eq. (20),

$$b = \frac{[2 \cdot \Delta\lambda \cdot 2\lambda_I]^{\frac{1}{2}}}{\lambda_I \lambda}. \quad (47)$$

If these formulas were used to obtain b -values, the values would be larger by about a factor $2^{\frac{1}{2}}$ than those of the earlier equations. The combination equations (18) which were used to test the hypothesis of additive b -values will not distinguish between the two sets except at very high b -values, where the factor $(E + E_I)$ under the square root in Eq. (19) begins to differ appreciably from two times the factor E under the square root in Eq. (46). But empirically, the determination of b -values by the methods of Sec. III gives more weight to the high values and will tend to mask any such deviation; and at the high values either theoretical picture might be expected to break down anyway. Consequently, Eq. (43) may be no more satisfactory than Eq. (13) in accounting for the Brooker deviations empirically, and the present wavelength data alone will probably not permit us to prove whether the postulate of a third structure S_3 and of long bond and other structures is or is not empirically necessary. It would probably be still more difficult to determine empirically from b -values whether the two excited states should be assigned different energies. The most sensible procedure is probably to use the methods of Sec. III for empirical determination of the b -values and to suppose that the interpretation of these values should change steadily in going from the cyanine to the polyene case.

Configuration Interaction in Polyenes

It is important to know what symmetric state mixes with the ground state in Eq. (43) and why. The interaction must be due to the excess density of negative charge in the density maxima of the polyene, which pulls the nuclei adjacent to the maxima closer together, producing alternating bond lengths and the alternating nuclear potential emphasized by H. Kuhn.³⁴⁻³⁶ Note that it is not just the zero-order negative charge density itself producing mixing by self-interaction; because when this is unaccompanied by bond-length alternation it produces quite negligible shifts in the spectra, as judged by the success of the free-electron zero-order predictions. In any case, such pure electronic effects should be of similar magnitude in all systems and would tend to cancel out in a differential analysis like that of the Brooker deviations in Sec. III and probably in the chain analysis of Sec. IV.

Undoubtedly, the induced alternating nuclear potential attracts further charge to these high-density regions. In perturbation language, this can only be described by saying that the potential mixes the zero-order ground state with one or more excited states of the same symmetry that have wave functions whose maxima and minima of *amplitude* (or "displacement")

coincide with those of the ground-state *density* distribution. A movement of charge is a mixture of states. Although a careful theoretical analysis needs to be made, a number of reasons can be given for supposing that the lowest such excited state may be the 1L_c -state of Fig. 1, and that this state can be identified with $\Psi_{\text{exc}}(\text{sym})$ of Eq. (43).

If the cyanine case could be carried into the polyene case by a continuously increasing perturbation, the states would mix and change their character adiabatically, so that there is, in principle, no difficulty in calling the state interacting with the ground state ${}^1B^\circ$ in the cyanines and 1L_c in the polyenes.

Nature of L -States

Theoretically there should be many 1L -states in alternant hydrocarbons.⁴⁸⁻⁵⁰ Each has the property that it is a 50-50 mixture of two hypothetical one-electron excited configurations of almost equal energy. For every such pair, two independent mixtures are possible, one with positive and the other with negative sign. One of these gives a "normal" state, 1C or ${}^1D^\circ$, etc., with "normal" transition moments depending in the usual way on gross molecular dimensions and parity; the other gives the 1L -states, which have a high-order cancellation of transition moments to other states, like high-order classical multipole oscillations, with the sign of the oscillating classical charge changing in every bond or at every atom.^{71,75}

The multiplicity of the ${}^1A-{}^1L$ transitions can be defined more precisely and related to some of the older structural formulations. In condensed-ring systems, benzene for example, the ground state is a *plus* mixture of two equivalent Kekulé structures as shown in Fig. 13. The lowest excited state, ${}^1L_b^\circ$, can be regarded as a *minus* mixture of the two.⁷⁹ This gives correctly the symmetry of the state, which is known from other evidence to be ${}^1B_{2u}$; since the minus mixture changes sign on reflection in every atom, which is the ${}^1B_{2u}$ characteristic. From the orbital point of view, this state can also be described as a particular mixture of the several $f-g$ orbital transitions of equal energy in benzene. The "transition density," $\Psi_A\Psi_{L_b}$, for absorption to this state, or the "polarization diagram" as it was called earlier, is shown in the upper right of Fig.

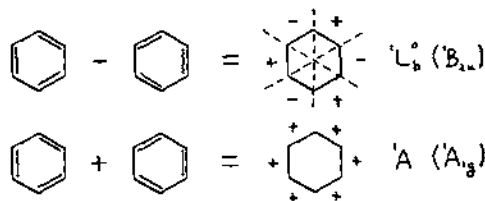


Fig. 13. Sklar relationship between resonance structure combinations and transition density diagrams in benzene.

⁷⁹ A. L. Sklar, J. Chem. Phys. 5, 669 (1937).

13. Since the transition dipole moments cancel, it is a forbidden transition. The plus and minus regions in this diagram show the multipole character of this transition.

The nodal lines in such a diagram, which are the intersections of the nodal planes with the plane of the diagram, are lines in which the state wave function changes sign on reflection. But nodal lines and planes can be defined also in a more general way,⁸⁰ so as to include less symmetrical systems, even when there are many electrons: The nodal planes have the property that, if all the electrons are placed in any such plane or planes, the wave function vanishes; and if the electrons are displaced by arbitrary small amounts out of the plane or planes, the wave function changes sign when all the displacements change sign. (And the planes may be more general surfaces.)

This definition can be applied to locate the nodes for an ${}^1A-{}^1L_c$ transition in a polyene. The lowest theoretically-predicted 1L_c -state is supposed to be a mixture of the $e-g$ and $f-h$ configurations. For hexatriene, it is a configuration with one electron raised from the orbital with $n=2$ to the orbital with $n=4$, minus a configuration with one electron raised from $n=3$ to $n=5$. If all the electrons are given the same x -coordinate—if they are put in the same y,z -plane—this 1L_c state free-electron wave function can then be written explicitly

$$\Psi_{L_c}(x_1=x_2=x) = \sin 2\pi x/L \sin 4\pi x/L - \sin 3\pi x/L \sin 5\pi x/L, \quad (48)$$

neglecting the filled orbitals and omitting the normalization constant. This is easily transformed trigonometrically to the form

$$\Psi_{L_c}(x_1=x_2=x) = \sin \pi x/L \sin 7\pi x/L, \quad (49)$$

and the sevenfold term will vanish at every atom of hexatriene when drawn as in Fig. 12. This suggests that the generalized nodal planes pass approximately through the atoms; and the same will happen for every polyene 1L_c -state. The ${}^1A-{}^1L_c$ transition density diagram may therefore have the classical counterpart shown in Fig. 14, where it is contrasted with the "normal" transitions.

Considering the relationships for the excited state of benzene, it may be significant that this diagram resembles the classical S_1 -minus- S_2 combination de-

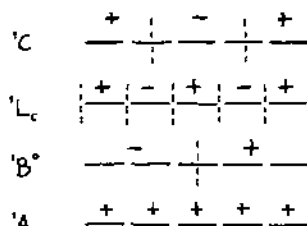
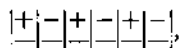


Fig. 14. Transition density diagrams for polyene states.

⁸⁰ K. Ruedenberg, private communication.

scribing the upper state of dyes:

minus $S_1 = - - - - -$
 equals $S_2 = - - - - -$



which has L -type properties since the combination wave function likewise changes sign at every atom. Figure 14 shows further that the 1L_c -state satisfies the requirement that the maxima and minima (of displacement) be located properly for producing a strong interaction with the ground-state-density-induced potential. Pariser⁵⁰ also points out that the ground state behaves like a minus state, that is, like the L -states, with respect to mixing and selection rules. So that in no respect does there seem to be any theoretical barrier to the inference that a rather specific interaction may be produced by the symmetric alternation-potential between the zero-order polyene states 1A_P and ${}^1L_{cP}$.

(D) Other Effects of Configuration Interaction

Limiting Alternation

A mixture of these two states, of form

$$\Psi_A = \Psi_{A_P} \cos \alpha + \Psi_{L_{cP}} \sin \alpha, \quad (50)$$

when given the proper phases, should then have still higher density than that of Ψ_{A_P} alone, in those regions where the ${}^1L_{cP}$ wave function displacement is given a plus sign in Fig. 14; and a lower density where it is given a minus sign. (The angle α now represents a change of density-oscillation amplitude, while the angle θ used in mixing structures represented a change of position of density maxima.) Whatever other states are mixed in, the density effect should be the same. In a self-consistent treatment, these density changes would increase the b -value in the ground state, which would increase the interaction again, and so on to some limiting density alternation and b -value where the attraction of the adjacent nuclei to an enhanced density maximum is balanced by their repulsion for each other and by the electronic repulsion and kinetic energy terms, as in a hydrogen molecule. It would be an interesting theoretical problem to compute this limiting self-consistent absolute b -value especially for polyene ground states.

The present results offer three semiempirical guides as to what kind of formulation is likely to be successful. First is the suggestion of the probable importance of interaction with particular states like 1L_c . Second is the suggestion from the qualitative theoretical success of Fig. 11 that the limiting b -value probably varies with the initial location, l , of the density maxima in the bonds, approximately as shown by Eq. (38). Third is the suggestion, from convergence, that the limiting alternation depends mainly on l alone and not on the

absolute size of the theoretical zero-order alternation; as though any alternation with a given l would be amplified up to the same self-consistent limit. Obviously, it is the limiting alternation and not the zero-order alternation that comes out of the empirical analysis.

This third conclusion seems to be the way to reconcile the Lennard-Jones result, that the theoretical zero-order alternation should decrease in long chains, with the empirical findings of H. Kuhn and Dewar and the present paper that the alternation of potential and bond length and the b -value do not decrease in long chains. Careful x-ray measurements on long polyenes would throw light on this question.

H. Kuhn's method of perturbation seems at first to give a different result from that here, with the first transition energy depending linearly on the amount of alternation, that is, on the b -value. But this is because he applies in principle a limiting (but arbitrary) alternation-potential parameter to a fixed zero-order wave function and density distribution. If the alternation parameter is taken proportional to the density alternation in the wave function, the energy must vary quadratically with each, and give a second-order effect like the present configuration interaction formulation when b is near zero. It remains to be seen whether the two approaches can be unified theoretically.

The meaning of the parameters used in the resonance theory of spectra and the relation of this theory to molecular orbital theory may need to be re-examined in the light of the present conclusions, since they suggest that the resonance theory states always contain an implicit second-order alternation-interaction or 1L_c -mixture (because of the localized electrons in the simple structures²⁷) which the states in the molecular orbital theories do not.

Configuration interaction has often been applied to molecular orbital theory without bond alternations. The present results suggest that when they are applied together, the size of the interactions and the intensity and energy changes for particular states should become especially striking.

These results may also have implications for the band theory of metals and semiconductors. It may not be true that the atoms in a long chain or extended system do not "know" how far they are from the end, as usually supposed. For a change of one atom at the end or edge may change the positions of density maxima throughout the system and affect the separation of electronic bands, the alternation of atomic spacings, and the state of charge at the opposite end or edge by large amounts. Surface layers and impurities or vacancies might therefore have strong effects dozens or hundreds of atoms away.

Spacing of Energy Levels

Another piece of evidence that may demonstrate specific interaction between the 1A and higher (hidden)

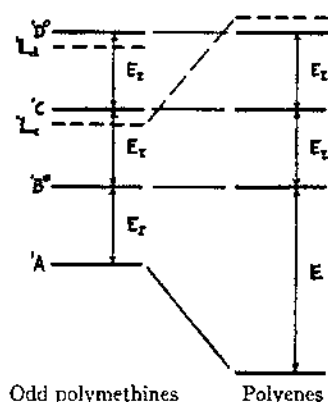


FIG. 15. Spacing of energy states in odd and even chain systems.

states in polyenes is the difference between the energy ratios of the first, second, third, and higher strong transitions and the corresponding ratios in the odd polymethine or cyanine dyes. This difference is shown in Fig. 15. The energy states appear to be spaced approximately equally in the cyanines. A transition which is probably ${}^1A-{}^1C$ is at almost exactly twice the frequency, E_T , of ${}^1A-{}^1B^0$, in several of the Brooker dye spectra given by Sklar,²⁵ and in the cyanine spectrum of Zechmeister and Pinckard,⁸¹ where it is known that there is a *cis*-modification present which would enhance the ${}^1A-{}^1C$ peak. This equal spacing is what would be expected for one-electron transitions between the equally-spaced orbitals, LCAO or free electron, of a linear system; and Nikitine's comparisons⁸² show the accuracy of this expectation. It would also be expected from the Lewis and Calvin correspondence-principle analogy to the fundamental and overtone oscillations of a classical linear antenna.

In the polyenes, however, when the 1A -state is depressed by interaction with the higher state, 1L_0 , the first transition energy, ${}^1A-{}^1B^0$, should become E ; the second transition energy, ${}^1A-{}^1C$, about $E+E_T$; the third, ${}^1A-{}^1D^0$, about $E+2E_T$; and so on. These predicted nonharmonic spacings are found to be quite accurate, as seen for example in the carotene spectra given by Zechmeister and Polgár,⁸³ where E is about 21 kK and E_T is about 9 kK. They have previously been a somewhat puzzling deviation from the simple molecular orbital expectations.

Obviously, energy-level displacements of this kind may have to be taken into account in theoretical calculations of resonance energies or ionization potentials, especially in polyenes.

Intensities

The mixture of a state such as ${}^1L_{CP}$ into the ground state should lower the ${}^1A-{}^1B^0$ intensity, since the

⁸¹ L. Zechmeister and J. H. Pinckard, *Experientia* 9, 16 (1953).

⁸² S. Nikitine, *J. chim. phys.* 48, 37 (1951).

⁸³ L. Zechmeister and A. Polgár, *J. Am. Chem. Soc.* 65, 1522 (1943).

${}^1L_{CP}-{}^1B^0$ intensity (with the zero-order wave functions) would be about zero, ${}^1L_{CP}$ being a high multipole state with many nodes. The intensities in polyenes and many even-atom conjugated systems are smaller than expected from simple molecular orbital theories by factors of 2 to 3,^{84,85} and it is usually assumed that this error will be corrected when enough configuration interactions are included. But perhaps it is only a few specific interactions of the type described here that lower the intensity. If the ground state takes on up to 50% ${}^1L_{CP}$ character, the intensity might be reduced by factors up to 2 in a chain polyene. A theoretical examination of this possibility and a search for similar specific intensity-reducing interactions in nonchain systems would be interesting.

VII. INTENSITY, BAND WIDTH, AND STRUCTURE NEAR THE ISOENERGETIC POINT

(A) McConnell Theory of Oscillator Strengths

The theory of oscillator strengths in a Brooker dye with changing solvents has been developed by McConnell⁸⁶ from the state formulation.

The general wave-function solutions of Eq. (37) for the ground and excited states of the dye, Ψ_A and Ψ_B , may be expanded in terms of the symmetric and anti-symmetric state wave functions at the isoenergetic point, Ψ_{A0} and Ψ_{B0} ,

$$\Psi_A = \Psi_{A0} \cos\phi + \Psi_{B0} \sin\phi \quad (51a)$$

$$\Psi_B = -\Psi_{A0} \sin\phi + \Psi_{B0} \cos\phi. \quad (51b)$$

The angle ϕ is $\theta-45^\circ$, because of the rotation by 45° from the structure wave functions Ψ_1 and Ψ_2 .

The ${}^1A-{}^1B$ transition energy is easily shown to be

$$E = E_T \cos 2\phi + b \sin 2\phi = [E_T^2 + b^2]^{1/2} = E_T \sec 2\phi. \quad (52)$$

The transition moment is of the form

$$Q_x = \int \Psi_A x \Psi_B d\tau = Q_{xI} (\cos^2\phi - \sin^2\phi) = Q_{xI} \cos 2\phi \quad (53)$$

since

$$\int \Psi_{A0} x \Psi_{A0} d\tau = \int \Psi_{B0} x \Psi_{B0} d\tau = 0 \quad (54)$$

by symmetry.

The integrated intensity, or oscillator strength, f , varies as EQ^2 ⁸⁴:

$$f = f_I \cos 2\phi. \quad (55)$$

⁸⁴ R. S. Mulliken and C. A. Rieke, *Rept. Progr. Phys.* 8, 231 (1941).

⁸⁵ N. S. Ham and K. Ruedenberg, *J. Chem. Phys.* 25, 1, 13 (1956), this issue.

⁸⁶ H. McConnell (1952, unpublished); also independently developed later by W. T. Simpson (unpublished). I am indebted to Dr. McConnell for permission to summarize his results in Eqs. (55) and (56).

Combining this with Eq. (52) gives McConnell's formula

$$\frac{f}{f_I} = \frac{E_I}{E} \quad (56)$$

Solvent effects other than the effect on b are not included in this treatment.

To test this formula, the absorption curves may be examined that were given by Bayliss and McRae⁵⁷ for the merocyanine dye with nuclei 22 and 24, $n=2$ (Fig. 5) in a series of solvents. The b -values varied in this series from near zero to 13 kK, and E increased by 30%. The integrated areas of the curves, determined from the rather small-scale published figures, decreased by only about $10 \pm 10\%$ in the series. The difference from Eq. (56) may not be outside the uncertainty in the areas. Since that equation rests on a particularly rigorous expansion involving a minimum of arbitrary assumptions, a more careful test of it would be desirable.

(B) Band Widths and Peak Intensity

Band Widths

But a most striking feature of dye spectra pointed out by Brooker and co-workers is the variation of peak intensity, not integrated intensity, near the isoenergetic point. For the dipolar dyes that cross the axis in Fig. 5, they plotted the peak intensity, against peak wavelength as the solvent varied. Such a set of points is shown in Fig. 16. It rises steeply to a peak or cusp at the isoenergetic point of maximum wavelength and then falls steeply, in many cases almost retracing its original path on the diagram. On a log-log plot, the steepness of the cusp at the isoenergetic point sometimes reaches slopes of 10^{10} or even 50.⁸⁷ The intensity behavior must imply a reciprocal behavior for the band width, since the integrated intensity is so nearly constant.

A glance at Fig. 12 shows why the band width should be least for cyanines and greatest for polyenes. The symmetric odd-atom chains have constant-density points in the bonds in both the ground and excited states, corresponding to 50–50 mixtures of the two structures, with each bond having 0.5 double-bond character in both states. The bonds have approximately equal length with no alternation in either state, and there is no strong tendency for the nuclei to move their positions on excitation. The strongest vibrational component in a transition will be the O–O component, with no strong vibrational excitation unless a ground-state alternation is stabilized in some attached ring system. The cyanine spectra are observed to have just such a single narrow peak, with half-peak-intensity band widths of 0.9 to 1.6 kK.^{1-3,57,81} Call the mean cyanine band width, w_0 .

⁸⁷ L. G. S. Brooker, private communication.

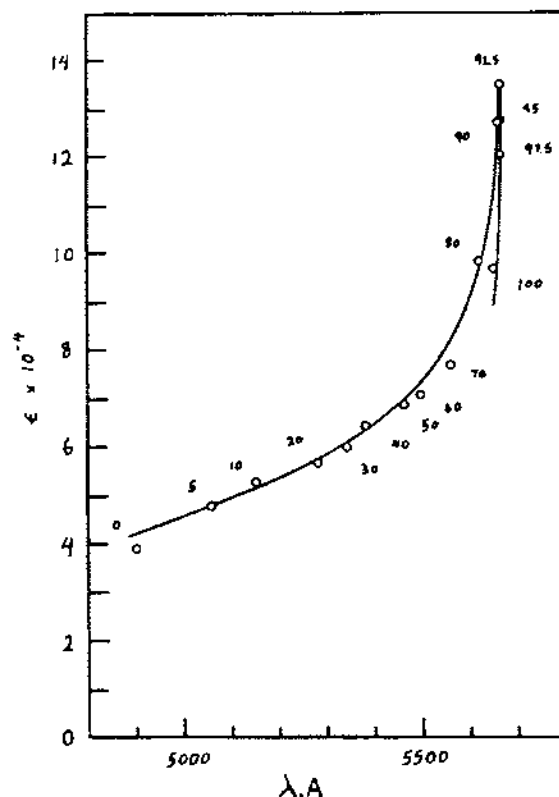


Fig. 16. Experimental absorption maxima of hydroxyl dye with nuclei 4C and HS (λ_{\max} and ϵ_{\max}) in pyridine-water mixtures, taken from Brooker¹¹; compared with theoretical ϵ_{\max} curve from Fig. 5 and Eqs. (57) and (58). Numbers beside the experimental points denote volume percent pyridine.

The symmetric even-atom chains, as shown by Fig. 12, have strongly alternating bond densities and bond lengths in their ground states, with the alternation reversing in sign in the excited states. By the Franck-Condon principle, the absorption peak will have strongly-marked vibrational structure with many quanta of the C=C stretching frequency excited. And the polyene spectra from dienes to carotenes, are commonly observed to have three to five vibrational peaks separated by this stretching frequency, with total transition half-widths of 4 to 6 kK.⁴⁵ Considering how sharp the single cyanine peaks are, it is hard to see how this marked band width and vibrational structure with these particular frequencies in the carotenes and longer polyenes can be accounted for without assuming strong bond alternation in the ground or excited states or both, as much as in the dienes, a rather directly empirical violation of the Lennard-Jones result.

These remarks on band width can be made quantitative. Suppose that the half-intensity width, w , of the absorption band is linearly related to the absolute value of b :

$$w = w_0 + k|b| = 1.0 \text{ kK} + 0.2|b| \quad (57)$$

where w_0 is taken as a constant band width for the simplest symmetric cyanine at room temperature, and

TABLE IV. Test of intensity predictions for dyes in changing pyridine-water mixtures.

Pyr. %	<i>b</i> (from deviations)	w [Eq. (57)]	E (obs)	ϵ_{\max} (pred) [Eq. (58)] $\times 10^{-4}$	ϵ_{\max} (obs) $\times 10^{-4}$
Merocyanine dye, nuclei 22 and 24, $n=2$					
0	13.6 kK	3.72 kK	21.3 kK	3.8	3.8
40	10.2	3.04	19.2	5.2	4.6
80	7.8	2.56	17.9	6.7	6.3
95	5.3	2.06	16.9	8.8	8.9
100	3.6	1.72	16.4	(10.8)	11.8
...	0.0	1.00	16.0	19.1	...
Hydroxystyryl dye, nuclei 4C and HS					
0	9.2	2.84	20.4	4.1	3.9
40	5.0	2.00	18.6	6.4	6.4
80	2.0	1.40	17.8	9.6	9.8
92	0.0	1.00	17.7	(13.5)	13.5
95	-1.1	1.22	17.7	11.1	12.8
97.5	-1.7	1.34	17.7	10.1	12.1
100	-2.5	1.50	17.7	9.0	9.7

the coefficient k is given the value necessary to raise w to about 5.0 kK when b assumes its polyene value of about 20 kK. A linear relation is plausible because b should be a measure of the displacement of any atomic nucleus between its equilibrium positions for the ground and the excited states, and the band width should be proportional to the slope of the upper state potential curve for the ground-state geometry, which would in turn be proportional to this displacement and so to the absolute value of b .

Peak Intensities

Since f is approximately equal to $w\epsilon_{\max}$, Eqs. (56) and (57) can be combined to give

$$\frac{\epsilon_{\max}}{\epsilon_{I\max}} = \frac{f}{f_I} = \frac{w_I}{w} = \frac{E_I}{E} \frac{w_0}{w_0 + k|b|} = \frac{E_I}{E} \frac{w_0}{w_0 + k[E^2 - E_I^2]^{\frac{1}{2}}} \quad (58)$$

The values on the right side may be taken from the Brooker deviation analysis of a particular dye in a particular solvent or may be computed for a given E_I and b . In Table IV and Fig. 16, the values of ϵ_{\max} so computed using Eqs. (57) and (58) are compared with the observed values for two of the dyes whose b -values in changing solvent mixtures were shown in Fig. 5. One of these is the dye studied by Bayliss and McRae. The calculated peak intensities in Table IV and the theoretical curve in Fig. 16 agree with the observed values within a mean deviation of 5%. If the particular w_0 for each dye were known and if k were more accurate, the agreement might be even better, especially for the high-intensity values.

For certain of Brooker's dyes, the isoenergetic curves showed no sharp cnsp but only broad maxima or coarse loops,¹¹ usually with low $\epsilon_{I\max}$. The present analysis suggests that these dyes should have peculiarly large half-widths, w_0 , probably for some one of the usual reasons, steric hindrance, or partial freedom of twist,

or alternating single and double bonds in some attached ring system.

Conversely, Eq. (58) predicts that the cusps of simple chain ions should be infinitely steep at the isoenergetic point. If the thermal motion that contributes to w_0 is reduced by lowering the temperature, it should be possible to produce cusps even more fantastically sharp than those already known.

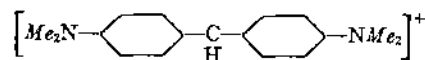
Consideration of the equilibrium nuclear configuration in the excited states of the molecules in Fig. 12 suggests that the absorption-fluorescence gap should be smallest for symmetrical cyanines or isoenergetic dyes, and that in changing solvents the fluorescence and phosphorescence peaks should stay closer to their isoenergetic points than the absorption peaks, and that their cusps should be steeper.

The intensity maximum usually does not coincide exactly with the energy minimum near an isoenergetic cusp; so that the cusp is slightly rounded and the two branches of the cusp are slightly separated, the pyridine branch for instance lying at longer wavelengths than the water branch for the dyes of Fig. 5 as shown in Fig. 16. Brooker has attributed this phenomenon to the greater stability of dipolar structures in the polar solvent,¹¹ but it might also be due to the higher refractive index of pyridine, which would affect E_I . A test of these alternative interpretations would be to see which branch of an isoenergetic curve would lie at lower energies in a mixed solvent where the less polar component has the lower refractive index.

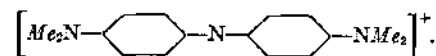
VIII. RELATION TO FIRST-ORDER PERTURBATIONS

This discussion would be incomplete without some remarks on the relation between second-order and first-order perturbation effects.

It is possible to have pure first-order changes in energy with no second-order mixing. One case often treated is that of central *aza*-substitution in the symmetric dyes,³⁸ like that which transforms Michler's Hydrol Blue



to Bindschedeler's Green



The structures S_1 and S_2 form 50-50 mixtures in the ground states and the excited states of both compounds. The effect of the *aza*-nitrogen is to make a first-order lowering of whichever state has the most excess charge in the center. Since the orbitals are alternately odd and even, if the ground state has excess charge there (starred center atom), the excited state will have none; and vice versa. So *aza*-substitution at an unstarred center atom, as in the Hydrol Blue, will give a red shift;

³⁸ H. Kuhn, *Helv. Chim. Acta* 34, 2371 (1951).

at a starred atom, a blue shift—assuming the ion is of the type that has its alternant-orbital filled. In a vinylogous series, a central aza red shift in the monomethine dye will be followed by a blue shift in the trimethine, a red shift in the pentamethine, and so on.

Successful first-order empirical and theoretical predictions of this type on chain and ring dyes have been made for many years.⁸⁸⁻⁹³ The shifts have been shown to be additive⁹⁰ and the theory has been extended to all positions of substitution in the molecule,⁹¹ and the alternant-orbital description of state densities now makes it quantitatively easy in many cases. (It would now be interesting to examine how far the shifts are equivalent to changes of chain length, in the spirit of Sec. III.) The further remarks here will be confined to one instructive example of aza-substitution that involves second-order mixing also.

This is the case of mono- and symmetric-di-aza-substitution at the starred atoms adjacent to the center of the symmetric trimethine dye with nuclei 4.⁹ The theory predicts that aza-substitution at one and then both of them will produce successive blue shifts; just as observed. The di-substitution shift is almost twice the mono-substitution shift, showing that there is indeed a large first-order perturbation effect.

But the special interest of these spectra lies in the fact that the mono-substitution shift is *more* than half as great as the di-substitution shift. This suggests that the unsymmetrical mono-substitution also produces a second-order blue shift associated with a nonzero b -value; which cannot be produced in the symmetrical unsubstituted or di-substituted dyes. The best way to study this second-order mixing is evidently to use the mean wavelength of the two symmetrical dyes as the λ_1 for the unsymmetrical one, thus eliminating the

first-order effect, so that the b -value for the mono-aza-substitution can be calculated in the usual way.

On the other hand, this analysis predicts that the effect of the second aza-nitrogen in symmetrical di-substitution will be *greater* than that of the first, if they are substituted in unstarred positions, so that they produce red shifts of the spectra. For the first nitrogen, the second-order blue shift might even overcome the first-order red shift.

It is clear that the question whether a perturbation is primarily first order or second order or a combination of the two, depends on the zero-order system it is applied to. The Brooker deviations are understandable as pure second-order mixing of wave functions simply because the Brooker procedure for obtaining λ_1 for the dyes, as represented by Eq. (2), is an ingenious and fairly rigorous way of eliminating the first-order effects of different end groups.

The power of the perturbation method in the theory of chemical comparisons or chemical series of any kind lies in the fact that each compound can form in turn the zero-order system which, in principle, can be transformed to the next compound by applying only a small perturbation. And a series of stepwise perturbations can eventually describe qualitatively and quantitatively a very large range of variation.

The method has proved especially useful in the problems studied here because the variation of one perturbation parameter, the b -value, links together quantitatively so many phenomena, Brooker deviations and basicities, intensity cusps, convergent series and nonharmonic energy spacings, and leads to so many predictions, from bond-length alternations to theoretical state interactions, that suggest further lines of study.

IX. ACKNOWLEDGMENTS

I am especially indebted to Dr. L. E. Orgel and to Dr. H. McConnell for many illuminating conversations on these questions.

⁸⁸ Th. Förster, Z. physik. Chem. B48, 12 (1941).

⁸⁹ G. N. Lewis, J. Am. Chem. Soc. 67, 770 (1945).

⁹⁰ M. J. S. Dewar, J. Chem. Soc. 1950, 2329.

⁹¹ E. B. Knott, J. Chem. Soc. 1951, 1024, 1028, 1586.

⁹² H. Kon, Sci. Rept. Tohoku Univ. 37, 171 (1953).