

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

## A Mathematical Treatment of the Color of the Merocyanine Dyes

BY WILLIAM T. SIMPSON

Long wave length singlet-singlet electronic transition energies and intensities are calculated for amide vinylog: the merocyanines. Procedures used are a valence bond type method and an equivalent single particle model. The characteristic shift to short wave lengths of absorption, with diminution of intensity, for non-polar merocyanines in solvents of decreasing dielectric constant is obtained. An initial shift of absorption to long wave lengths is predicted to occur with the first decrease of dielectric constant, or what is equivalent, a negative Brooker deviation is predicted to occur for unsymmetrical cyanines in which there is only a slight defect in the symmetry of the extreme resonance structures. A qualitative understanding of these results is facilitated by the use of perturbation theory in conjunction with the single particle model.

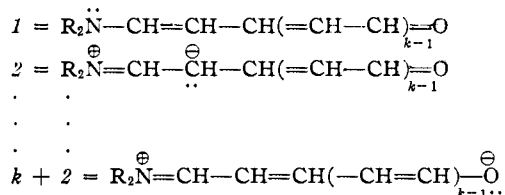
### Introduction

The object of this paper is to give a mathematical theory of the electronic absorption spectra, both as to position and intensity of the visible bands, of simple substances related to the merocyanine dyes.<sup>1</sup> In Part I a secular equation procedure is followed. The treatment is fundamentally that given by Pauling, Förster, Sklar and Herzfeld, and others,<sup>2</sup> except that the necessary modifications are introduced to adapt the calculations to the peculiarity of the merocyanines, the presence of charge separation; and the language of matrix mechanics is used.

In Part II many of the ideas in Part I will be expressed in terms of the single particle model which was discussed earlier under the name: "The Modified Lewis and Calvin Method."<sup>3</sup> A proof, analogous to one sketched in another connection relating the free-electron and LCAO molecular orbital theories,<sup>4</sup> of the substantial equivalence of the secular equation procedure and the single particle model will be given. It is believed that the single particle model offers interesting possibilities for the interpretation of spectra of the type under consideration, particularly from the standpoint of perturbation theory.

### Part I

**The Energy Matrices.**—An amide vinylog with chain length specified by  $k$  is schematically characterized by the mesomers (valence bond structures)  $i$  in which series the negative charge migrates progressively from left to right:



The energy of a mesomer is regarded as depending upon the position of the non-bonding electron pair and the amount of charge separation. Thus the energy matrix without interaction between mesomers is ( $D$  is the dielectric constant)

(1) THIS JOURNAL, **73**, 5326 (1951).

(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939); Th. Förster, *Z. physik. Chem.*, **47B**, 245 (1940); **48B**, 12 (1940); K. F. Herzfeld and A. L. Sklar, *Rev. Mod. Phys.*, **14**, 294 (1942); *J. Chem. Phys.*, **10**, 508, 512 (1942); L. M. Kushner and C. P. Smyth, THIS JOURNAL, **71**, 1401 (1949).

(3) W. T. Simpson, *J. Chem. Phys.*, **16**, 1124 (1948).(4) W. T. Simpson, *ibid.*, **17**, 1218 (1949).

$$\mathbf{G}'' = \begin{pmatrix} Q_N & & 0 \\ & Q_C & \\ 0 & & \ddots \\ & & & Q_O \end{pmatrix} - \frac{e^2}{D} \begin{pmatrix} 1/r_1 & & & 0 \\ & 1/r_2 & & \\ & 0 & \ddots & \\ & & & 1/r_{k+2} \end{pmatrix}$$

where, for example,  $Q_N$  is the energy exclusive of the explicit charge separation part ( $-e^2/Dr_1$ ) of the mesomer for which the electron pair is on the nitrogen. Before transforming  $\mathbf{G}''$  to a more usable form it will be convenient to regard a given dye as all-*trans* with  $120^\circ$  bond angles, and to neglect the difference between the C-C, C-N and C-O bond distances calling them all  $a$ . The distance of charge separation  $r_i$  in the  $i$ th mesomer by trigonometry is then  $3^{1/2}(i-1)a$ , so that

$$1/r_i = (2/3^{1/2}a) (1/(2i-2))$$

It will be necessary to replace  $r_i = 0$  (the value inferred from the mesomer  $i = 1$ ) by  $(3^{1/2}ar)/2$ , which is the same as assuming that there is a certain amount of residual charge separation  $r$  implied by the mesomer 1. Adoption of an abbreviated notation for diagonal matrices

$$\begin{pmatrix} a & & & \\ & b & & \\ & & c & \\ & & & \ddots \\ 0 & & & & \end{pmatrix} \equiv [a, b, c, \dots]$$

then leads to  $\mathbf{G}'' = [Q_N, Q_C, \dots, Q_O] - 2e^2/(3^{1/2}aD) \times [1/r, 1/2, 1/4, \dots, 1/(2k+2)]$ , which with  $p = 2e^2/(3^{1/2}aD)$  and  $\mathbf{I}$  the unit matrix is

$$[Q_N, Q_C, \dots, Q_O] - p/r \mathbf{I} + p[0, 1/r - 1/2, \dots, 1/r - 1/(2k+2)]$$

Because of the fact that all interaction terms will be assumed equal it is convenient to measure energies in units of the interaction energy  $\alpha < 0$ ; and because most of the  $Q$ 's are  $Q_C$ , to adopt  $(1/\alpha)(Q_C - 2e^2/(3^{1/2}aD))$  as the zero of energy. With these changes the energy matrix including interaction

$$\mathbf{G}' = \mathbf{G}'' + \begin{pmatrix} 0 & \alpha & 0 \\ \alpha & 0 & \alpha \\ 0 & \alpha & 0 \\ & & \ddots & \\ & & & & \end{pmatrix}$$

becomes

$$\mathbf{H}' = \mathbf{H}'' + \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \\ & & \ddots & \\ & & & & \end{pmatrix}$$

where

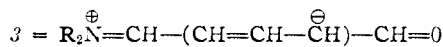
$$\mathbf{H}'' = [(Q_N - Q_C)/\alpha, 0, 0, \dots, (Q_0 - Q_C)/\alpha] + (p/\alpha)[0, 1/r - 1/2, \dots, 1/r - 1/(2k + 2)]$$

The constant  $p$  is  $0.9644 \times 10^6 (1/D)$  cm.<sup>-1</sup>.

The form of the interaction matrix can be explained on a wave mechanical basis by assuming that the Hamiltonian is a sum of terms "along the chain" and that the wave functions are each products of terms "along the chain." The interaction between



and



for example, is considered to be given by

$$\int (\psi_1 \psi_2 \dots \psi_x \dots \psi_n)_2 (H_1 + H_2 + \dots H_{x,y} + \dots + H_n) X (\psi_1 \psi_2 \dots \psi_x \dots \psi_n)_3 d\tau$$

where  $x$  and  $y$  refer to the allyl anion parts which are enclosed in parentheses. The assumed orthogonality of 2 and 3 comes from the  $x, y$  part, so only  $H_{x,y}$  gives a non-vanishing matrix element.

The neglect of carbonium ion ( $\overset{\oplus}{C}$ ) mesomers in the series  $i$  of mesomers initially chosen is, to some extent, only apparent. Choice of allyl anion as the basic interacting unit makes it possible to neglect the details of the transfer of charge in the passage from one extreme allyl anion mesomer to the other, but this passage of charge may well involve a carbonium ion. The matrix element for interaction is assumed to be independent of the dye chain length, which is plausible; but is also assumed not to be changed if the allyl resonance occurs at the ends of the dye. This last assumption is certainly incorrect, but the error appears off the diagonal so that its effect is less serious.

Before proceeding to the discussion of the results of the computation (solution of the secular equation) it is well to note that the simple amide vinyls, which are the objects of the present study, should be compared with Brooker's non-polar merocyanines. Remarks about strongly polar merocyanines are deferred until Part II, where the effects to be expected from  $Q_N$  or  $Q_0$  being very different from  $Q_C$  are described.

**Energies and Intensities.**—Diagonalization of  $\mathbf{H}'$  leads to transition energies which for a given  $D$  depend qualitatively on the value chosen for the residual charge separation in the uncharged mesomer. In particular, if  $r$  is small, there is a shift of the absorption maximum to longer wave lengths with decreasing dielectric constant; with increasing asymmetry of the extreme mesomers. Any considerable shift of this nature (negative Brooker deviation)<sup>5</sup> is contrary to experiment, although there seems to be some evidence for a slight negative deviation with first asymmetry of extreme mesomers for unsymmetrical cyanines. (This is most apparent when deviations are computed from the mean of the energies rather than wave lengths of absorption of the parent symmetrical dyes.) It is found that  $r$  has to be un-

reasonably large in order for there to be no initial negative deviation with the first slight asymmetry of extreme mesomers. For example, it is found from first order perturbation theory that in order completely to prevent a negative deviation,  $r$  for the nine-carbon dye ( $k = 4$ ) has to be about 5.8 (5a). (It seems as if  $r = 2$ , corresponding to the explicit charge separation in the mesomer 2 should be an upper limit to  $r$ .)

The effect of the perturbing matrix  $\mathbf{H}''$  for low dielectric constant media (in which  $\mathbf{H}''$  is no longer a small perturbation) is markedly to increase the transition energies (the normal positive Brooker deviation) and lower the intensities; these changes relative to the substance characterized by  $\mathbf{H}'' = 0$ . The effect of increasing  $r$  is to *diminish* the magnitude of the ultimately large positive Brooker deviations.

The  $\mathbf{H}'$  matrices for the merocyanines given by  $k = 2$  and  $k = 3$  with  $Q_N = Q_C = Q_0$  were diagonalized for the particular value,  $r = 1$  (0.866a). The results are given in Table I, for various values of  $-p/\alpha$  (and hence of  $\text{const} \times (1/D)$ ).

TABLE I  
ENERGIES, TRANSITION ENERGIES AND INTENSITIES FOR  $r = 1$

$-p/\alpha$	$W_1$	$W_2$	$-\Delta W$	$\lambda_{\text{max.}}$ (m $\mu$ )	const. $\times E$
$k = 2$					
0	1.6180	0.6180	1.0000	(500)	0.8000
0.5	1.3514	.3801	0.9713	515	.8120
1.0	1.1237	.1350	.9887	506	.7590
1.5	0.9383	-.1232	1.0615	471	.6461
2.0	.7924	-.3949	1.1873	421	.5145
2.5	.6790	-.6766	1.3556	369	.3987
$k = 3$					
0	1.7321	1.0000	0.7321	(600)	1.1606
0.5	1.4236	0.7245	.6987	629	1.1885
1.0	1.1621	.4409	.7212	609	1.0597
1.5	0.9561	.1401	.8160	538	0.8082
2.0	.8000	-.1763	.9763	450	.5696
2.5	.6823	-.5007	1.1830	371	.4025

If a value of  $r$  much smaller than unity were chosen, the negative deviation (which is at least 29 m $\mu$  for  $k = 3$ ) would be so large as to be in substantial disagreement with experiment, while a value of  $r$  larger than two seems to be "theoretically" unreasonable. To test the effect of varying  $r$ , the  $\mathbf{H}'$  matrix for  $k = 2, r = 2$  was diagonalized for  $-p/\alpha = 1$  and 2.5 with the results:  $\Delta W = 1.0460$  (478 m $\mu$ ) and  $\Delta W = 1.19575$  (418 m $\mu$ ), respectively. Comparison with Table I corroborates the statements made above about the effect of increasing  $r$ .<sup>6</sup>

The intensities,  $E$ , were calculated using the relative intensity amplitude matrix:  $[0, 1, 2, \dots, k + 1]$ . The intensity values in the table are uncertain in the last place. The behavior of the derivative,  $dE/d\lambda_{\text{max.}}$ , is in fair agreement with the experimental results of Brooker<sup>1</sup> (see Fig. 1).

(6) In the range of small  $-p/\alpha$ , second order perturbation theory can be applied and is in qualitative agreement with the accurate method of diagonalization. For the dye  $k = 2$  the transition energy is thus calculated to be:  $-\Delta W$  (in  $\alpha$ ) = 1.0000 +  $(-p/\alpha)(0.1340 - 0.2236/r) - (-p/\alpha)^2(0.0027 - 0.0625/r)$ .

(5) L. G. S. Brooker, *Rev. Mod. Phys.*, **14**, 275 (1942).

Incidentally, the approach together of the curves in the region of large deviation (short wave length) seem to indicate that for small enough  $D$  it makes little difference how long a dye is structurally; the length of the effective path of oscillation of charge is controlled by the charge separation energy, so that the longer members of an homologous series approach identity as dynamical systems.

The "sensitivity rule" of Brooker<sup>5</sup> is to be correlated with the initial shift to longer wave lengths as  $-p/\alpha$  increases ( $D$  decreases). The ground state for the dye  $k = 3$ , for  $r = 1$  and  $-p/\alpha = 1$  is (not normalized)  $\psi_g = (1.0000, 1.1621, 0.9315, 0.6190, 0.3038)$ .<sup>7</sup> This means that the ratio of the contributions of the extreme (first and fifth) mesomers is 9.2 to 1 in favor of the mesomer without charge separation, and yet there is still no positive Brooker deviation (see Table I). If  $r$  is larger this effect is less pronounced; nevertheless, one sees from these calculations that the inference of equality of contribution for extreme mesomers from the absence of Brooker deviation must be made cautiously.

Incidentally, for  $k = 3$  and  $\Delta W = -0.7321$ ,  $\alpha = 0.1667 \times 10^5 \text{ cm.}^{-1}$ , a reasonable assumed experimental transition energy, the relationship between  $-p/\alpha$  and  $D$  is  $D = 4.24 (-\alpha/p)$ . It has been shown above that for a reasonable  $r$  no very considerable normal Brooker deviation (say  $> 28 \text{ m}\mu$ ) results unless  $-p/\alpha > 1$  ( $D < 4.24$ ). The fact that very considerable deviations can be obtained in methanol ( $D = 31$ )<sup>8</sup> need not be taken as a disagreement between experiment and theory, but instead can mean that the real  $D$  experienced by the merocyanines in highly polar solvents may be an order of magnitude smaller than the solvent  $D$ . Looking at the small side of the scale it is seen that  $D \rightarrow 1$  is entirely adequate to account for large negative deviations (or in the present case, more strictly, hypsochromic shifts) of the order of magnitude observed.<sup>5</sup> Thus for  $k = 3$  (Table I) a shift of  $150 \text{ m}\mu$  is predicted to occur when  $-p/\alpha$  changes from 0 to 2.0 which, using  $D = 4.24 (-\alpha/p)$ , is a change in  $D$  from  $\infty$  to 2.12.

### Part II

**Analogy by Finite Differences.**—The development analogy between the secular equation approach and a single particle model is most conveniently made for the unperturbed case,  $Q_N = Q_C = Q_0$ , and  $1/D = 0$ .

The one-dimensional Schrödinger equation is approximated by a set of difference equations<sup>9</sup> beginning with

$$(h_0 - 2h_1 + h_2)/\Delta^2 + (2m/\hbar^2)Wh_1 = 0$$

where  $h_i$  is the  $i$ th probability amplitude ordinate and  $\Delta$  the lattice constant. The  $V$  term is omitted

(7) The  $i$ th component of the row vector is the coefficient of the eigen  $\psi$  of  $G''$  belonging to  $G''_{ii}$ , or, which is the same thing, is the coefficient of the  $i$ th mesomer.

(8) L. G. S. Brooker and R. H. Sprague, *THIS JOURNAL*, **63**, 3203 (1941). It should be remarked that phenol blue, the substance studied in this reference, differs from the example in that certainly the approximation  $Q_N = Q_C = Q_0$  becomes questionable.

(9) L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 202.

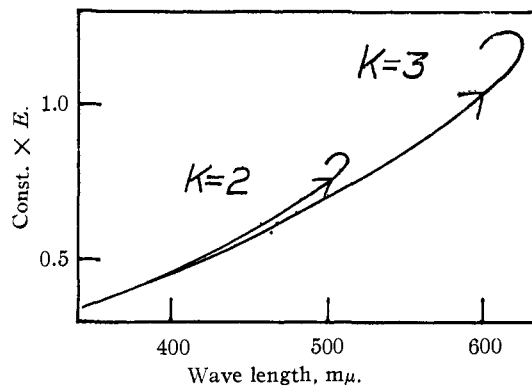


Fig. 1.—Theoretical transition energy-intensity relationship for two merocyanines. Arrows point in direction of increasing effective dielectric constant.

for a free particle. If box quantization is introduced by setting  $h_0 = h_s = 0$  there results a set of simultaneous equations in the  $h$ 's; and the condition that these have a solution is the vanishing of the determinant of the coefficients. For a box length  $l$  and for  $\Delta_4 = l/4$  the determinant is

$$\begin{vmatrix} -x & 1 & 0 \\ 1 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} = 0,$$

where  $W = \hbar^2/(2\Delta_4^2m)(-x + 2)$ ; so that the energy of the ground state is given by the largest positive  $x$ . Again, for the same dynamical system but a new lattice constant  $\Delta_5 = l/5$  the determinant is

$$\begin{vmatrix} -y & 1 & 0 & 0 \\ 1 & -y & 1 & 0 \\ 0 & 1 & -y & 1 \\ 0 & 0 & 1 & -y \end{vmatrix} = 0$$

where  $W = \hbar^2/(2\Delta_5^2m)(-y + 2)$ . The determinants are identical to those used in part I for the unperturbed merocyanines:  $k = 1$  and  $k = 2$ , respectively.

In the treatment of part I the interaction constants are said to be equal; although in Table I  $\alpha$  is selected so that the unperturbed  $\lambda_{\max}$ 's will, for  $k = 2$  and  $k = 3$ , respectively, be 500 and 600  $\text{m}\mu$ . The process of constructing the analogy is first carried out under the assumption of constant  $\alpha$ .

It is therefore necessary to equate coefficients of  $(-x + 2)$  and  $(-y + 2)$  in the equations for  $W$ , which gives  $\Delta_4^2m_1 = \Delta_5^2m_2$ . The single particle counterparts of the two merocyanines are now different dynamical systems, and  $m_k$  is the mass that goes with the dye  $k$ .

The question of interpretation of the equation in  $\Delta^2m$  cannot be answered unambiguously. One might for example wish to make  $l$  change with the length of the dye, looking for a constancy of  $m$  as an heuristic justification of the procedure. There is not a constancy of  $m$  under this assumption, even when  $\alpha$  is adjusted so as to make the calculated  $\lambda_{\max}$ 's vary accurately with chain length. The result is not unexpected, because of the reasonably good fit of the free electron model: in which  $m$  is constant and  $l$  changes with the dye chain

length, but the additional factor of the squares of appropriate quantum numbers has been introduced.

The assumption will now be made that  $l$  is constant. Thus the dye  $k$  which has  $k + 2$  mesomers and  $k + 2 = n$  mobile electron pairs is represented by a particle in a box with length  $l$ . If the theory in finite difference approximation is to be completely equivalent to the treatment in part I, constancy of

$$\Delta_{k+3}^2 m_k = (l/(k+3)^2) m_k$$

is required. This is now equivalent to assuming that the single particle mass varies so that  $m_k/(k+3)^2$  is constant. Recall that  $m_k$  is the mass of a single particle corresponding to the dye  $k$  with  $n = k + 2$  so that the variation of  $m$  is expressed by  $m_k = \text{const} \times (n+1)^2$ .

The analogy is considered sufficient to warrant the replacement of the secular equation procedure by one which uses the differential form of the Schrödinger equation. The final form of the single particle model employs to advantage a somewhat modified  $m_k$ ,  $n$  relationship. The procedure used in part I gives too large a value for the ratios of transition energies of succeeding members of a vinylogous series (correction for this effect is made in column 5 of Table I) and this is exaggerated in the passage to the limit  $\Delta \rightarrow 0$ . The transition energies are observed to be given, roughly, by  $\Delta W_k = \text{const} \times (1/n)$ . The transition energies for particles of varying mass in a box of length  $l$  are given by  $\Delta W = \text{const} \times (1/m)$  so the modified relation  $m_k = nM$  gives essentially perfect agreement with experiment in the matter of the vinylene shifts. In fact, from the observed  $\Delta\lambda(\Delta k = 1) = 100 \text{ m}\mu$ , and the assumption that  $M$  is the mass of an electron pair, it is found that  $l = 2.13 \text{ \AA}$ ; a value which, it has been argued,<sup>3</sup> is reasonable.

The model will be used in the next section as a basis for qualitative discussions of several of the points raised in Part I.

**Perturbation Theory for the Single Particle Model.**—The potential in the unperturbed case and the wave functions squared for the ground and excited states are given in Fig. 2a. If a stabilization is introduced in the two regions  $-l/2$  and  $+l/2$  (Fig. 2b)  $\lambda_{\text{max}}$  is shifted toward longer wave lengths. This conclusion follows

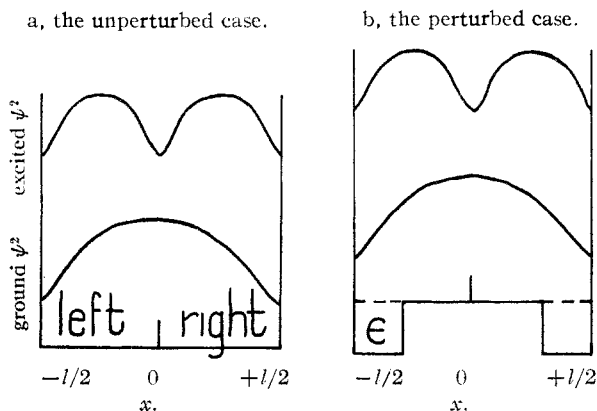


Fig. 2.—Potential diagrams to illustrate "the steeper the deeper."

from the fact that for both ground and excited states the areas in the left and right regions under  $\psi^2$  are each one-half. Inspection of Fig. 2 shows that the stabilization of the excited state

$$2 \int_{-l/2}^{-l/2+\epsilon} \psi_{\text{excited}}^2 \Delta V dx$$

outweighs the stabilization of the ground state, thus bringing the levels together. This first example of the use of perturbation theory derives in pictorial fashion the empirical-theoretical rule of Brooker and Sklar<sup>5</sup>: "the steeper the deeper." The depressions in the left and right regions are directly to be correlated with changes in the dyes which (referring back to the secular equation theory) make  $Q_L$  and  $Q_R$  more negative than intermediate  $Q$ 's.

The effect of adding a region of stabilization on the left only (Fig. 3a, a merocyanine: the curved base of the diagram represents an  $e^2/Dr$  term in the energy and hence the effect of charge separation) is likewise to shift  $\lambda_{\text{max}}$  toward longer wave lengths. The "sensitivity rule" has been correlated in Part I with the initial small shift to longer wave lengths predicted to occur with the first asymmetry of extreme mesomers. This small shift is now seen to be a consequence of the "steeper the deeper" rule. If the region of stabilization is modified so as to correspond to a larger  $r$  (residual charge separation) (Fig. 3b) which modification is idealized (Fig. 3c), then one sees according to first order perturbation theory that the shift to longer wave lengths is prevented (the perturbation affects ground and excited states equally) in agreement with the result obtained in Part I.

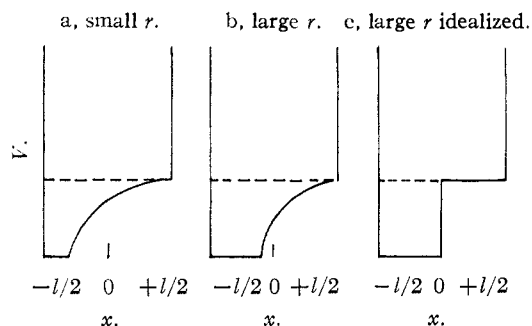


Fig. 3.—Potential diagrams showing different amounts of residual charge separation  $r$ .

The direction of wave length shift for a larger perturbation of the shape given in Fig. 3 can be obtained from second-order perturbation theory. The theorem that  $\psi_{\text{ground}}$  "seeks" the region of lowest potential is used, together with the orthogonality of  $\psi_{\text{ground}}$  and  $\psi_{\text{excited}}$ . The  $\psi$ 's then have the form shown by the full lines in Fig. 4. The dotted lines are the unperturbed  $\psi$ 's. Application of first order perturbation theory with the corrected wave functions shows a proportionately large stabilization of the ground state, and a proportionately small stabilization of the excited state, pushing the levels apart and resulting in a shift of  $\lambda_{\text{max}}$  to shorter wave lengths: the Brooker deviation. Numerical illustrations are given in Part I

in finite difference approximation, and one illustration has been given previously (for the case depicted in Fig. 3c) in differential form.<sup>3</sup>

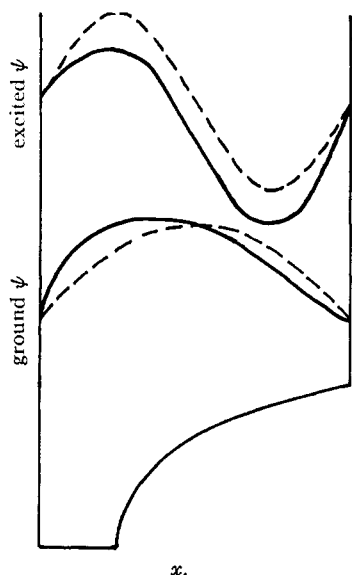


Fig. 4.—Changes in  $\psi$  as a result of charge separation.

It is now possible very simply to investigate the effect, neglected in Part I, of departures from the assumption  $Q_N = Q_C = Q_0$ . For if a stabilizing  $\Delta Q$  on the right is introduced, Fig. 3a say, can be

a, high  $D$ , inverted behavior.      b, intermediate  $D$ , symmetrical behavior.      c, low  $D$  normal behavior.

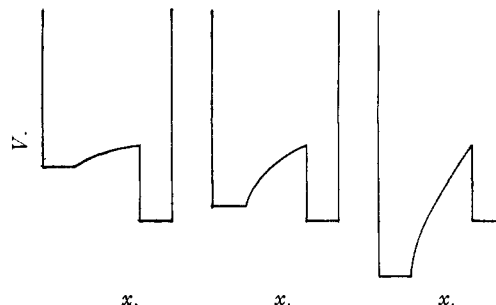


Fig. 5.—Changing dielectric constant in a model substance which is considered to represent a strongly polar merocyanine.

converted in essence into Fig. 2b. Moreover, depending upon the dielectric constant, a single substance can be altered in the remarkable fashion demonstrated by Brooker<sup>1</sup> (Fig. 5). As  $D$  is decreased (5a to 5b) it is seen that  $\lambda_{\max}$  moves to longer wave lengths, an inversion of the "normal" behavior. Continued decrease in  $D$  (5b to 5c) finally gives the normal effect, a shift of  $\lambda_{\max}$  to shorter wave lengths.

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## Internal Dispersion Forces. The Polyenes

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Internal dispersion forces in polyenes (butadiene, hexatriene, etc.) are sufficient to account qualitatively for observed alternations in bond lengths, positions of first singlet-singlet absorption bands, and resonance energies. The question of the relative importance of conjugative interaction and internal dispersion effects is therefore raised. Configurational interaction in unsaturated compounds may be explainable in part as arising from internal dispersion forces.

### Introduction

Bond distances in molecules can be considered to represent a compromise between attractive and repulsive forces of various sorts. Included in the effects which counterbalance the bonding tendency of the center carbon-carbon link in *n*-butane are exchange repulsions<sup>1</sup> between perfectly paired electrons in the bonds centering on the 2- and 3-carbon atoms. This repulsion is analogous to the repulsions encountered in the close approach of "closed shell" atoms or molecules.

Part of the attraction between the left and right region of the molecule is undoubtedly due to dispersion forces, *i.e.*, to the tendency for instantaneous dipoles in the two regions to be in phase. A change in the polarizability of the regions such as is brought about in the abstraction of four hydrogens to produce butadiene still leaves the same number of electron pair bonds on each of the center carbons, and so may be considered to affect the attractive force, with only a second order influence

on the repulsion. Thus some of the observed shortening of the middle link in butadiene may be attributed to an *internal* dispersion force.

In order for such a force to exist, it is necessary that the individual double bonds be polarized. If the bonds are compared with isolated double bonds, this polarization implies a mixing with excited states. It is seen that if the excited states of a double bond are considered to represent a weakening in binding energy, then a natural result of the dispersion force shortening of the 2,3-bond in butadiene is a lengthening of the double bonds. The question as to the relative importance of conjugation effects and internal dispersion forces then arises.

### A Procedure for Calculating Energies

It might be thought that a comparison of the importance of conjugation and internal dispersion forces could be made by an appeal to  $\pi$ -electron spectra, which in the case of so-called conjugated polyenes are considered to be fairly well understood on the basis of a pure conjugation model.<sup>2</sup> In

(1) J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935) eqn. (40) *et seq.*

(2) *E.g.*, the valence bond method or the simple LCAO molecular orbital method.