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Color and Constitution of Polymethine Dyes

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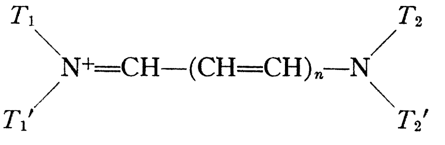
PART I

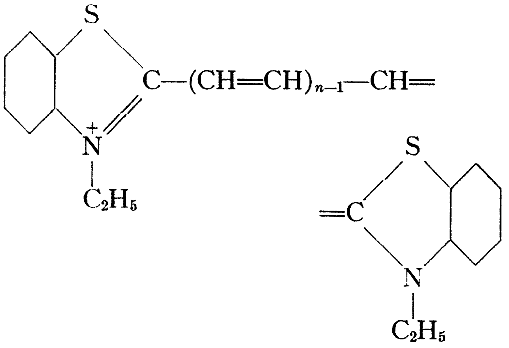
Introduction

THE typical polymethine dye, represented[1] by ion (I), may be discussed theoretically by either the valence bond method of Heitler-London-Slater-Pauling (HLSP) or by the molecular orbital method, (LCAO), of Hund-Mulliken and Hückel.[2] Since the phenomena described in the preceding paper[3] can be qualitatively understood more easily from the former method we shall first limit our discussion to the HLSP method and only in the last section summarize the results of the LCAO molecular orbital method, which, however, from a quantitative point of view, are better.



$$\begin{matrix}T_1 & & T_2\\ & N^{+}{=}CH{-}(CH{=}CH)_n{-}N & \\ T_1' & & T_2'\end{matrix}$$

(I)



(I′)

Since the atoms in the chain, formed by the nitrogen atoms in ion (I) and the carbon atoms between them, are joined by a system of alternately single and double bonds we can expect the charge distribution of the electrons on the carbon atoms to be just like that of the atoms in benzene. That is, we can expect the chain to be planar and each carbon atom to have one "unsaturation electron."[4] As discussed in reference 4, the visible and near ultraviolet absorption is associated with the system of unsaturation electrons, which can be treated independently of the electrons whose charge distribution is concentrated in the plane of the chain. Besides the $(2n+1)$ unsaturation electrons on the $(2n+1)$ carbon atoms of the chain in ion (I) there is also another one on the positively charged nitrogen and a pair on the nitrogen atom.

In addition to the structural formula drawn for ion (I), one can equally well write a second structure which differs from the one drawn in that an unsaturation electron has been moved from the right- to the left-hand nitrogen atom and the bonds readjusted. In the case of a symmetrical ion $(T_1=T_2)$ these two structures are degenerate and the ion is analogous to benzene which has the two Kekulé structures as degenerate ground structures. A difficulty, however, arises in carrying over from benzene to ion (I) the view that the longest wave-length electronic absorption is associated with a transition between the two molecular states which arise from a resonance splitting of the degenerate ground structures.[4] The electron distributions in the two (I) structures, which differ in that an electron has moved from one end of the molecule to the other, do not overlap appreciably. The resonance splitting of these two structures would thus be expected to be negligible instead of the observed value of the order of a few volts.

Pauling,[5] however, has pointed out that one must consider, in addition to the two structures (I), the following set of intermediate structures $(X_{2j+1})(j=0 \text{ to } n)$.

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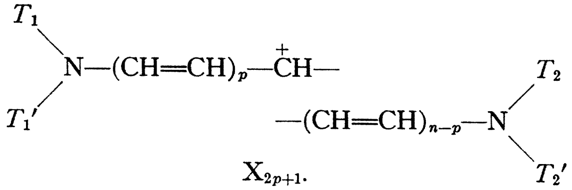
[1] It is understood that the groups T which are attached to the nitrogen atoms may bend back and join to the chain as in ion (I′).

[2] L. Pauling-Gilman, *Organic Chemistry*, Vol. 2, p. 888; R. S. Mulliken, J. Chem. Phys. **7**, 570 (1939); K. F. Herzfeld, *ibid.* **10**, 508 (1942); A. L. Sklar, *ibid.* **10**, 521 (1942).

[3] L. G. S. Brooker, Rev. Mod. Phys. **14**, 275 (1942).

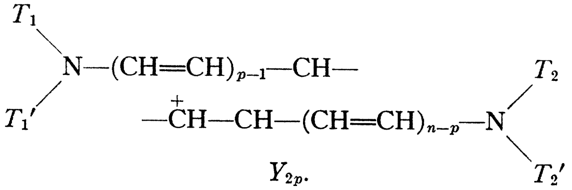
[4] A. L. Sklar, Rev. Mod. Phys. **14**, 232 (1942); J. Chem. Phys. **10**, 521 (1942).

[5] L. Pauling, Proc. Nat. Acad. Sci. **25**, 577 (1939).



X_{2p+1}.

Since the overlap of electrons on atoms separated by even two interatomic distances is very small, we shall also have to include the set of structures $(Y_{2j})(j=1 \text{ to } n)$:



Y_{2p}.

For every structure in the set consisting of (I), (X), and (Y) there is a second structure which differs from the former in that an electron has been moved to the neighboring atom on the left. Thus, although the two (I) structures do not appreciably overlap directly, one (I) structure overlaps with (X_1), (X_1) with (Y_2), (Y_2) with (X_3), and so on until (X_{2n+1}) interacts with the other (I) structure. The two ground structures (I) can split through this chain of interactions with the intermediate structures (X) and (Y).

In all we have $2n+3$ structures, two (I), $(n+1)$(X), and n(Y) structures. If we neglect all integrals, Coulomb and exchange, which are smaller than the product of the first power of the overlap integral of electrons on neighboring atoms times the ordinary integrals, Coulomb or exchange, and also neglect terms containing overlaps of electrons on non-neighboring atoms, the molecular energies resulting from resonance among the $2n+3$ structures are given by the roots of the secular determinant[4] (II).

$$\begin{vmatrix}
e_1-E; & \alpha_1\,; & 0\,; & 0; & \cdots 0; & 0\,; & 0\,; & 0 \\
\alpha_1\,; & f-E; & \alpha\,; & 0; & \cdots 0; & 0\,; & 0\,; & 0 \\
0\,; & \alpha\,; & f-E; & \alpha; & \cdots 0; & 0\,; & 0\,; & 0 \\
0\,; & 0\,; & \alpha\,; & \ddots & \vdots & & & \\
\vdots & \vdots & \vdots & & \ddots & & & \\
0\,; & 0\,; & 0\,; & \cdots & \alpha; & f-E; & \alpha\,; & 0 \\
0\,; & 0\,; & 0\,; & \cdots & 0; & \alpha\,; & f-E; & \alpha_2 \\
0\,; & 0\,; & 0\,; & \cdots & 0; & 0\,; & \alpha_2\,; & e_2-E
\end{vmatrix} = 0. \qquad \text{(II)}$$

α, α_1, α_2 are, respectively, the interaction energies between an intermediate structure, and either a second intermediate, or one of the two ground structures; e_1 and e_2 are the energies of the two ground structures (I); and f is the energy of an intermediate structure,[6] (X) and (Y). Since E is the energy of all the unsaturation electrons in the molecule, the transition energy in question is the difference between the two smallest values of E.

The roots of determinant (II) have been discussed in detail as a function of the number of rows in an earlier paper[7] for various ranges of the parameters $R=\alpha/(e_1-f)$ and $R'=\alpha/(e_2-f)$. The results will now be applied to a discussion of Brooker's results.[2]

PART II

Symmetrical Ions

If we, for the moment, limit our discussions to symmetrical ions, in which the two ground structures (I) are necessarily degenerate and in addition assume that the excited structures (X) and (Y) are considerably higher in energy than the ground structures (i.e., R is small), then we

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[6] It is sufficiently accurate for our purposes to take the energy of all excited structures, (X) and (Y), to be the same, since small differences in their energy should not affect our discussions.

[7] K. F. Herzfeld, J Chem. Phys. **10**, 508 (1942).

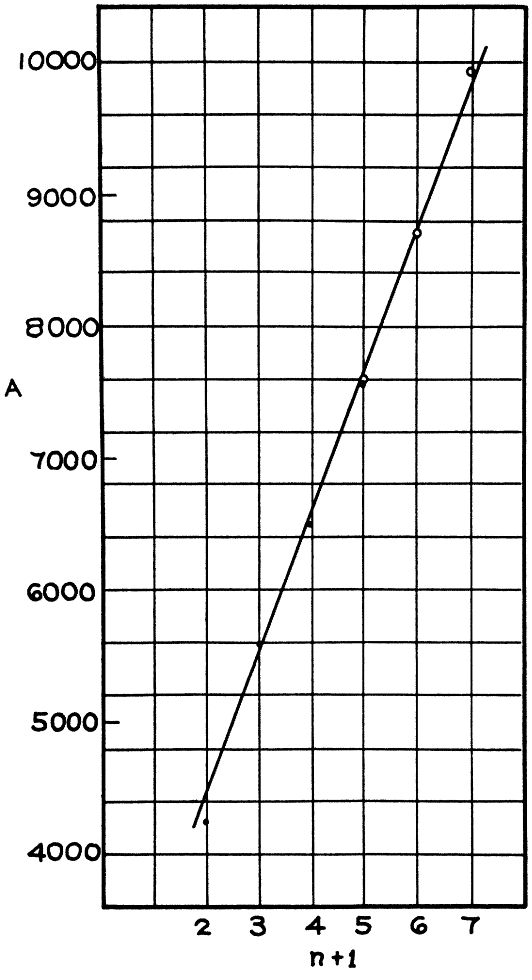
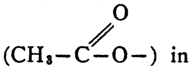


FIG. 1. The solid points in the figure give the wave-length of the absorption peak for ion I′ as a function of the number of double bonds between the nitrogen atoms (NH). The empty circles give the same data for an ion which differs from ion I′ only in having an acetoxy group


$(CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-})$

in place of the hydrogen atom on the sixth carbon atom of the polymethine chain.

can reach certain qualitative conclusions concerning the electronic band system with the longest wave-length. This band system arises from a transition between the two levels into which the doubly degenerate ground structures are split by resonance interaction. Since the two ground structures do not interact directly but only through a chain of interactions with the excited structures, one should expect the resonance splitting of the ground structures to decrease as one increases the number of intermediate interactions of like character through which the chain of interactions must be handed on. As the chain length of ion (I) increases the number of excited structures also increases, each interacting only with its "neighboring" structure. One should, accordingly, expect the resonance splitting to decrease as the chain length increases and the absorption to shift toward the red.

The usual dependence of the absorption peak of *symmetrical* polymethine ions on the chain length, illustrated[8] in Fig. 1 by the thiocyanines, ion (I′), is in accord with this expectation.

Figure 1 shows that for the symmetrical thiocyanine ions the wave-length of the absorption peak varies linearly with the chain length. Theoretically, at least in HLSP approximation,[9] the algebraic relationship between the peak wave-length and chain length depends on the order of magnitude[10] of R, the ratio between the interaction energy α and the energy difference between ground and excited structures $(e-f)$. For the small values of R under discussion the HLSP method gives an exponential dependence of the transition energy on the number of carbon atoms in the chain for large values of $N=2n+1$.

The theoretical (HLSP) value for the transition energy is directly proportional to[11] α, but the ratio of the transition energies of a given ion to its next homologue (n increased by one) does not explicitly depend on α. In HLSP approximation this ratio does, however, depend on R. The ratio of the transition energies for an ion with $N=7$ to one with $N=9$ varies from 1.2 to 1.4 as R varies from one-half to ten. The experimental value of the ratio of the peak wave-lengths of ion (I′) with $N=9$ to ion (I′) with $N=7$ is[12] 1.19.

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[8] The data in Fig. 1 were obtained at the Eastman Kodak Laboratories and communicated to the author by Dr. L. G. S. Brooker.

[9] In LCAO approximation the observed linear relation is obtained for all values of R.

[10] In order to simplify the calculation of the roots of determinant (II) the end interaction integrals α_1 and α_2 are equated to α, since the α's are of the same order of magnitude and since a small difference between them would not be expected to affect the general questions treated here, except for very small values of n.

[11] A surprisingly large value of α is required to bring the HLSP value for the transition energy into line with experiment (cf. reference 4); this difficulty does not appear in LCAO approximation.

[12] In LCAO approximation the ratio is insensitive to R and gives, for this case, values which vary only between 1.20 and 1.24, as R changes, in good agreement with experiment for all values of R.

From the discussion at the beginning of this section, one would also expect the resonance splitting of the ground structures to decrease as the energy difference between ground and excited structures ($f-e$) increases. This is borne out by the calculations of reference 7.

PART III

Unsymmetrical Ions

The charge distribution on the nitrogen atoms in ion I depends, to some extent, upon the character of the groups joined to them. If the groups T_2 which are joined to the right-hand nitrogen atom in ion (I), differ from those, T_1, attached to the left-hand one, then the ionization energies of the two nitrogen atoms will, in general, be different. We should, accordingly, expect that, in the case of an unsymmetrical ion, the two ground structures have somewhat different energies, e_1 and e_2. Since the resonance splitting of the energies of the ground structures, which determines the energy difference between the ground and lowest excited state, depends on and is superimposed on the difference (e_1-e_2), we should clearly expect that the lack of degeneracy of the ground structures in unsymmetrical ions should cause differences in kind between the class of unsymmetrical and that of symmetrical ions.

If we, then, set[10] $\alpha_1=\alpha_2=\alpha$ in the secular determinant (II) but keep e_1 and e_2 different, we obtain a transition energy for the unsymmetrical ion. The results depend upon the order of magnitude of $R=\alpha/(e_1-f)$ and $R'=\alpha/(e_2-f)$. We shall limit our discussions in this section to the case which is easiest to discuss qualitatively, namely, that of small values of R and R', which is the case when the intermediate structures, (X) and (Y), are considerably higher in energy than the ground structures (I). In this case it turns out that the transition energy, ΔE_N, is:

$$2\Delta E_N=\{(e_1-e_2)^2+(\alpha\sigma_N)^2\}^{\frac{1}{2}} +\{(e_1-e_2)^2+(\alpha\sigma_N')^2\}^{\frac{1}{2}}, \quad (1)$$

where $\alpha\sigma_N$ (or $\alpha\sigma_N'$) is essentially the transition energy of the symmetrical ion with end groups which are equal to the left- (or right-) hand side of the unsymmetrical ion.

The transition energies of the two parent symmetrical ions, for a common chain length, differ because the energy difference of the two ground and many excited structures, ($e-f$), is different in the two cases. In order to observe the effect of the energy difference (e_1-e_2) one should, then, compare the unsymmetrical ion to a hypothetical symmetrical ion whose degenerate ground structures have the energy. $(1/2)(e_1+e_2)$, the mean of those of the ground structures of the unsymmetrical ion. Now the hypothetical symmetrical ion will have an absorption peak which is intermediate between those of the two parent symmetrical ions.

The difference between the peaks of the two symmetrical ions may also be in part due to the fact that the interaction energies (α_1 and α_2) between electrons on a nitrogen and its neighboring carbon atom, are different in the two cases. It seems quite probable, however, that an ion in which α_1 differed from α_2 would absorb at some sort of mean of the frequencies of those ions which had both its end α's equal, respectively, to α_1 and α_2.

The properties then which are peculiar to *unsymmetrical* ions will be sought experimentally by comparing the absorption peak of the unsymmetrical ion with the mean of its two symmetrical parents.[3]

It is too complicated to say theoretically which type of mean should be used in the experimental comparison of an unsymmetrical ion with its parent symmetrical ions. It has, however, been found empirically that, for quite a large number of "slightly" unsymmetrical polymethine ions,

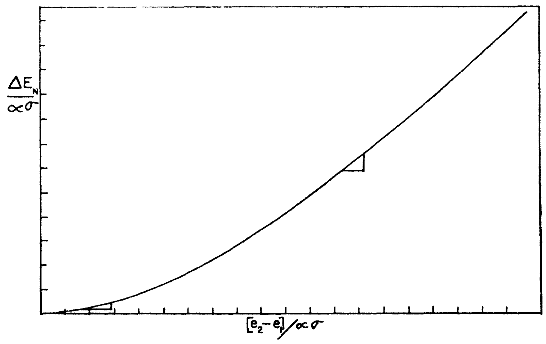

FIG. 2. Dependence of the transition energy, ΔE_N on the energy difference between the two ground structures, e_1-e_2. Each scale division represents one-tenth. The abscissa runs from 0 to 1.9, the ordinate from 1.0 to 2.2.

the wave-length of peak absorption is very closely the arithmetic mean of the wave-length of the peaks of the parent symmetrical ions,[13] when (e_1-e_2) is sufficiently small.

This suggests that the absorption wave-length of unsymmetrical ions be compared to the arithmetic mean of the wave-length of its parents since it will be shown in the following[14] that the effect of (e_1-e_2) on the transition energy of unsymmetrical ions is a second-order one.

For dyes with very different ends, however, such differences do exist. Brooker[2] has emphasized that the peak of the unsymmetrical ion often "deviates" to high frequencies by significant, and occasionally very large, amounts from the mean of the absorption peaks of the two parent symmetrical ions which have ends in common with the left or right half, respectively, of the unsymmetrical ion.

This is in agreement with formula (1), since ΔE_N is greater than $(\alpha/2)(\sigma_N+\sigma_N')$, the arithmetic mean[15] for the transition energies of the parent dyes.

It is also clear that deviation to shorter wave-lengths due to the fixed energy difference (e_1-e_2), becomes larger as the two $\alpha\sigma_N$ become smaller. Now, as discussed in the preceding section, $\alpha\sigma_N$ decreases as the chain length N increases. We should, accordingly, expect the deviation to increase as the chain length increases. This has been found to be the case by Brooker and is illustrated in Fig. 4 of the preceding paper.[3]

Since the $\alpha\sigma_N$ decreases with increasing N, one can see from Eq. (1) that as N increases, ΔE_N decreases. Now in a symmetrical ion $(e_1=e_2)$, ΔE_N would approach zero as N increases indefinitely but in an unsymmetrical ion ΔE_N should decrease and asymptotically approach the magnitude of the energy difference (e_1-e_2). It has indeed been found by Brooker that for a series of unsymmetrical ions differing only in the value for N (homologous series), the absorption peaks appear to converge to a finite wave-length limit as N increases whereas the peaks for a corresponding series of symmetrical ions do not converge when plotted on a wave-length scale.[16]

Equation (1) also affords an explanation of Brooker's sensitivity rule which states that the change in the deviation produced by introducing a given alteration in the molecular structure of a symmetrical ion $(e_1=e_2)$ or a "slightly" unsymmetrical ion $(e_1\neq e_2)$ is much smaller than the change in deviation produced by making the same change in the molecular structure of a highly unsymmetrical ion $(e_1\neq e_2)$.

This may be seen for a chain which is not too large to be a consequence of the fact that the resonance interaction $\alpha\sigma$ and the energy difference (e_1-e_2) enter into the transition energy as a sum of squares. When the difference (e_1-e_2) is small compared to the $\alpha\sigma$, a given increase in (e_1-e_2) affects ΔE_N much less than would the same increase if (e_1-e_2) were already of the same order of magnitude as $\alpha\sigma$ or larger. That is, if one plots the transition energy against (e_1-e_2) for fixed[17] $\alpha\sigma_1$ and $\alpha\sigma_2$ one gets, because of the quadratic relationship, the curve of Fig. 2 from which it is clear that the effect on the transition energy of increasing (e_1-e_2) by an amount Δe is very much less when (e_1-e_2) is zero or small than is the effect when (e_1-e_2) is already appreciable.

Another interesting effect may be obtained if we look into the resonance stabilization of the ground state. Although the transition energy ΔE_N is always larger for unsymmetrical ions $(e_1\neq e_2)$ than for symmetrical ones, the resonance depression of the lowest level is always less when $e_1\neq e_2$ than when $e_1=e_2$.[18] One should accordingly expect that symmetrical ions, in virtue of their larger resonance stabilization, should be more stable than unsymmetrical ones. The former should, for example, be more resistant to fading.

An interesting application of this effect should show up in the measurements of the pH at which the ion is half transformed by acid or alkali (pK value). The polymethine dyes act as indicators in both the acid and alkali range and so have two pK values. Now the difference between the two pK values for a given ion measures (except for a factor RT) the free energy difference involved in changing two of the given ions into two new ions. The new ions differ

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[13] B. Beilenson, N. I. Fisher, and F. M. Hamer, Proc. Roy. Soc. **A163**, 138 (1937).

[14] See discussion of the "sensitivity" rule.

[15] The difference between the harmonic and arithmetic mean of the transition energies is not very great except in extreme cases.

[16] Cf. Fig. 9 of reference 3.

[17] σ_1 and σ_2 are taken to be equal in drawing the figure.

[18] Cf. Eqs. 20 and 45 of reference 7.

from the original given ion in that a proton or hydroxyl has been attached, or perhaps a proton deleted; in any case, however, the resonance system no longer runs through the original chain. In other words, the resonance stabilization which is present before the original ion is transformed and which is, at most, only in small part present after transformation, will resist any change. The entropy change also plays a role through the symmetry number since the product formed is unsymmetrical regardless of whether the original ion is or is not. It is easily checked, however, that the effect of the symmetry number amounts at most to a few tenths of a *p*H unit and is in the opposite direction to the effect of the energy. One can thus understand and expect the applicability to the polymethines of the following rule which Schwarzenbach has found for the triphenylmethane dyes:[19] "The difference between the *p*K values in two regions is larger for symmetrical than for unsymmetrical dyes."

On the basis of the foregoing discussion one should, furthermore, expect, at least so far as the energy is concerned, the following rule: The *p*K values for acid transformation of a homologous series of polymethine ions should decrease and those for basic transformation should increase as the chain length increases. In this it is assumed that entropy changes will not upset this result which is due to stabilization energies.

PART IV

Theory of Symmetric Ions

We wish now to calculate the energy levels of the symmetric ion according to the HLSP method. As mentioned before, the energy values are the roots of determinant (II), in which e is the energy of the ground structures (I), f that of the excited structures (X), (Y), and α the interaction integral between structures.

The method of solution is as follows: One finds exactly the same determinant (II) in the solution of a classical chain vibration problem. Consider $N+2$ particles of mass *1*. The first is tied by a spring to a position of equilibrium in space, to which it is pulled by a restoring force $-(e-\alpha)X$ (X being its deflection). It is also tied to its neighbors by a spring with a restoring force $-\alpha(X-x_1)$. The next particle, which represents the first carbon atom, is tied to its point of equilibrium in space by a spring with a restoring force $-(f-2\alpha)x_1$ and to its neighbors by springs exerting forces $-\alpha(x_1-X)$ and $-\alpha(x_1-x_2)$, and so down the chain to the last particle, which is pulled back to its equilibrium position by a force $-(e-\alpha)Y$ and is acted upon by a force $-\alpha(Y-x_N)$ from the preceding particle.

The secular equation for this problem is exactly our determinant, with ω^2 instead of E, ω being 2π times the frequency.

This problem has been treated by Bartholomé and Teller.[20] The method of solution can be described as follows. One looks for all possible standing waves in the chain. If the end springs were equal to the interior springs, the wave-length (speed of propagation) of the standing waves would be the same in all parts of the chain. However, because the end particles are attached with a different force, the wave-length (speed of propagation) is different for the end members. Nonetheless, the total number of half wave-lengths has to be an integer.[21] Once the wave-length is known, the frequency of the vibration (and E of the quantum problem, corresponding to ω^2) can be found easily. By such a procedure, the determinant is not directly attacked.

In a given mode of vibration—which corresponds to a given quantum state—the particle number s will have a given amplitude x_s. In quantum theory this amplitude is proportional—apart from normalization—to the coefficient with which the structure number s contributes to this state.

One finds, from the differential equations of the vibration problem, the connection between the wave-length of the standing wave and the energy to be

$$E=f+2\alpha\cos k, \tag{2}$$

where k is the "wave vector" of the standing

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[19] G. Schwarzenbach, Zeits. f. Electrochemie **47**, 40 (1941). A similar argument can be made for Schwarzenbach's examples.

[20] E. Bartholomé and E. Teller, Zeits. f. physik. Chemie **B19**, 3 (1931).

[21] If we had a continuous medium, the problem would be that of finding the standing waves in a stack made up of a glass block with thin plates of different refractive index at the end.

wave. It is determined by

$$\cos\frac{N+1}{2}k = R\cos\frac{N+3}{2}k \tag{3}$$

for "symmetric" vibrations, where the two ends of the chain are in the same phase, and by

$$\sin\frac{N+1}{2}k = R\sin\frac{N+3}{2}k \tag{4}$$

for "antisymmetric" vibrations, where the two ends of the chain are in opposite phase.

Here, R is given by $\alpha/(e-f)$. For $R<1-(2/N+3)$, the two lowest states are not given by (3), (4). For $1-(2/N+3)<R<1$, the lowest state is not contained in (3). To find these states it is necessary to replace e^{ik} by a real quantity v in (2), (3), (4). One finds then the values of k and ΔE, the energy difference between the two lowest states, approximately. The results are obtained for the energy of the first transition according to HLPS.

$$R\ll 1. \quad \Delta E = 2\alpha(1-R^2)^2R^N, \tag{5}$$

$$R=1. \quad 4\alpha\sin^2\frac{\pi}{2(N+2)}, \tag{6}$$

$$R\gg 1. \quad 4\alpha\sin\frac{3}{2}\frac{\pi}{N+3}\sin\frac{\pi}{2(N+3)}. \tag{7}$$

All of these ΔE go to zero with increasing N; i.e., the wave-length

$$\lambda = hc/\Delta E$$

goes to infinity, but it does so for $R<1$ exponentially, for $R\geqq 1$, like N^2. For $R<1$, we have also calculated the case in which α_1, the overlap of the two end groups, is different from α, that of the inner groups. One finds, nonetheless, the same dependence on N as given above, only the constants are different.

If we set

$$\gamma = (\alpha_1{}^2-\alpha^2)/\alpha_1{}^2$$

one has to replace R by

$$\frac{(1+4\gamma R^2)^{\frac{1}{2}}-1}{2\gamma R}$$

and 2α by

$$\alpha\frac{4R^2\gamma}{1+4\gamma R^2-(1+4\gamma R^2)^{\frac{1}{2}}}.$$

In the LCAO approximation, we use a skeleton made up of ions only. This skeleton has then $(N+2)$ orbits, into which $N+1$ electrons are put. In this procedure one unpaired electron on one N has been left on the ion. With this treatment one gets again determinant (II), and the calculations of the states and orbits can be taken over formally but there is a considerable difference in the interpretation. The expression, which in the HLSP method describes a state, now describes a molecular orbital. The role of the valence structure s is played now by the atomic orbital of the atomic ion s. The quantities x_s, the relative amplitudes of the classical oscillation, which in HLSP give the contribution of the different structures to a state, now give the coefficients of the sth atomic orbital in a molecular orbital.[22] As a consequence of this, e and f are now the ionization energies of the N and C atoms and α is the overlap of the atomic wave functions. In the ground state, therefore, the $(N+1)/2$ lowest molecular orbitals are filled. In the first excited state, one electron is taken from the molecular orbital $(N+1)/2$ and put into $(N+3)/2$. The previous calculations of the energy of these orbitals (states in HLPS) remain unchanged. The transition energy is to a first approximation:

$$\text{for } R\ll 1,\ \Delta E = 2\alpha\sin\frac{\pi}{N+1}, \tag{8}$$

$$\text{for } R=1, \quad 4\alpha\cos\frac{\pi}{(N+2)}\sin\frac{\pi}{2(N+2)} \quad \text{(exact value)}, \tag{9}$$

$$\text{for } R\gg 1, \quad 2\alpha\sin\frac{\pi}{N+3}. \tag{10}$$

For large N, the ΔE values for the three cases are, in lowest approximation, $\sim N$, which is the value found theoretically for a polyene chain. Figure 1 shows that experimentally the connection between the wave-lengths $(hc/\Delta E)$ and N is a straight line. However, U. Fano pointed out

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[22] This corresponds to the Bloch method in metals.

in the discussion that this straight line does not go through the origin. If one takes higher members in the development in powers of N, one finds

$$R<1.\quad \lambda=\frac{hc}{2\pi\alpha}\left[N+1+\frac{\pi^3}{6}\frac{1}{N+1}\left(1-\frac{48R}{\pi}\right)\right], \tag{8'}$$

$$R=1.\quad \lambda=\frac{hc}{2\pi\alpha}\left[N+2+\frac{13}{24}\frac{\pi^2}{N+2}\right], \tag{9'}$$

$$R>1.\quad \lambda=\frac{hc}{2\pi\alpha}\left[N+3-\frac{2}{R^2}+\frac{1}{N+3}\left(\frac{\pi^2}{6}-\frac{6}{R^2}\right)\right]. \tag{10'}$$

Figure 1 can be represented by

$$\lambda=550(N+5). \tag{11}$$

The constants in Eqs. (8′) (9′) (10′), which are added to N, are smaller than 5. Therefore, the theory is not accurate enough to give this feature.

Nonetheless, the general behavior of the symmetric ions is represented much better by the LCAO than by the HLSP method, not only because of the general dependence on N but also numerically.[4]

A different assumption about the energy of the different structures in HLSP approximation was also tested. It was assumed that the (X) structures had the same energy e as the ground structures instead of having the energy of the more highly excited structures (Y), namely, f. With this assumption, there are then $N+2$ structures, those with energies e and f alternating. The result is (independent of the size of R):

For HLSP approximation (difference between the two lowest states)

$$\Delta E=\frac{1}{2}\left[\left\{(e-f)^2+16\alpha^2-16\alpha^2\sin^2\frac{\pi}{N+3}\right\}^{\frac{1}{2}}-\left\{(e-f)^2+16\alpha^2-16\alpha^2\sin^2\frac{2\pi}{N+3}\right\}^{\frac{1}{2}}\right], \tag{12}$$

which, for large N, approaches

$$\Delta E=4\alpha^2\{(e-f)^2+16\alpha^2\}^{-\frac{1}{2}}\frac{3\pi^2}{(N+3)^2}. \tag{12'}$$

For LCAO (transition between the $(N+1)/2$th and $(N+3)/2$th level),

$$\Delta E=-\frac{e-f}{2}+\frac{1}{2}\left[(e-f)^2+16\alpha^2\sin^2\frac{\pi}{N+3}\right]^{\frac{1}{2}}. \tag{13}$$

In the limit of large N, this gives

$$\frac{4\alpha^2}{e-f}\frac{\pi^2}{(N+3)^2} \tag{13'}$$

and is therefore of the same character as (7), and yields $\lambda\sim N^2$ instead of $\sim N$.

PART V

Theory of Unsymmetrical Ions

Here we make the e of the two ends unequal, $e_1>e_2$, but keep the end interaction integrals α still the same as those within the carbon chain. The result is that the standing wave is no longer symmetrical (or antisymmetrical) with respect to the center of the chain. The situation is as if, in the continuous optical analogy mentioned before, the two end plates had different refractive indices.

If we call

$$R=\frac{\alpha}{e_1-f},\quad R'=\frac{\alpha}{e_2-f}, \tag{14}$$

$$\sigma^2=4R^{2N}(1-R^2)(1-RR') \tag{15}$$

and σ'^2 the quantity with R' and R exchanged, we obtain for the transition energy of unsymmetrical ions for large N according to HLPS the following values.

$R\ll1$

$R'\ll1$

$$\begin{aligned}\Delta E=&\tfrac{1}{2}\{(e_1-e_2)^2+\alpha^2\sigma^2\}^{\frac{1}{2}}\\&+\tfrac{1}{2}\{(e_1-e_2)^2+\alpha^2\sigma'^2\}^{\frac{1}{2}}\\&-\tfrac{1}{2}RR'\left\{(e_1-e_2)^2+\alpha^2\sigma^2\frac{R^2}{R'^2}\right\}^{\frac{1}{2}}\\&-\tfrac{1}{2}RR'\left\{(e_1-e_2)^2+\alpha^2\sigma'^2\frac{R'^2}{R^2}\right\}^{\frac{1}{2}}.\end{aligned} \tag{16}$$

$RR'=1$

$$\Delta E=\alpha\left[R+\frac{1}{R}-2\cos\frac{\pi}{N+2}\right]. \tag{17}$$

(exact value)

$R>1,\ R'>1$

$$\Delta E=3\alpha\left(\frac{\pi}{N+3}\right)^2\times\left[1+\frac{1}{R}+\frac{1}{R'}\right]^{-2}. \qquad (18)$$

$R<1,\ R'>1,\ RR'\neq 1$

$$\Delta E=+\alpha\left(R+\frac{1}{R'}\right)-2\alpha\cos\frac{\pi}{N+2}. \qquad (17')$$

(17′) is equal to (17). Therefore in all cases where at least one of the R values is not larger than 1, ΔE approaches a finite limit as N increases indefinitely.

On the other hand, the LCAO method gives for unsymmetric ions the following transition energies.

$R<1,\ R'<1$

$$\Delta E=2\frac{\alpha\pi}{N+1}(1-RR')(1+R^2)^{-\frac{1}{2}}(1+R'^2)^{-\frac{1}{2}}, \qquad (19)$$

$RR'=1$

$$\Delta E=2\alpha\sin\frac{\pi}{N+1}, \qquad (20)$$

$R>1,\ R'>1$

$$\Delta E=\frac{2\alpha\pi}{N+3}\left(1-\frac{1}{RR'}\right)\times\left(1+\frac{1}{R^2}\right)^{-\frac{1}{2}}\left(1+\frac{1}{R'^2}\right)^{-\frac{1}{2}}, \qquad (21)$$

$R<1,\ R'>1,\ RR'\neq 1$

$$\Delta E=4\alpha\sin\frac{\pi}{2(N+2)}\cos\frac{\pi}{N+2}.^{23} \qquad (22)$$

All of these approach zero with $N=\infty$, i.e., the wave-length approaches infinity in the same way as for symmetric ions. This can be understood from the nature of the approximations made.

PART VI

Discussion

We therefore find the following situation. Both the HLSP approximation and the LCAO approximation give the general behavior for the symmetrical ion, namely, that the wave-length goes to infinity for increasing N (just as in polyenes), but HLSP gives the wrong functional dependence. LCAO gives λ correctly as $K(N+C)$ but is not able to provide the correct value of the constant C.

For the unsymmetrical ion, only the formula according to HLSP can explain the experimental result that there is a finite wave-length limit with increasing chain length, while for LCAO there is no essential difference in the behavior of symmetric and antisymmetric ions. No closer check on the functional dependence of λ on N has been made in this case.

It must be pointed out that the LCAO method as used here does not take into account repulsion between electrons and the wave functions are not antisymmetrized. Whether the inclusion of the repulsion and antisymmetrization would help matters cannot be said.

Also, the effect of the overlap integral, discussed by Professor Mulliken in this symposium, is not taken care of in setting up the determinant (II).

Historical Note

The case of the polyenes—i.e., neutral chains in which the ends are of the same nature as the inner members—has been extensively discussed by Hückel, Mulliken, Lennard-Jones, and co-workers and Coulson.[24] Mulliken has discussed chains with different ends but his interest was not directed to the influence of this difference.

Th. Foerster[25] has made a very interesting investigation of the dyes considered here, and also of phenylmethane dyes. He has used methods very similar to those used here, but the dependence on chain lengths was outside his interest.

Lennard-Jones and Coulson have refined the treatment of the polyene dyes considerably beyond the methods used here.

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[23] In J. Chem. Phys. **10**, 518 (1942), Eq. (71), sin and cos are exchanged in the first line.

[24] E. Hückel, Zeits. f. Physik **70**, 204 (1931); **76**, 628 (1932). Zeits. f. Electrochemie **43**, 752 (1937). R. S. Mulliken, J. Chem. Phys. **7**, 364, 570 (1939). J. E. Lennard-Jones, Proc. Roy. Soc. **158**, 280 (1937). J. E. Lennard-Jones and J. Turkevich, Proc. Roy. Soc. **158**, 297 (1937). C. A. Coulson, Proc. Roy. Soc. **164**, 383 (1938); **169**, 413 (1939).

[25] Th. Foerster, Zeits. f. physik. Chemie **B47**, 245 (1940).