NOTE ON THE CORRELATION OF π-ELECTRONS IN ORGANIC DYES

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I. Preliminaries.

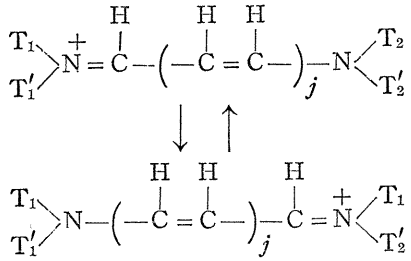
The quantitative theory for the light absorption of organic molecules has based on the two well known quantum-mechanical approximations of the bond orbital and the molecular orbital methods. The absorption bands of some unsaturated hydrocarbons such as benzene, anthracene, phenanthrene, butadiene, fulvene, azulene etc., have been investigated quantitatively by these two methods. The application of these theories to polymethine dyes, however, has given too high calculated values of the wave-lengths of the absorption maxima to interpret the experimental data of these compounds.

On the other hand, the model[1)2)] based on the assumption of the free electron gas such as in metals,[3)] could lead to a rather satisfactory interpretation of the colour[7)8)] of symmetrical polymethines,[1)4)] porphyrines,[5)] polyenes,[2)] and polyacenes.[6)] In those theories, however, the correlation among π-electrons is completely neglected and the free π-electrons are merely subjected to the Pauli principle.

In this paper the author presents a theory taking into account the correlation among electrons, based on the free electron model.

II. The Correlation of π-Electrons in the Polymethine Dyes and Similar Compounds.

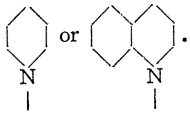
For the sake of simplicity, we shall take, as an example, polymethines as shown in Fig. I.



(Ia)

(Ib)

FIG. I. Polymethine Dye.

The end radicals $T_1 \diagdown \atop T_1' \diagup$N— and $T_2 \diagdown \atop T_2' \diagup$N— are the groups containing a nitrogen atom N. It happens sometimes that they may take ring structures as  or . For the symmetrical polymethines $T_1 = T_2$ and $T_1' = T_2'$.

In the molecule as shown in Fig. I, the number of π-electrons, contributing to the resonance structures (I a) and (I b) etc., is $(j+4)$; $(j+1)$ electrons being contributed from $(j+1)$ carbon atoms and three from two nitrogen atoms. For the symmetrical polymethines $T_1 = T_2$ and $T_1' = T_2'$.

In the usual quantum-mechanical description of these kinds of dyes, the π-electrons find themselves in the attractive field of the molecular framework of the positively charged carbon and nitrogen atoms as well as in the repulsive field of electrons which are forming σ-bonds. The π-electrons as a *free electron gas*, stretch along the polymethine chain in the shape of a charged cloud.

The wave function ψ of the π-electrons is expressed by:

$$\Delta\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0, \tag{1}$$

where m is the mass of electron, E the eigenvalue of energy, and V the potential, being a function of coordinates. For symmetrical polymethine dyes, the one-dimensional wave function of the electrons is assumed to subject to a constant potential with infinitely high barriers nearly at the both ends of the molecule. Accordingly the potential is expressed by:

$$V = \begin{cases} \text{constant for} & 0 \leqq x \leqq L, \\ +\infty & \text{elsewhere,} \end{cases} \tag{2}$$

where x is the distance along the zig-zag line of the chain links of the molecular skeleton, and L the length of the polymethine chain measured along x.

For unsymmetrical polymethines, sometimes the potential is assumed as a periodically varying one[9] along the zig-zag chain of the dye molecule, leading to the solution expressed by Mathieu function.

Now we shall consider, how the potential changes by taking into account the effect of the correlation among π-electrons. The quantum-mechanical mean potential of an electron, say at the state i, due to the other kind of electron cloud, which has an energy level E_j and is at a volume element $d\tau_j$, is designated by

$$\psi_j^* U_{ij} \psi_j d\tau_j, \tag{3}$$

where ψ_j is an eigenfunction associated with the energy E_j, and U_{ij} the interaction potential between the states of the level E_j and of the level considered E_i. The collective interaction due to the electron cloud at the state j is obtained by integrating (3) over $d\tau_j$, and is given by

$$\int \psi_j^* U_{ij} \psi_j d\tau_j. \tag{3'}$$

Accordingly we should sum up (3') over available energy levels. Hence, we obtain

$$\sum_j \int \psi_j^* U_{ij} \psi_j d\tau_j, \tag{4}$$

where $\sum_j$ means the summation over all the filled levels except that of the state i (including spin) occupied by the electron, which is considered as an *Aufpunkt*.

By using (4), we may write, instead of (1), the wave equation for the electrons considered, say at the state i, as follows:

$$\Delta\psi_i + \frac{8\pi^2 m}{h^2}\left\{E - \left(V + \sum_j \int \psi_j^* U_{ij}\psi_j d\tau_j\right)\right\}\psi_i = 0, \tag{5}$$

taking into account the potential of π-electron themselves. In (5), ψ_i means the wave function associated with the energy E_i.

The interaction potentials U_{ij} are of the form $1/|r_{ij}|$ or presumably $e^{-\kappa|r_{ij}|}/|r_{ij}|$, where r_{ij} is the distance between the electrons at the states i and j, with a constant κ. Sometimes, it may be roughly assumed that the interaction potentials are all constant for any j. And it is the equation (5), with which the present author wishes mainly to concern.

The last term of the left-hand side in (5), can be treated, as usual, successively (by the iteration) or by the perturbation method. Here, however, as another approximation, we shall take a rather bold assumption for this term. We shall put for (4),

$$\alpha\psi_i^*\psi_i = \sum_j \int \psi_j^* U_{ij}\psi_j d\tau_j, \tag{6}$$

where α is a constant. This means that the interaction potentials among the level E_i and all other levels E_j are averaged over j and are put equal to the *self-energy* of the electron ψ_i at the energy level E_i. The method used here may possibly correspond to the Hartree approximation.

III. Symmetrical Polymethines.

For the symmetrical polymethines, the end groups in Fig. I, are $T_1 = T_2$ and $T_1' = T_2'$. From (5) and (6), we shall write the one-dimensional wave equation for the electrons,

$$\frac{d^2}{dx^2}\psi + \beta^2(E' - \alpha\psi^2)\psi = 0, \tag{7}$$

with

$$E' = E - V, \quad \beta^2 = \frac{8\pi^2 m}{h^2},$$

and

$$V = \begin{cases} \text{constant} & 0 \leqq x \leqq L, \\ +\infty & x < 0 \quad \text{and} \quad L < x. \end{cases} \tag{8}$$

The solution of (7) is given by an elliptic function:

$$\psi(x) = sn(\beta\gamma x + \gamma', k), \tag{9}$$

with

$$E' = \gamma^2(1 + k^2), \tag{10}$$

and

$$k^2 = \frac{\alpha}{2\gamma^2}, \tag{11}$$

where γ and γ' are integration constants.

From the assumed type of potential (8), we have conditions for ψ:

$$x=0;\ \psi=0 \quad \text{and} \quad x=L;\ \psi=0.$$

These conditions immediately result in

$$\gamma'=0,$$

and

$$\gamma=\frac{2}{\beta L}\{rK+isK'\}, \tag{12}$$

where r and s are integers including zero, $i=\sqrt{-1}$, and

$$\left.\begin{aligned} K&=\int_0^{\pi/2}\frac{du}{\sqrt{1-k^2\sin^2 u}},\\ K'&=\int_0^{\pi/2}\frac{du}{\sqrt{1-k'^2\sin^2 u}},\end{aligned}\right\} \tag{13}$$

with

$$k'=\sqrt{1-k^2}.$$

Now we should take $s=0$, considering that we have already put $\alpha\psi^2$ instead of $\alpha\psi^*\psi$ in (7), which means $\psi(x)$ is a real valued function of x.
An integration constant γ is thus determined by (11), (12), and (13).

From the resultant expression (9) for the eigenfunction, we obtain the potential of the type:

$$V'=V+\alpha\cdot sn^2(\beta\gamma x,\ k). \tag{9'}$$

Accordingly, returning again to the equation (5), we shall assume, instead of (6), this type of potential (9') for the electron-correlation. And further, if necessary, it may be proposed to use the potential of this type of elliptic function even for the field originated from the molecular skeleton and σ-bonds. This means that, as the potential of molecular field for the unsymmetrical polymethine dyes, we may take the potential of the type of elliptic function, instead of that of trigonometric function.[9]

By using (9'), rather than the expression (6), the equation (5) becomes again linear. So it is possible to normalize the solution of this equation, thus

$$1=\int_0^L A^2 sn^2(\beta\gamma x,\ k)dx=A^2\frac{1}{\beta\gamma k^2}[\beta\gamma L-\mathrm{E}(am\beta\gamma L,\ k)],$$

where A is the normalization factor.

IV. Approximate Calculation for Symmetrical Polymethines.

(a) Case I. $\alpha\to 0$.

As a special case, we shall take $\alpha\to 0$, then we obtain from (8)$\sim$(12),

$$k\to 0,\quad k'\to 1,$$

$$K \to \frac{\pi}{2}, \quad K' \to \infty,$$

$$\gamma = \frac{r}{\beta L}\pi, \tag{14}$$

$$\phi(x) = sn\left(\frac{\gamma\pi}{L}x,\ 0\right) = \sin\frac{\gamma\pi}{L}x, \tag{15}$$

$$E^{(0)\prime} = \gamma^2 = \frac{h^2}{8m}\frac{r^2}{L^2}. \tag{16}$$

The first absorption band is associated with the jump of one electron from the highest occupied level, No. $\frac{n}{2}$, to the lowest vacant level, No. $\left(\frac{n}{2}+1\right)$. We have the energy difference $\Delta E_1^{(0)}$ between these levels:

$$\Delta E_1^{(0)} = \frac{h^2}{8mL^2}(n+1). \tag{17}$$

From the Bohr relationship, the wave-length $\lambda_1^{(0)}$ of the maximum of the first absorption band is expressed by

$$\lambda_1^{(0)} = \frac{hc}{\Delta E_1^{(0)}} = \frac{8mc}{h}\frac{L^2}{n+1}, \tag{18}$$

where h is Planck's constant, and c the velocity of light.

After determining the normalization factor $\sqrt{\frac{2}{L}}$, the intensity of the absorption band, which is measured by the oscillator strength, is calculated. For the *trans*-configuration of the dye molecule, the oscillator strength $f^{(0)}$, associated with the quantum jump: level No. $\frac{n}{2} \to$ No. $\left(\frac{n}{2}+1\right)$ (n: even), is given by

$$f^{(0)} = \frac{8}{3\pi^2}\cdot\left(\cos^2\frac{\varepsilon}{2}\right)\cdot\frac{n^2(n+2)^2}{(n+1)^3}, \tag{19}$$

where $180^\circ - \varepsilon$ is the valency angle between successive chain links.

(*b*) *Case II.* $0 < \alpha \ll 1$.

For $\alpha \ll 1$, $k \ll 1$, and $k' \approx 1$, we obtain, retaining the terms up to $O(k^2)$,

$$\phi(x) \fallingdotseq \sin\frac{\gamma\pi}{L}x\cdot\left\{1+\frac{k^2}{4}\cos^2\frac{\gamma\pi}{L}x\right\}, \tag{20}$$

with

$$E^{(1)\prime} = \gamma^2(1+k^2) \fallingdotseq \frac{h^2\gamma^2}{8mL^2}\left(1+\frac{3}{2}k^2\right), \tag{21}$$

and

$$K \fallingdotseq \frac{\pi}{2}\left(1+\frac{k^2}{4}\right).$$

Accordingly the first absorption band, associated with the electron jump: level No. $\frac{n}{2}$ to the lowest vacant level No. $\left(\frac{n}{2}+1\right)$, can be calculated. The energy difference

$\Delta E_1^{(1)}$ and the wave-length $\lambda_1^{(1)}$ of the maximum of the absorption band are as follows:

$$\Delta E_1^{(1)} = \frac{h^2}{8mL^2}(n+1)\left(1+\frac{3}{2}k^2\right), \tag{22}$$

$$\lambda_1^{(1)} = \frac{8mc}{h}\frac{L^2}{n+1}\left(1-\frac{3}{2}k^2\right). \tag{23}$$

The normalization factor A is determined by

$$A^2\int_0^L \sin^2\frac{r\pi}{L}x\cdot\left\{1+\frac{k^2}{2}\cos^2\frac{r\pi}{L}x\right\}dx = 1,$$

i.e.

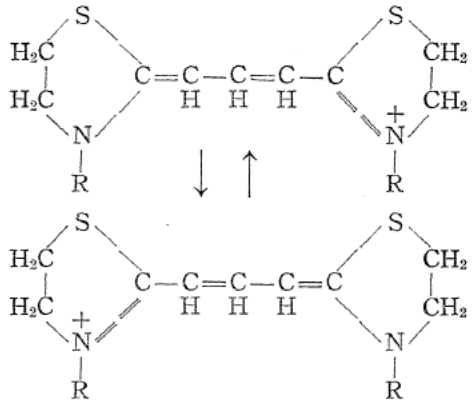
$$A = \sqrt{\frac{2}{L}}\cdot\left\{1-\frac{k^2}{16}\right\}.$$

And the oscillator strength $f^{(1)}$ associated with this electron transition for the *trans*-configuration of the dye molecule, is obtained:

$$f^{(1)} = \frac{8}{3\pi^2}\cdot\left(\cos^2\frac{\varepsilon}{2}\right)\cdot\frac{n^2(n+2)^2}{(n+1)^3}\cdot\left[1+\frac{3}{2}k^2+\right.$$
$$\left.+\frac{3k^2}{8}(n+1)^2\left\{\frac{1}{(n-1)^2(2n+1)^2}+\frac{1}{(n+3)^2(2n+3)^2}\right\}\right]. \tag{24}$$

V. Comparison with Experiments.

We shall take, for example, the thiazolino-cyanine dye as shown in Fig. II.



(II a)

(II b)

FIG. II. 1, 1'-dialkyl-2, 2'-trimethine-thiazolino-cyanine.

In this molecule, $L = 8l$, where l is the bond length of the chain elements, and is put equal to 1.39 Å, which according to Pauling[10] is the bond length of a C·····C bond, with the bond number 1.5, as is found in benzene. The number of electrons, which contribute to the resonance structures (II a) and (II b) etc., is $n = 8$ as mentioned in § II. The C—C=C valency angle is $180° - \varepsilon = 124°$. By using the universal constants, h, c, and m, as the usual ones,[11] we obtain from (18) and (19),

$$\lambda_1^{(0)} = 4530 \text{ Å},$$
$$f^{(0)} = 1.85.$$

On the other hand, the data of the wave-length of the maximum of the first absorption band obtained by Brooker,[12)13)14)] and the oscillator strength[8)] are

$$\lambda_{\text{exp.}} = 4450 \text{ Å},$$
$$f_{\text{exp.}} = 1.2.$$

If we use (23) in order to make agree with the experiment, we should choose

$$k^2 = 0.0118,$$

for this case, and accordingly

$$\alpha = 0.12 \text{ eV}.$$

While, we obtain from (24),

$$f^{(1)} = 1.88.$$

The experimentally found value $f_{\text{exp.}}$ for the oscillator strength, is smaller than those calculated $f^{(0)}$ and $f^{(1)}$ for the all-*trans*-configuration. The *trans*-configuration corresponds to the highest value of the oscillator strength more than the other configurations having some *cis*-links. The lower value thus shows that the dye used in the experiment probably was a mixture of *cis*- and *trans*-isomers.

In comparing the value of α with the energy difference (17) for the transition in question, *i.e.* $\Delta E_1^{(0)} = 2.74$ eV., and considering that the binding energy for a conjugated double bond, is 3.73 eV., we can find that the value of α, which corresponds to the mean energy of the electron-correlation, may be not so unreasonable.

As another example, we shall take the symmetrical carbo-cyanine dyes, whose cations have the equivalent limitting structures as shown in Fig. III.

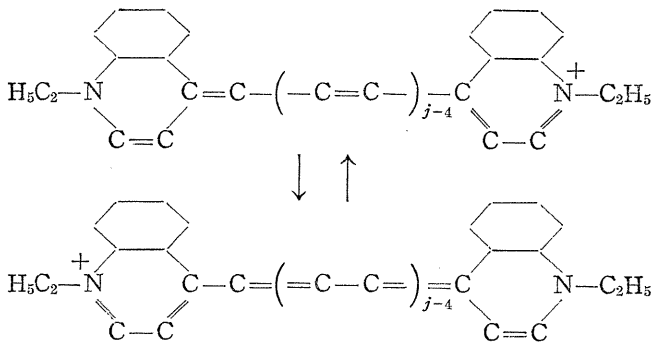


FIG. III. Symmetrical 4, 4'-Carbo-cyanine.

A generalization of the equation for the length of the polymethine chain leads to the following expression:

$$L = (2j+2)l,$$

where j is the number of double bonds counted along the chain in either of the

limitting structures (III a) and (III b) in Fig. III. The number N of π-electrons contributing to the resonance structures is $N=2j+2$. For this type of dyes, we obtain the wave-length λ_1 of the maximum of the first absorption band from (18) and (23) respectively,

$$\lambda_1^{(0)} = 637\frac{(2j+2)^2}{2j+3} \quad (\text{Å unit}), \tag{25}$$

$$\lambda_1^{(1)} = 637\frac{(2j+2)^2}{2j+3}\cdot\left(1-\frac{3}{2}k^2\right) \quad (\text{Å unit}). \tag{26}$$

Calculated values by (25) for $j=4$, 5, and 6, are shown in the following:

$$j=4: \quad \lambda_1^{(0)} = 5790 \text{ Å},$$
$$j=5: \quad \text{〃} = 7060 \text{ Å},$$
$$j=6: \quad \text{〃} = 8320 \text{ Å}.$$

On the other hand, the experimental data given by Brooker[12)-14)] are:

$$j=4: \quad \lambda_1^{\text{exp.}} = 5910 \text{ Å in } CH_3OH,$$
$$j=5: \quad \text{〃} = 7050 \text{ Å in } CH_3OH,$$
$$j=6: \quad \text{〃} = 8130 \text{ Å in } CH_3OH.$$

By using these figures both from (25) and from the experiment, so as to make agree with the values from (26), we should choose the values for α as follows:

$$j=4: \quad \alpha = -0.13 \text{ eV},$$
$$j=5: \quad \text{〃} = 0.009 \text{ eV},$$
$$j=6: \quad \text{〃} = 0.15 \text{ eV}.$$

The order of magnitude of α for small j ($j=5$, and 6 etc.), is less than 10% of the kinetic energy of an electron as mentioned above and is not so unreasonable.

In the case of $j=4$, it seems that the theory based on the free electron model presumably underestimates the wave-length of the first absorption maximum of the spectrum. And it is considered that this underestimation resulted in the negative value of α. While, on the contrary, this model overestimates the wave-length of the absorption maximum for the dye molecules with sufficiently long chain. The formulae (18) and (25) show that the wave-length of the absorption maximum increases in proportion to the chain length as the shape of melecules becomes longer. For example, the carotin molecule, which has eleven conjugated double bonds ($j=11$), gives the experimental data for the wave-length of the absorption maxima as follows:

$$\lambda = 5110,\ 4780,\ 4420 \text{ Å} \quad \text{for } \alpha\text{-carotin in } CS_2,$$
$$\lambda = 5200,\ 4850,\ 4540 \text{ Å} \quad \text{for } \beta\text{-carotin in } CS_2.$$

While the calculated value (25) for the wave-length of the first absorption maximum appears in the infra-red region. Because of the discrepancy between the theory based on the free electron model[16)] and the experiments for the long chain molecules, it is presumably of no use to estimate the order of magnitude of the

energy of electron-correlation for large j. Moreover, as no reliable data for $j \geqq 7$ of the symmetrical 4, 4′-carbo-cyanine in Fig. III, are found at present, we can hardly say anything about the order of magnitude of the energy of the electron-correlation of this kind of dyes having the longer chain length.

In concluding the paper the present author intends to point out that the potential expressed by (9′), may be of some use for the potential of the electron correlation for the unsymmetrical polymethines, as well as for the symmetrical ones. And further, sometimes, the type of the potential (9′) may be conveniently applied,[15] *mutatis mutandis*, to the unsymmetrical polymethines as a mean molecular field acting on the π-electron considered. In this case, the solution of the wave equation takes the same feature as in (9), and the corresponding energy difference and wave-length are given by (22) and (23).

This type of potential (9′) may, also, be of some use in the theory of electrons in metals. This problem, as well as that of the unsymmetrical polymethines, polyenes, and related compounds, shall be discussed later elsewhere.

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15) The potential of $sn^2(x, k)$-type may be most profittably applied to polyene molecules.
16) *Note added in Proof*—Recently at the annual meeting of the Phys. Soc. of Japan, held at Oct. 30, 1952, G. Araki and T. Murai mentioned that the electron-correlation was conveniently taken into account by Tomonaga's method.[17] Based on the free electron model containing only one parameter, they showed that the calculated values of the wave-length of the maximum absorption agreed fairly well with experimental data over a wide range of the chain length of carotinoid molecules.
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