

A Quantum-Mechanical Theory of Light Absorption of Organic Dyes and Similar Compounds*

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(Received February 21, 1949)

The most important organic compounds which absorb visible light can be classified into three groups typified: (a) by symmetrical polymethines, (b) by porphyrines, (c) by polyenes.

Recently it was shown that the position of the absorption maxima of *symmetrical polymethines and related compounds* (symmetrical cyanine and oxanole dyes; Michler's hydrol blue and derivatives; malachite green and other triphenyl methane dyes; etc.) can be calculated by adopting a model of the dye molecule which is analogous to the free-electron gas model used in particular by Sommerfeld to describe the condition of metals. The π -electrons of the polymethine chain are considered as a one-dimensional free-electron gas which extends itself along the length of the chain.

In the normal state the stablest energy states of the electron gas each contain two electrons in accordance with Pauli's exclusion principle. The remaining states are empty. The existence of the first absorption band is a consequence of the jump of a π -electron from the highest energy level occupied in the normal state to the lowest empty level.

For the wave-length of the maximum of the first absorption band of this group of dyes, the relationship obtains that

$$\lambda_1 = (8mc/h)(L^2/[N+1]),$$

where L is the length of the polymethine zig-zag chain, N , the number of π -electrons, m , the mass of the electron, c , the velocity of light, h , Planck's universal constant. Good agreement with experimental results for λ_1 is obtained by the use of this equation.

The problem of *porphyrine and phthalocyanine* compounds can also be dealt with on the basis of a free-electron gas model. We treat the π -electrons of the porphyrine ring as electrons which are confined to move in a closed ring-shaped path in a field of constant potential energy.

In the case of *polyenes and related compounds* (Carotenes, unsymmetrical cyanines and oxanoles, merocyanines, azo- and stilbene dyes, etc.) a description by means of a free-electron gas model is no longer permissible. The electron gas in this case suffers a disturbance from its condition in the case of the first and second groups of dyes, and, to allow for this, the π -electrons are considered placed in a one-dimensional potential having a sine curve periodicity. The wave-length λ_1 is expressed by

$$\lambda_1 = \left[\frac{V_0}{hc} \left(1 - \frac{1}{N} \right) + \frac{h}{8mc} \frac{N+1}{L^2} \right]^{-1},$$

where V_0 is the amplitude of the sine-shaped potential along the chain.

This relation is confirmed by the experimental data. It also gives an explanation for the markedly different manner (compared with the symmetrical polymethines) in which the position of the absorption bands of polyenes and related compounds depends on the chain length.

The results of the classical color theory of Witt are capable of a simple explanation when considered in the light of the electron gas model.

THE problem of setting up a quantitative theory for the light absorption of organic molecules has been attempted only in a few instances. The most important results are those of Sklar¹ and Förster² who found quantitatively the absorption bands of some unsaturated hydrocarbons (benzene, anthracene, phenanthrene, butadiene, fulvene, and azulene). Their calculations were based on the two well-known quantum-mechanical approximations of the bond orbital and molecular orbital methods. Later these methods were applied to polymethine dyes.³ It turns out, however, that the calculated values of the wave-lengths of the absorption maxima of these compounds are about four times larger than the experimentally determined ones. This would mean that according to these calculations the dyes would absorb in the infra-red and not in the visible spectrum. So far then, these methods, when applied to dyes, do not seem to give satisfactory results.

Recently, by using the concept of the free-electron

gas, as used in particular by Sommerfeld⁴ for metals,⁵ the author has shown^{6,7} that this can lead to a satisfactory interpretation of the color of the symmetrical polymethine dyes.⁸ The model based on the electron gas was then refined⁹ and will now be shown to be capable of being extended to give a quantitative theory of light absorption of the most important groups of colored organic compounds typified by the symmetrical polymethines, porphyrines, and polyenes.

⁴ A. Sommerfeld and H. Bethe, *Handbuch der Physik* (1933), Vol. 24, second edition.

⁵ The density of the π -electrons in aromatic compounds and the diamagnetic anisotropy of such molecules has been treated on the basis of free-electron gas models by: (a) O. Schmidt, *Zeits. f. physik. Chemie* (B) 39, 59 (1938); 42, 83 (1939); 44, 185, 194 (1939); 47, 1 (1940). (b) L. Pauling, *J. Chem. Phys.* 4, 673 (1936); (c) K. Lonsdale, *Proc. Roy. Soc.* 159, 149 (1937).

⁶ H. Kuhn, *Helv. Chim. Acta* 31, 1441 (1948), lecture at the chemistry colloquium at the University of Basel on January 22, 1948.

⁷ H. Kuhn, *J. Chem. Phys.* 16, 840 (1948).

⁸ Very recently J. R. Platt, *J. Chem. Phys.* 17, 484 (1949), has used a free-electron gas model for treating the absorption of polyacenes, and W. T. Simpson, *J. Chem. Phys.* 16, 1124 (1948), has treated polymethines in a similar way as it has been done earlier by H. Kuhn (references 6 and 7). N. S. Bayliss, *J. Chem. Phys.* 16, 287 (1948), has treated the absorption of polyenes on the basis of a free-electron gas model. However, as we shall see in Section C-3, the use of such a model is not permissible in this case.

⁹ H. Kuhn, *Chimia* 2, 11 (1948). For an extension of the treatment to molecules with branched π -electron gas see H. Kuhn, *Helv. Chim. Acta* 32, nr. 7 (1949) (in print).

* Translated from the German by Alexander Silberberg.

¹ A. L. Sklar, *J. Chem. Phys.* 5, 669 (1937).

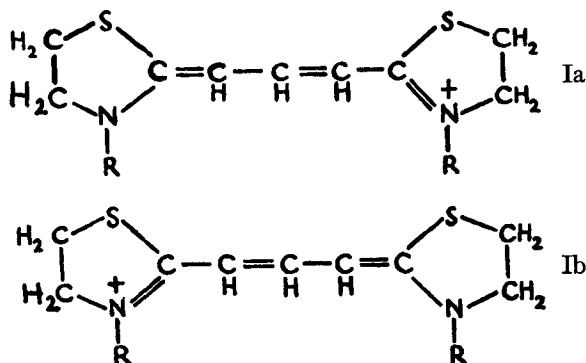
² Th. Förster, *Zeits. f. Elektrochemie* 45, 548 (1939); *Zeits. f. physik. Chemie* (B) 41, 287 (1938).

³ K. F. Herzfeld, *J. Chem. Phys.* 10, 508 (1942); A. L. Sklar, *J. Chem. Phys.* 10, 521 (1942); K. F. Herzfeld and A. L. Sklar, *Rev. Mod. Phys.* 14, 294 (1942).

A. SYMMETRICAL POLYMETHINE DYES AND SIMILAR COMPOUNDS

1. Qualitative Description of the Electron Gas Model

We consider as a particularly simple example the symmetrical polymethine dye Ia, Ib. The cation, which is responsible for the color, is considered to be resonating between two limiting structures, Ia and Ib, each of which makes the same contribution to the normal state of the cation.



Each structure results from the other when the single and double bonds of the polymethine chain change over. This picture shows that we are not dealing with a conjugated chain of double and single bonds, but with a chain of equal bonds, whose nature is intermediate between double and single bond. Their character compares with the C—C bonds in benzene.

A qualitative quantum-mechanical picture of this bond condition is illustrated in Fig. 1. The atoms constituting the polymethine chain lie with their centers in a plane and are joined by σ -bonds. Each carbon atom of the chain and the two nitrogen atoms at the ends are the center of three such σ -bonds as indicated by the lines in Fig. 1(a).

To form the σ -bonds each carbon atom and each of the two terminal nitrogen atoms uses three of its valency electrons. The fourth valency electrons of the carbon atoms in the chain and the remaining electrons in the outer shells of the two nitrogen atoms find themselves in the electrostatic field of the molecular skeleton. These electrons (π -electrons) are attracted by the positively charged carbon and nitrogen atoms, but are repelled by the electrons forming the σ -bonds. Due to the influence of the above electrostatic attractions and repulsions, the π -electrons form an "electron gas" which in the shape of a charged cloud stretches along the polymethine chain both above and below the plane xy of the molecule.

If such a molecule absorbs visible light, it means that the light vector concerned interacts with the easily displaceable π -electrons of the electron gas, which is thereby brought into a state of excitation.

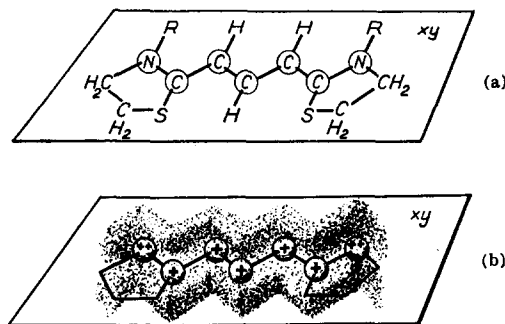


FIG. 1. Cation of the cyanine dye Ia, Ib. (a) Molecular skeleton. (b) The π -electron gas extends along the polymethine chain above and below plane xy in the form of a charged cloud. Light absorption is caused by the electrical vector of the incident light acting on the easily displaceable π -electrons.

2. Quantitative Treatment

The Bohr relationship between the wave-length λ of an absorption maximum and the excitation energy ΔE of the corresponding excited state (i.e., the difference in energy between the particular excited state considered and the normal state) is

$$\lambda = hc/\Delta E, \quad (1)$$

where h is Planck's constant, and c is the velocity of light. This relation permits us to predict the absorption spectrum (i.e., the position of possible absorption maxima) from the excitation energies of the possible excited states of the π -electrons.

In order to find the energy of the possible excited states of the electron gas, a few simplifying assumptions have to be made. Firstly, we restrict the π -electrons so that they can only move in the direction of the chain, i.e., only along the zig-zag line of the polymethine chain. Secondly, we assume that the potential energy of an electron remains constant as it moves along the chain, and that it rises sharply to infinity as it comes to the ends of the chain. That means that we replace the π -electrons of the polymethine chain by electrons moving in a one-dimensional box of length L , where L is the length of the polymethine zig-zag chain (Fig. 2).^a

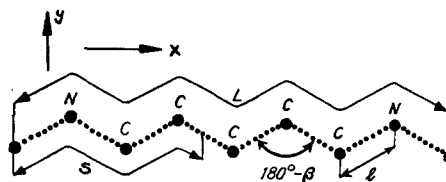


FIG. 2. According to the model the π -electrons can only move along and in the direction of the polymethine zig-zag chain of length L . The potential energy along the length L is considered constant.

^a The potential energy along the chain does not actually rise sharply to infinity at the ends of the resonating portion. It shows a more or less steep increase at these points, depending on the nature of the groups in the neighborhood of the terminal nitrogen atoms. For most of the cases dealt with here these groups are simple saturated structures, and we can assume that L is measured by the length of the polymethine zig-zag chain between the nitrogen atoms plus one bond distance to either side (see Fig. 2).

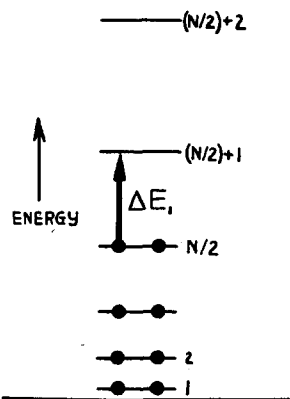


FIG. 3. Cation of the cyanine dye Ia, Ib. Energy levels in which a π -electron of the electron gas can remain. In the normal state the $N/2$ stablest levels are filled by two electrons each, as required by the Pauli exclusion principle. The remaining levels are empty. (N is the number of π -electrons in the gas).

The existence of the first (by far the strongest) absorption band is a result of the jump of an electron from the highest occupied level, No. $N/2$, to level No. $([N/2]+1)$.

With these assumptions it is easy to set up and solve the Schrödinger equation for the π -electrons, and the energy values which a particular electron can assume are simply calculated.^b Figure 3 shows the energy levels of some of the lowest quantum states.

According to the Pauli exclusion principle, not more than two of the electrons of the π -electron gas can co-exist in the same quantum state, and thus be at the same energy level. In the normal state all the lowest levels will then be filled, with two electrons each, to a certain height, depending upon the number of electrons available. All higher levels in this normal state will be empty. If N is the number of π -electrons making up the gas (in the case of the dye Ia, Ib, N is 8), then for the normal state the $N/2$ lowest levels contain two electrons each; the other levels are empty (see Fig. 3, the electrons are represented by dots).

The existence of the first absorption band, which is practically the only important one, is associated with the jump of one electron from the highest occupied level, No. $N/2$, to the lowest free level, No. $([N/2]+1)$. For the energy difference, ΔE_1 , between level No. $N/2$ and the next highest one we obtain, on account of the assumptions made, the relation

$$\Delta E_1 = (\hbar^2/8mL^2)(N+1), \quad (2)$$

where m is the mass of the electron, L (see above) is the length of the polymethine chain measured along zig-zag line of the chain links. By substituting (2) in (1) we immediately obtain an expression for the wave-length of the maximum of the first absorption band

$$\lambda_1 = \frac{hc}{\Delta E_1} = \frac{8mc}{h} \frac{L^2}{N+1}. \quad (3)$$

The intensity of the absorption band, which is measured by the oscillator strength, f , is also easily calculated on the basis of this model.

For the special case of a polymethine chain where every bond in the chain has a *trans*-configuration (like the chain represented in Figs. 1 and 2) the oscillator

^b For details see reference 6.

strength is given by

$$f_1 = \frac{8}{3\pi^2} \cos^2(\beta/2) \cdot \frac{N^2(N+2)^2}{(N+1)^3}, \quad (4)$$

where $180^\circ - \beta$ is the valency angle between successive chain links. If the polymethine chain does not exhibit *trans*-configuration at every bond, but if at some, or even all links, the *cis*-structure prevails, the oscillator strength (which on our model is easily calculated for all configurations) must always be less than according to (4).

The manner in which Eq. (4) can be derived will now be briefly indicated. From general quantum theory the transition probability, with which an electron under the influence of light passes from a lower quantum state A to a higher state B , is easily calculated and obviously determines the oscillator strength $f_{A \rightarrow B}$ corresponding to this transition. Hence,

$$f_{A \rightarrow B} = \frac{8m\pi^2}{3\hbar^2} \Delta E_{A \rightarrow B} (|X_{A \rightarrow B}|^2 + |Y_{A \rightarrow B}|^2 + |Z_{A \rightarrow B}|^2), \quad (4.1)$$

where

$$X_{A \rightarrow B} = \int \psi_A \psi_B^* x d\tau, \quad (4.2)$$

$$Y_{A \rightarrow B} = \int \psi_A \psi_B^* y d\tau, \quad (4.3)$$

$$Z_{A \rightarrow B} = \int \psi_A \psi_B^* z d\tau. \quad (4.4)$$

In the above $\Delta E_{A \rightarrow B}$ is the energy difference of the two states and $\psi_A(x, y, z)$ and $\psi_B(x, y, z)$ are the wave functions of the electron in state A and B , respectively, when the molecule is fixed relative to an xyz coordinate system. The symbol $d\tau$ is used to represent the volume element $dx dy dz$ in space, and the integrals are to be taken over the whole space.

Here we are concerned with the transition of a π -electron of the polymethine chain from quantum state No. $N/2$ to state No. $([N/2]+1)$. The energy difference $\Delta E_{A \rightarrow B}$ in this case equals ΔE_1 as given by Eq. (2), and the wave functions of the electron in the two states, according to our one-dimensional electron-gas model, are:

$$\psi_{N/2} = (2/L)^{1/2} \sin((\pi s/L)N/2), \quad (4.5)$$

$$\psi_{N/2+1} = (2/L)^{1/2} \sin((\pi s/L)([N/2]+1)), \quad (4.6)$$

where the variable s is the distance between a point on the zig-zag chain L and one of its ends when measured along the zig-zag path of the chain (see Fig. 2). The xyz coordinate system is now so placed relative to the molecule that the origin is at one end of the chain and that the x axis coincides with the direction of the chain as shown in Fig. 2. Consequently,

$$x = s \cos(\beta/2). \quad (4.7)$$

Formula (4.2) suitably applied to these conditions transforms to

$$X_{N/2 \rightarrow N/2+1} = \int_{s=0}^L \psi_{N/2} \psi_{N/2+1}^* x ds. \quad (4.8)$$

Substituting Eqs. (4.5), (4.6), and (4.7) in (4.8) and integrating we obtain

$$X_{N/2 \rightarrow N/2+1} = -(2L/\pi^2) \left(\cos \frac{\beta}{2} \right) (N(N+2)/(N+1)^2). \quad (4.9)$$

Similar calculations applied to formulas (4.3) and (4.4) show that in this case $Y_{N/2 \rightarrow N/2+1}$ and $Z_{N/2 \rightarrow N/2+1}$ are zero.

Introducing these results in Eq. (4.1) gives the following result for $f_{N/2 \rightarrow N/2+1}$

$$f_{N/2 \rightarrow N/2+1} = \frac{4}{3\pi^2} (\cos^2 \beta/2) \frac{N^2(N+2)^2}{(N+1)^3} \quad (4.10)$$

As there are two electrons in the quantum state No. $N/2$, both of which can carry out this transition, the total oscillator strength

f_1 assigned to the first absorption band must be double the value of $f_{N/2 \rightarrow N/2+1}$ in Eq. (4.10), i.e., the value of f_1 is as in Eq. (4).

The value of $f_{A \rightarrow B}$ as given by Eq. (4.1) corresponds to a random orientation of the dye molecules relative to the incident light which may be polarized or unpolarized. Different are the conditions in the case when all the dye molecules are orientated parallel to one another and when the electric vector of the incident light is parallel to, say, the x direction of the coordinate system mentioned in connection with Eq. (4.1). The oscillator strength of the transition would then be

$$f_{x, A \rightarrow B} = (8m\pi^2/h^2)\Delta E_{A \rightarrow B}|X_{A \rightarrow B}|^2. \quad (4.11)$$

Similarly,

$$f_{y, A \rightarrow B} = (8m\pi^2/h^2)\Delta E_{A \rightarrow B}|Y_{A \rightarrow B}|^2, \quad (4.12)$$

$$f_{z, A \rightarrow B} = (8m\pi^2/h^2)\Delta E_{A \rightarrow B}|Z_{A \rightarrow B}|^2. \quad (4.13)$$

In the case of a polymethine chain with an all-*trans*-configuration, we have from Eq. (4.9) etc., that $X_{N/2 \rightarrow N/2+1} \neq 0$; $Y_{N/2 \rightarrow N/2+1} = Z_{N/2 \rightarrow N/2+1} = 0$. Hence, it follows from Eqs. (4.11), (4.12), and (4.13) that $f_{x, N/2 \rightarrow N/2+1} \neq 0$; $f_{y, N/2 \rightarrow N/2+1} = f_{z, N/2 \rightarrow N/2+1} = 0$. This expresses the fact that under these circumstances only the component of the incident light in the direction of the chain interacts with the molecule and hence light whose electric vector is parallel to the chain axes of the molecules will be most strongly absorbed while light whose electric vector is perpendicular to these axes will not be absorbed at all.⁶

Beyond the first absorption band we expect further though weaker bands at shorter wave-lengths which are caused by a π -electron jumping, say, from energy level No. $([N/2]-1)$ to level No. $([N/2]+1)$, or to No. $([N/2]+2)$ etc., or, say, from level No. $N/2$ to level No. $([N/2]+2)$, or to No. $([N/2]+3)$ etc.

From our model it follows that these transitions in part have polarization or components of polarization perpendicular to that of the first absorption band, and that the intensity of these bands will differ largely as we go from one *cis-trans*-isomer to the other.

3. Comparison with Experiment

All the factors entering Eqs. (3) and (4) can easily be determined in an actual case: h , c , and m are universal constants; L , the length of the polymethine chain is found from the known bond distances; and N , the number of π -electrons of the electron gas, results directly from the structural formula.

In the case of the dye Ia, Ib we find for L from Fig. 2,

$$L = 8l, \quad (5)$$

where l is the bond length of the chain elements. (l equals 1.39×10^{-8} cm, which according to Pauling¹⁰ is the bond length of a C—C bond, with bond number 1.5, as is found in benzene.) Further, as already mentioned, $N = 8$. Each carbon atom in the chain yields its fourth valency electron, and the two nitrogen atoms at the ends together give three. Finally $(180^\circ - \beta) = 124^\circ$, which is the C—C=C valency angle.

Using these values, as well as the usual ones of h , c , and m , in Eqs. (3) and (4), we obtain,

$$\left. \begin{array}{l} \lambda_1 = 4530\text{\AA} \\ f_1 = 1.86 \end{array} \right\} \text{theoretical.}$$

⁶ Similar conclusions have been derived on the basis of the molecular and bond orbital methods. See Mulliken, reference 20.

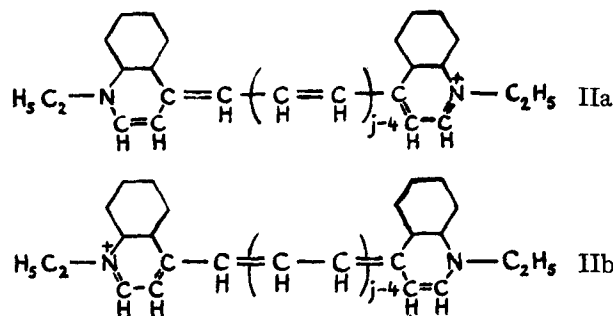
¹⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), second edition.

For this dye Brooker¹¹ obtained the values,^d

$$\left. \begin{array}{l} \lambda_1 = 4450\text{\AA} \\ f_1 = 1.2 \end{array} \right\} \text{experimental,}$$

which are in good agreement with the calculated ones. The experimentally found value for f_1 is smaller than that calculated for the all-*trans*-configuration shown in Fig. 1. It will be remembered that in connection with Eq. (4) we pointed out that such a *trans*-configuration yields the highest value of f_1 as against any configuration having some *cis*-links. The lower value thus shows that the dye which was used in the experiment probably was a *cis-trans*-isomer mixture.

As a further example we take the symmetrical carbocyanine dyes whose cations have the equivalent limiting structures



As in the case of the dye Ia, Ib we have a polymethine chain wherein each C—C bond can be considered to be of bond number 1.5 as in the benzene nucleus.

As a generalization of Eq. (5) we find the following expression for L , the length of the polymethine chain (see Fig. 2),

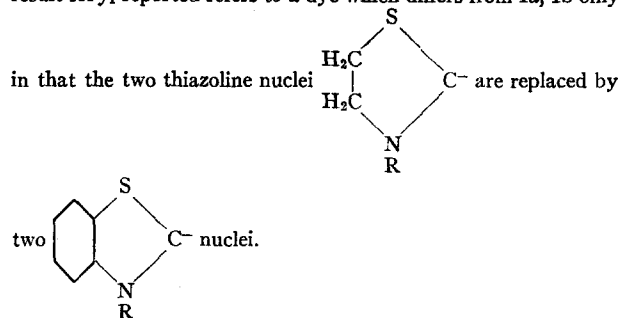
$$L = (2j+2)l, \quad (6)$$

where j is the number of double bonds counted along the chain in either of the limiting structures. Further,

$$N = 2j+2. \quad (7)$$

¹¹ L. G. S. Brooker, *Rev. Mod. Phys.* **14**, 275 (1942); R. E. Burk and O. Grummitt, *Advances in Nuclear and Theoretical Organic Chemistry* (Interscience Publishers, Inc., New York, 1945), Chapter 4; Brooker, Sprague, Smyth, and Lewis, *J. Am. Chem. Soc.* **63**, 1116 (1940); Brooker, Keyes, and Williams, *J. Am. Chem. Soc.* **64**, 199 (1942).

^d The result given for the wave-length of the absorption maximum refers to the dye Ia, Ib; the corresponding value of the absorption intensity could not be found in the literature, and the result for f_1 reported refers to a dye which differs from Ia, Ib only



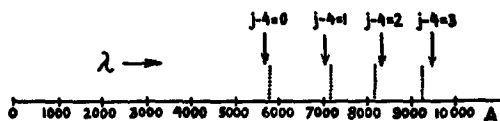


FIG. 4. Cation of the dye IIa, IIb. Position of the maximum of the first absorption band in the cases, $j-4=0, 1, 2, 3$. Dotted lines: Experimentally found position (according to Brooker). Arrows: Calculated from Eq. (8).

From Eqs. (6), (7), and (3) we obtain

$$\lambda_1 = 637 \frac{(2j+2)^2}{2j+3} \text{ (angstrom).} \quad (8)$$

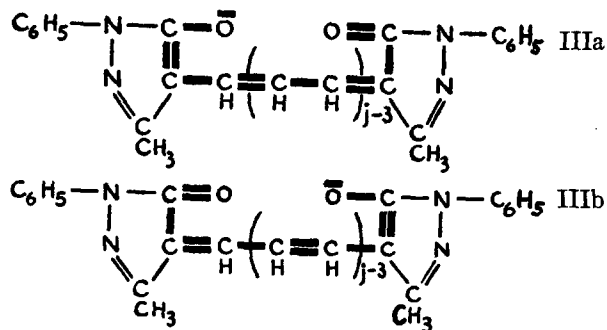
In Fig. 4 the dotted lines show the absorption maxima found experimentally by Brooker¹¹ for the cases ($j-4$) = 0, 1, 2, and 3. The values for the absorption maxima calculated from (8) are shown by arrows. In all cases excellent agreement between theory and experiment is found.

Figure 5 gives the experimental absorption curve in the case ($j-4$) = 1. Arrow No. 1 shows the position of the band maximum on the basis of the electron gas

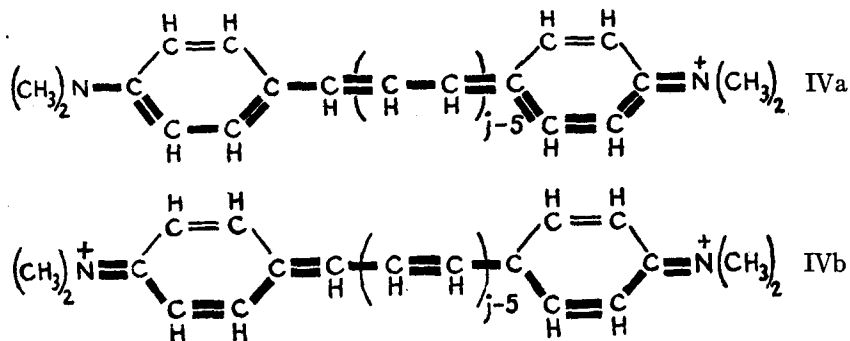
model. Arrows No. 2, 2', and 3 give the positions of the maximum calculated on the basis of the bond orbital and molecular orbital methods, respectively, by using the equations of Herzfeld and Sklar.⁶

Besides the cyanines a further number of dye types are known where the electron gas model can be considered to yield relatively sound results, and where good agreement with experiment is found. We will select the following dyes as examples.^f

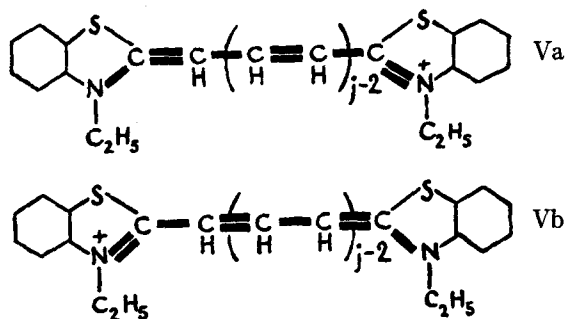
Oxanole dyes:



Michler's hydrol blue and derivatives:



Cyanine dyes:



⁶ K. F. Herzfeld and A. L. Sklar, *Rev. Mod. Phys.* **14**, 294 (1942), Eq. (8) or (10), Eq. (7). For the exchange energy (which enters the equation based on the bond orbital method) we have used the values $\alpha=36$ kcal./mole (arrow No. 2) and $\alpha=49$ kcal./mole (arrow No. 2'). The former is based on the experimentally found resonance energies of a number of aromatic hydrocarbons (compare, e.g., Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), p. 256),

the latter is based on the absorption spectra of aromatic hydrocarbons (compare, e.g., Förster, reference 2). For the overlap energy (which enters the equation based on the molecular orbital method) the value $\beta=20$ kcal./mole (arrow No. 3) was found from resonance energies using the same source as above.

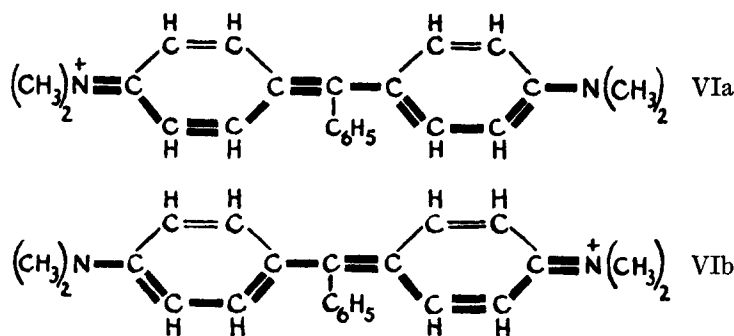
The values of these parameters deduced by introducing the experimental value of λ_1 of the dye considered in Herzfeld and Sklar's equations are as follows: $\alpha=210$ kcal./mole; $\beta=81$ kcal./mole.

^f In order to get satisfactory agreement with experiment it is necessary in some of these and in other cases to make allowance for the influence of neighboring substituting groups (compare reference a). In the case of dye Va, Vb, for example, due to the easily polarized benzene nuclei at both ends of the polymethine chain, the potential energy of the π -electrons increases less rapidly at the ends of the chain than when these benzene nuclei are absent. We take this into account by increasing the length L by a constant amount $(\frac{2}{3})l$ over its value given by Eq. (6) in the absence of these nuclei. We then write $L=(2j+2+\frac{2}{3})l$. More generally, $L=(2j+2+\alpha)l$ and thus,

$$\lambda_1 = 637 [(2j+2+\alpha)^2 / (2j+3)] \text{ (angstrom),}$$

where α is a constant for each series of symmetrical polymethines, depending upon the nature of neighboring substituting groups. α turns out to be within the limits -1 and $+1$ for most series. (Cf. also reference 6, p. 1451 ff.)

Malachite green:



In each case, the molecule is shown as two equivalent limiting structures, labeled a and b, which are formed, one from the other, when the single and double bonds interchange. The resonating portion is indicated by heavy lines. It must be mentioned that in the cases of dyes IV and VI the resonating portion is actually extended over both sides of the benzene nuclei: there is thus a branched π -electron gas. The simplified treatment as an unbranched gas, that is by neglecting the π -electrons of the double bonds indicated by thin lines, leads in such cases to similar results as are obtained by a more refined treatment⁹ based on a branched electron gas model.

We mentioned in Section 2 that a medium which contains dye molecules orientated parallel to one another should in the region of the first band absorb light whose electric vector is parallel to the axes of the molecules more strongly than light whose electric vector is perpendicular to the chain axes. This is actually the case as has been shown by Land and West.¹² These authors have prepared molecular dispersions of cyanine and other dyes in polyvinyl alcohol foils and have orientated the axes of the dye molecules by stretching the foils in a certain direction. They found that the absorption of light whose electric vector was parallel to the direction of strain was by far stronger than the absorption of light whose electric vector was perpendicular to this direction.

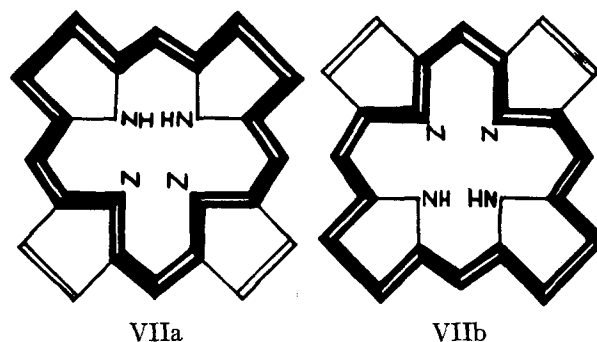
Observations of the fluorescence of polymethine dyes orientated in polyvinyl alcohol lead to conclusions similar to those deduced from the above-mentioned measurements of the dichroism of such dispersions. This has been shown by experiments on a number of dyes which were kindly supplied by Dr. J. D. Kendall (Ilford Ltd., London) and by the CIBA A. G. Basel. It has been found that a foil of cyanine dye molecules (orientated in polyvinyl alcohol as mentioned above) when illuminated with unpolarized ultraviolet light in most cases gives out a strong fluorescence. This fluorescent light is almost completely polarized in such a way that its electric vector is parallel to the direction of strain, i.e., parallel to the axes of the chains of the dye molecules.

This can be readily understood if we consider that the wavelength region of the fluorescent light is in the neighborhood of the first absorption band of the dye investigated (though shifted somewhat toward longer wave-lengths) so that it is on hand to presume that the fluorescence band is simply the reverse electronic transition corresponding to the absorption band. The fluorescence band would then be the result of a jump of an electron from level No. $([N/2]+1)$ back to level No. $N/2$. It is thus not surprising when the polarization of the fluorescence and absorption bands are the same as the experiments mentioned show.

¹² E. H. Land and C. D. West, *Alexander's Colloid Chemistry*, Reinhold, New York, 1946, Vol. VI, p. 160.

B. PORPHYRINES AND SIMILAR COMPOUNDS

In the case of the porphyrines and the phthalocyanines we find conditions similar to those in the cases so far considered. These molecules also may be shown as resonating between two equivalent limiting structures,



by an interchange of the alternating single and double bonds indicated by the heavy lines. These bonds in character between single and double bonds form the closed ring system shown.

For a quantitative treatment we again make the simplifying assumption that the π -electrons can move only in the direction of the closed chain, and that the potential energy is constant along its whole length. This model leads to an explanation of the color of the blood porphyrines.*

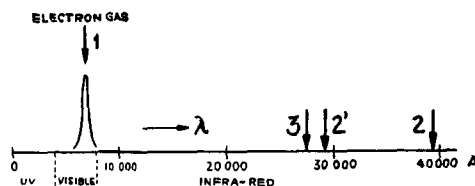


Fig. 5. Cation of the dye IIa, IIb in the case when $j-4=1$. The drawn-out curve is the experimentally found absorption curve. The arrows indicate the positions of the absorption maximum calculated on the basis of the various methods: Arrow No. 1: Electron gas model (according to Eq. (3) or (8)). Arrows No. 2 and 2': bond orbital method. Arrow No. 3: molecular orbital method.

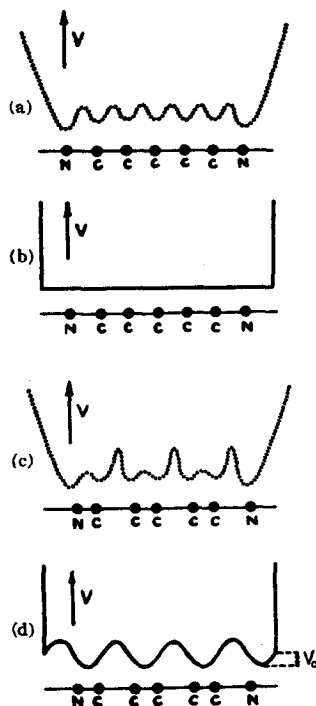
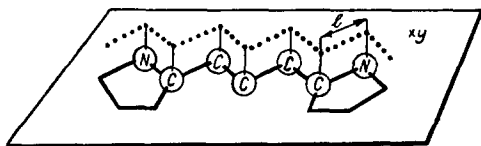
* The mean position of the absorption bands of the porphyrines in the visible spectrum can be interpreted, although their complexity cannot be explained, on the basis of the simple model

C. UNSYMMETRICAL POLYMETHINE DYES, POLYENES, AND RELATED COMPOUNDS

1. More Detailed Discussion of the Free-Electron Gas Model for Symmetrical Polymethines

For the quantitative discussion of the light absorption by symmetrical polymethines, a model was set up on the assumption that the potential energy V of a π -electron is constant along the chain and rises sharply to infinity at the ends (Fig. 7(b)). In the following we will discuss how far we were justified in making this simplification.

We will lead a π -electron along the polymethine chain, e.g., along the zig-zag line indicated in Fig. 6 for the case $j=3$. Its potential energy will vary as shown in Fig. 7(a), i.e., it will alternately decrease and increase as the electron approaches and moves away from



FIGS. 6 and 7a-d. Symmetrical and unsymmetrical polymethines. We follow a π -electron as it moves along the dotted line in Fig. 6, i.e., as it moves along the chain of what can be a symmetrical or unsymmetrical polymethine.

If the chain is that of a *symmetrical* polymethine, the potential energy, V , will alternately increase and decrease along the chain as indicated in Fig. 7(a). For the quantitative treatment of the optical behavior we consider this curve replaced by the lines of Fig. 7(b) (V constant along the chain, and rising to infinity at the ends).

If the chain is that of an *unsymmetrical* polymethine (where the bond distances are alternatively longer and shorter), V will vary along the chain as shown in Fig. 7(c). In the quantitative treatment of the optical behavior we think this curve replaced by the curve indicated by the lines of Fig. 7(d). (V has a sine wave variation of amplitude V_0 along the chain, and rises sharply to infinity at the ends).

Note coincidence of the crests and troughs of the sine curve with the longer and shorter bonds, respectively.

discussed. This can be done with a model which in particular takes into account the π -electrons associated with those double bonds in VIIa, VIIb not indicated heavily, and which further allows for the fact that the H atoms in the center of the ring system are actually equally shared by the four N atoms. For a detailed discussion of this see a paper to be published shortly in *Helv. Chim. Acta*.

the positively charged carbon and nitrogen atoms. At the ends of the polymethine chain the potential energy rises rapidly and forms a barrier to an outward moving electron.

A quantum-mechanical treatment of an electron in such a periodically varying potential¹² has been worked out by Morse.¹³ He showed that here the levels group themselves into bands. Each band contains $(2j+2)$ levels. For the case considered in Fig. 8(a) $j=3$, and the number of levels in each band is 8. (Only the 8 levels of the first band and the lowest two levels of the second are shown in Fig. 8(a).) The grouping of levels into bands is characteristic of a periodically varying potential, and will not be found when the potential is constant (Fig. 8(b)).

The normal state of the π -electron gas corresponds to the arrangement in Fig. 8(a) where the first energy band is half-filled with the electrons. The first absorption band, as well as further bands, are associated with electron jumps from the highest occupied levels to the next and higher levels. In the case of the symmetrical polymethines, which we are considering, this would mean jumps between levels in the central region of the first energy band. The distances between levels situated in the region of the middle of an energy band are very nearly the same as the distances between energy levels in the case of a free-electron gas. Hence we were justified in assuming the simplified model of a free-electron gas when dealing with the light absorption of the symmetrical polymethine dyes.¹

2. Qualitative Discussion of the Quantum-Mechanical Aspect of Unsymmetrical Polymethine Dyes

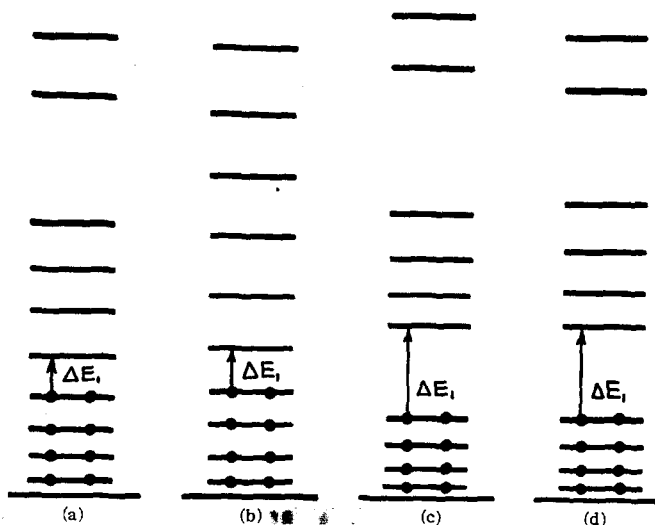
Somewhat more complicated conditions are found in the case of unsymmetrical polymethines and related

¹² The potential along the chain is of course not strictly periodic, because it was not entirely correct to assume that the bonds along the resonating portion of a symmetrical polymethine have all the same double bond character (bond number 1.5) and that consequently all C—C bond distances along the chain are equal. According to a suggestion by L. Pauling (*Proc. Nat. Acad. Sci.* 25, 577 (1939); H. Gilman, *Organic Chemistry* (John Wiley and Sons, Inc., New York, 1938), Chapter 22), we have to consider besides the two equivalent resonating structures with the positive charge on either of the two terminal nitrogen atoms, intermediate structures with the positive charge on some other one of the atoms of the resonating portion. The effect of these intermediate structures is to change somewhat the double bond character and consequently the bond distance of each chain bond, depending on the position of the bond in the chain. Here we shall neglect the influence of these intermediate structures on the bond distances, but it should be pointed out that they should be considered in a more precise treatment.

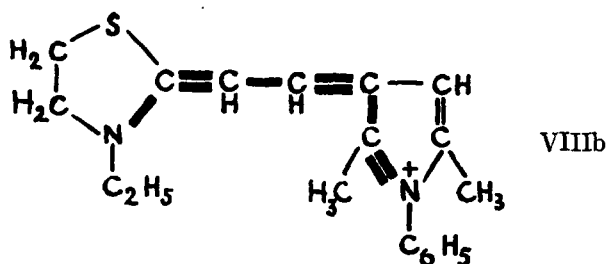
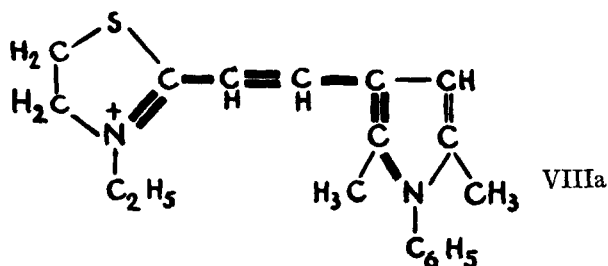
¹³ P. M. Morse, *Phys. Rev.* 35, 1310 (1930).

¹ The same applies in the case of radical-like colored compounds such as Wurster's red, Tschitschibabin hydrocarbon, quinyhydrone, the colored reduction product of π, π' dipirydil, and similar substances. Here too the levels of the first energy band are only partly filled in the normal state and the model of the free-electron gas can be considered to describe the light absorption of these compounds. Values obtained (see reference 9) by this method are indeed also in good agreement with experiment.

FIG. 8(a), (b), (c), (d). Energy levels of an electron in the potential fields shown in Fig. 7(a) to (d). (Fig. 8(a) corresponds to Fig. 7(a), Fig. 8(b) to Fig. 7(b), etc.). Representation is schematic with distances between higher levels shown reduced.



compounds. Let us, for example, consider the dye with the cation:



As was the case for the cations of symmetrical polymethines it is possible to write two limiting structures VIIIa and VIIIb which arise from a changing over of double and single bonds in the chain. Unlike the case of the symmetrical compounds, however, we now find that the two limiting structures are not equal in energy, and they will not make equal contributions to the normal state. For example VIII, Brooker¹¹ found that structure VIIIa contributes more than VIIIb.

In view of this we can no longer expect that as in the case of symmetrical polymethines the chain should consist of like C—C bonds of bond number 1.5. What we find are alternating somewhat longer and somewhat shorter bonds with predominating single and double bond character, respectively. The longer and shorter bonds are there where the single and double bonds are written in the structure which contributes more to the normal state.

We shall see that this alternation of longer and shorter C to C distances brings about a disturbance in the behavior of the π -electron gas along the chain. If we lead a π -electron along the chain in the manner discussed in Section 1 in connection with Fig. 6, we will find that for the unsymmetrical polymethine the potential energy varies not as in Fig. 7(a) but as in Fig. 7(c), i.e., the periodic variation is complete only after passing two carbon atoms as against one when the polymethine is symmetrical.

This difference in length of the period of the potential along the chain, distinguishing the cases of a symmetrical and an unsymmetrical polymethine, causes each of the energy bands found for the symmetrical compound to divide into two separate energy bands for the corresponding unsymmetrical compound. (See Fig. 8(c)).

In the normal state of the unsymmetrical polymethine the first energy band formed, as above, is now completely filled with the available π -electrons, and all the other bands are empty, as illustrated by Fig. 8(c). The first absorption band results, as always, when an electron jumps from the highest occupied to the next free level, i.e., in this case from the highest level of the first energy band to the lowest level of the second energy band. This distance, however, is larger than the distance between the corresponding levels in the case of a free-electron gas (Fig. 8(b)). Hence, we are no longer able to use the free-electron gas as the basis of our approximation.

3. Quantitative Treatment

As seen above, the π -electrons are actually in a potential field whose periodicity is as shown by Fig. 7(c). It is permissible, however, as an approximation, to assume a one-dimensional potential field which has a sine wave variation along the chain, as indicated in Fig. 7(d). The maxima of this sine curve correspond to the middles of the longer C—C bonds; the minima, to the middles of

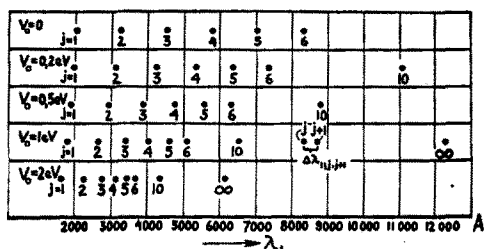


FIG. 9. Dependence of λ_1 on V_0 for various values of j , according to Eq. (11). Note that the increment $\Delta\lambda_{1;j,j+1}$ decreases the more rapidly with increasing values of j , the larger V_0 is.

the shorter. At both ends of the chain the potential energy is assumed to rise to infinity as in the case of the free-electron gas model (Fig. 7(b)). The small effect that this approximation has on the position of the energy levels is shown schematically for the two cases Fig. 7(c) and Fig. 7(d) in Figs. 8(c) and 8(d), respectively. Using the procedure of Morse¹³ we obtain, in good approximation,

$$\Delta E_1 = \frac{\hbar^2}{8mL^2}(N+1) + V_0 \left(1 - \frac{1}{N}\right), \quad (9)$$

where ΔE_1 is the energy difference between the highest energy level of the first energy band and the lowest level of the second energy band. L is (as before) the length of the polymethine chain measured along the zig-zag line of the chain links, N is the number of π -electrons, V_0 is the amplitude of the sine curve used to approximate the variations of the potential energy. V_0 is a measure of the asymmetry of the dye, i.e., of the relative contributions of the two limiting structures. If we put V_0 equal to zero corresponding to the case of a symmetrical polymethine, we find, as would be expected, that Eq. (9) reduces to Eq. (2).

If we substitute (9) in (1) we obtain for the wavelength of the first absorption band⁹

$$\lambda_1 = \frac{1}{(V_0/hc)(1-1/N) + (h/8mc)([N+1]/L^2)}. \quad (10)$$

Further, if we substitute for L and N from (6) and (7), respectively, and introduce the values of the constants h , c , and m , Eq. (10) transforms to

$$\lambda_1 = \frac{1.23 \times 10^4}{19.3[(2j+3)/(2j+2)^2] + V_0[1-1/(2j+2)]}, \quad (11)$$

where λ_1 is in angstrom units, V_0 is in electron volts.

Figure 9 illustrates the dependence according to Eq. (11) of λ_1 on j for various values of V_0 . In the case of dyes typified by the *symmetrical* polymethines ($V_0=0$), we see that the first absorption band is displaced toward higher wave-lengths by a certain amount $\Delta\lambda_{1;j,j+1}$ as we move up step by step (increasing j) in a particular series. $\Delta\lambda_{1;j,j+1}$ can in practice be considered constant for these series. In the case of dyes typified by the *unsymmetrical* polymethines, the amount $\Delta\lambda_{1;j,j+1}$ decreases as we move up a homologous series, i.e., increase j . The larger V_0 (i.e., the larger the contribution of the one limiting structure relative to the other), the more marked is the rate with which $\Delta\lambda_{1;j,j+1}$ decreases.

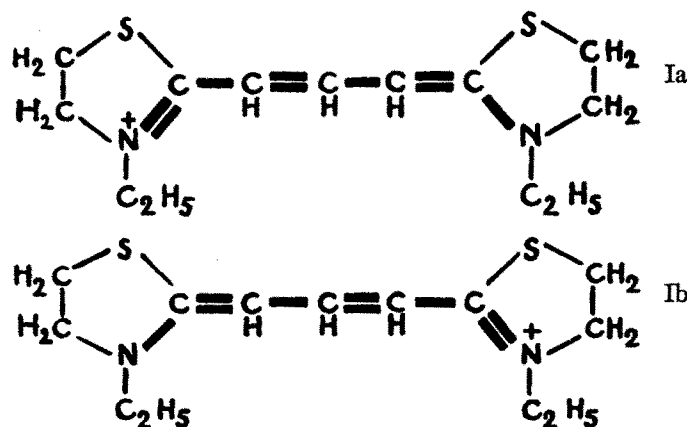
The first absorption band of a dye typified by the unsymmetrical polymethines will thus *always be found at a shorter wave-length* than the band of the corresponding symmetrical compound of the same length of chain. The displacement toward shorter wave-lengths will be the bigger the more the one limiting structure outweighs the other.

4. Comparison with Experiment

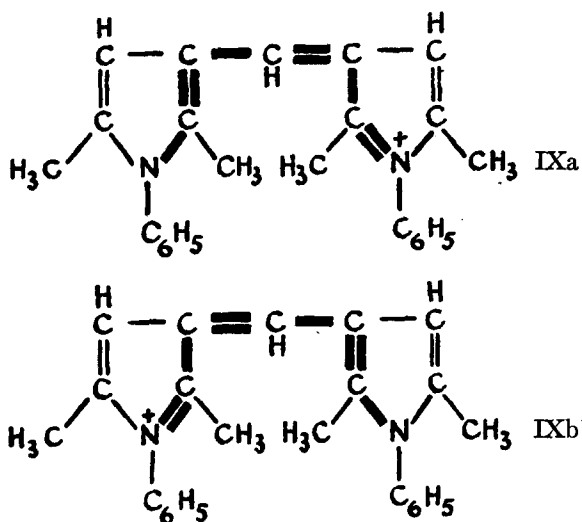
The expected displacement toward shorter wave-lengths in going from a dye of the symmetrical polymethine type to the corresponding unsymmetrical compound has already been observed by Schwarzenbach¹⁴ and Brooker¹¹ for a large number of examples. We shall limit ourselves to a discussion of a few selected cases.

Unsymmetrical Cyanines, Oxanoles, Merocyanines, and Anhydro Bases of Symmetrical Cyanines

As a first example let us again consider the unsymmetrical cyanine VIIIa and VIIIb. This can be regarded as a hybrid of the two dyes

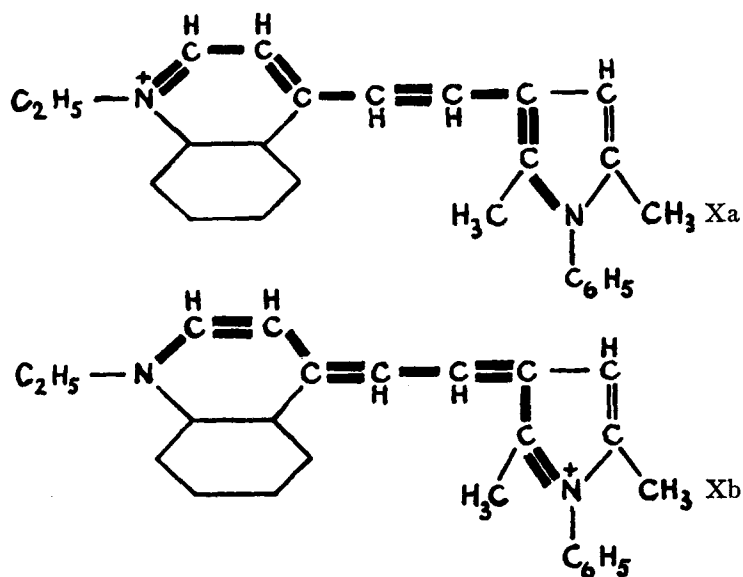


¹⁴ G. Schwarzenbach, *Zeits. f. Elektrochemie* 47, 40 (1941); Schwarzenbach, Lutz, and Felder, *Helv. Chim. Acta* 27, 576 (1944).

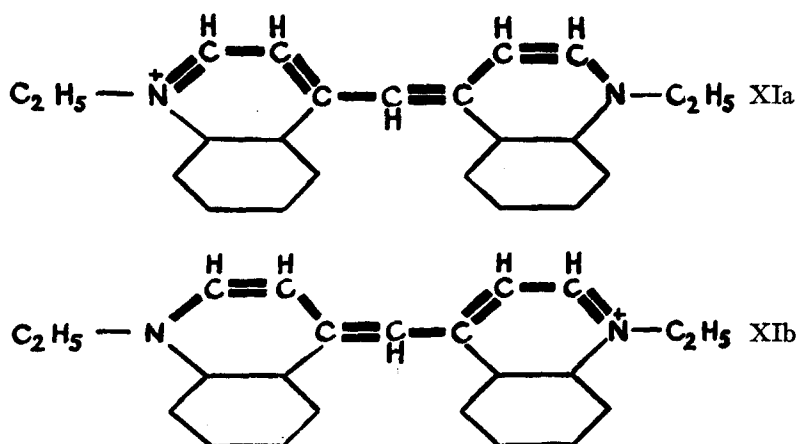


For the two symmetrical dyes ($V_0=0$) we obtain from Eqs. (8) or (11) a theoretical result, $\lambda_{1, \text{theor}}=4530\text{\AA}$. In good agreement with this we have, according to Brooker¹¹ the experimental value $\lambda_{1, \text{exp}}=4450\text{\AA}$ for the dye Ia, Ib; and $\lambda_{1, \text{exp}}=4490\text{\AA}$ for the dye IXa, IXb. For the unsymmetrical dye VIIIa, VIIIb, on the other hand, we find¹¹ $\lambda_{1, \text{exp}}=4170\text{\AA}$, which as expected constitutes a considerable displacement toward shorter wave-lengths. To assess quantitatively the asymmetry of our dye VIIIa, VIIIb we introduce the experimentally found wave-length λ_1 into Eq. (11) and thus find that the amplitude $V_0=0.26 \text{ ev}$.

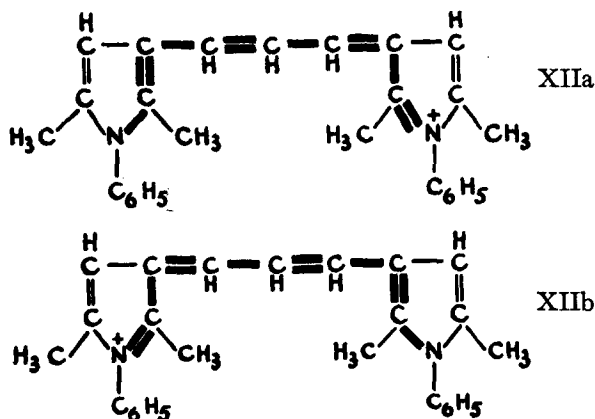
As a further example, we consider the dye



which is the hybrid of the dyes

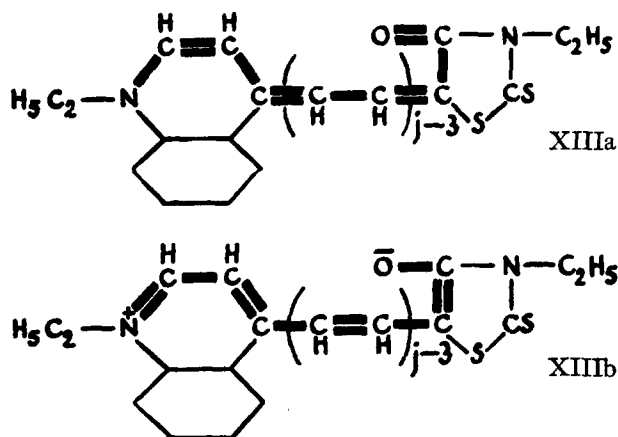


and



For the two symmetrical dyes we obtain from Eq. (8) the value $\lambda_{1, \text{theor}} = 5790\text{\AA}$. This is in satisfactory agreement with the experimental results $\lambda_{1, \text{exp}} = 5910\text{\AA}$ (dye XIIa, XIIb), and $\lambda_{1, \text{exp}} = 5750\text{\AA}$ (dye XIIa, XIIb). For the unsymmetrical cyanine Xa, Xb the largely differing value $\lambda_{1, \text{exp}} = 5020\text{\AA}$ is found.¹¹ Using this result to determine V_0 from Eq. (11), we find $V_0 = 0.37$ ev, i.e., a value larger than that for the dye VIIIA, VIIIB considered above. From this follows, as has already been found by Brooker,¹¹ that in the normal state Xa outweighs Xb by more than VIIIA outweighs VIIIB.

Similar relationships were found by Brooker¹¹ to exist for a large number of further cyanines and merocyanines. Of particular interest is the behavior of the merocyanines of the general structure XIIIa, XIIIb:



In these compounds it is found that the maximum of the absorption band occurs there in the spectrum, where it would be expected on the assumption of a symmetrical structure, and is thus not displaced to shorter wavelengths as in the other cases. This shows¹¹ that the two limiting structures XIIIa and XIIIb take equal shares and that the polymethine chain as in the case of symmetrical cyanines is made up of like C—C bonds of bond number 1.5 (see reference *h*).

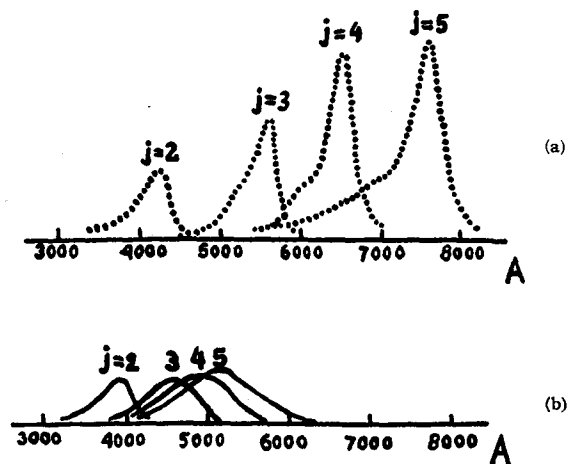
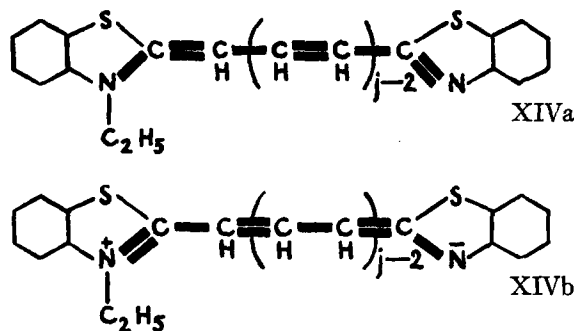


FIG. 10. Absorption curves according to Brooker: (a) symmetrical cyanines Va, Vb (dotted curves), (b) the corresponding anhydro bases XIVa, XIVb (full line curves).

Free Cyanine Bases

It is interesting to compare the exceptional case of the merocyanines XIIIa and XIIIb with the case of the anhydro bases of the symmetrical cyanines; for example, the compounds of general structure XIVa, XIVb:



The limiting structure XIVa (corresponding to XIIIa) clearly contributes much more to the normal state than the dipolar structure XIVb (corresponding to XIIIb).¹ We thus expect a very pronounced decrease in the dis-

TABLE I.

Polyene	j'	$\lambda_1(\text{\AA})$ exper.	$\lambda_1(\text{\AA})$ calculated from Eq. (14) for $V_0 = 2.00$ ev
Butadiene	2	2170	2330
Hexatriene	3	2600	2820
Octatetraene	4	3020	3200
Axerophthene	5	3460	3500
Anhydro Vitamin A	6	3690	3750
β -Carotene	11	4510	4510
Dehydro- β -Carotene	12	4750	4610
Dehydrolycopene	15	5040	4860

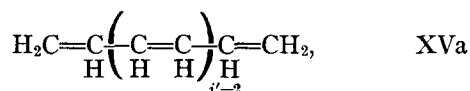
¹ In changing over from structure XIVa to structure XIVb energy must be expended in the separation of the opposing electric charges.

placement $\Delta\lambda_{1;j,j+1}$ as the polymethine chain grows longer, i.e., as we increase j .

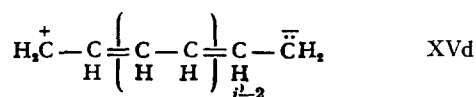
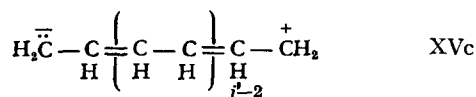
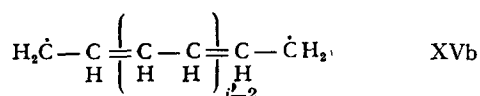
The experimentally determined¹¹ absorption peaks of the bases XIVa, XIVb are shown for the case when $j=2, 3, 4$, and 5 in Fig. 10(b). For the sake of comparison peaks (taken from Brooker¹¹) of the corresponding symmetrical cyanines Va, Vb are shown in Fig. 10(a). The relative position of the maxima of these curves are as expected. By introducing the observed λ_1 -values of the maxima of the absorption curves of the anhydro bases in Eq. (10), we obtain approximately 1 ev for the amplitude V_0 of the potential energy along the chain.^k

Polyenes

Still more marked than in the case of the anhydro bases of the symmetrical cyanines, is the predominance of the reference structure XVa



in the case of the polyenes. This reference structure contributes decidedly more to the normal state than any limiting structure that arises from an interchange of single and double bonds such as, e.g.,



The difference between longer C—C bond distances ("single bonds") and shorter bond distances ("double bonds") is here, then, particularly pronounced. We thus expect a still stronger convergence of the displacement $\Delta\lambda_{1;j,j'+1}$ with increasing j' than in the case of the anhydro bases of the cyanines.

In Table I, column 3, we have collected¹ the experi-

^k In the quantitative treatment we have taken into account the disturbing effect of the two benzene nuclei situated at the end of the polymethine chain, as had to be done in the case of the corresponding symmetrical cyanine Va, Vb (cf., reference f).

¹ The results are for solutions in hexane. They are taken from the following: J. R. Platt and H. B. Klevens, *Rev. Mod. Phys.* **16**, 182 (1944); P. Karrer and E. Jucker, *Carotinoide* (Verlag. Birkhäuser, Basel, 1948). The result for Axerophthen (the hydrocarbon of fundamental importance in Vitamin A) is taken from P. Karrer and J. Benz, *Helv. Chim. Acta.* **31**, 1048 (1948), and is for a solution in ethanol. The result for anhydro-Vitamin A was very kindly communicated to me by Dr. M. Kofler of Firma Hoffman LaRoche Basel.

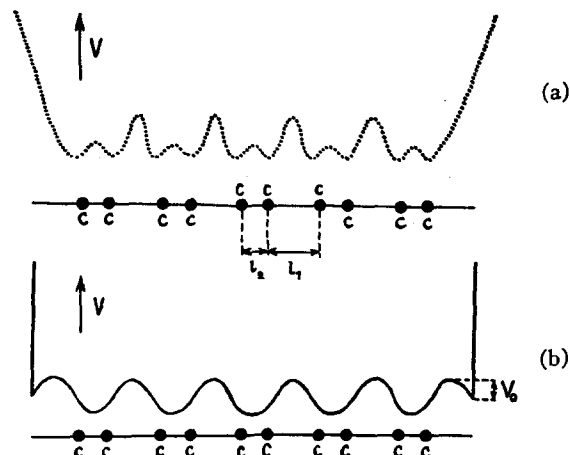


Fig. 11. Potential energy fields of the polyenes. The potential energy of a π -electron as it moves along the zig-zag chain of the polyene is shown in (a). For the quantitative treatment, the curve (a) is considered replaced by the sine curve (b) of the same periodicity.

mentally determined maxima^m of the first absorption bands of a number of polyenes with j' -values from 2 to 15. (j' is the number of conjugated double bonds). These results show the expected relationship. They deviate more than any of the other examples dealt with in this section from the results that would be expected on the basis of a free-electron gas model. In the case of dehydrolycopene ($j'=15$), for example, calculating λ_1 from Eq. (3) which assumes a free π -electron gas we obtain 20300Å, while the experimental result, $\lambda_1=5040\text{Å}$, is four times smaller. To consider the π -electron gas of a polyene as a free-electron gas for a quantitative treatment as has recently been attempted by Bayliss⁸ would thus not seem permissible.

As in the preceding cases we consider the π -electrons placed in a one-dimensional potential field with a sine wave variation. If we designate the C—C bond distance of the "single bond" with l_1 , and the "double bond" distance with l_2 , we find, according to Fig. 11, the following expression for L .ⁿ

$$L = (j' + \frac{1}{2})(l_1 + l_2). \quad (12)$$

From measurements by Schomaker and Pauling¹⁵ on butadiene, it follows that $l_1=1.46 \times 10^{-8}$ cm, $l_2=1.35 \times 10^{-8}$ cm. Further, we have for the number of π -electrons,

$$N = 2j'. \quad (13)$$

^m The first absorption band of the polyenes possesses as a rule three neighboring peaks. These, however, have to be attributed to the same electron jump. The result given for λ_1 in such a case refers to the centroid of the total band. In the instances of the polyenes, here investigated, the wave-length of this centroid coincides with the wave-length of the center one of the three peaks.

ⁿ As previously discussed the points where the potential can be assumed to be infinite are taken one bond distance to either side of the terminal C-atoms of the conjugated chain system.

¹⁵ V. Schomaker and L. Pauling, *J. Am. Chem. Soc.* **61**, 1769 (1939).

Substituting (12) and (13) in (10) and using the above values for l_1 and l_2 , we obtain the expression

$$\lambda_1 = \frac{1.23 \times 10^4}{18.8(2j'+1)^{-1} + V_0(1-(2j')^{-1})}, \quad (14)$$

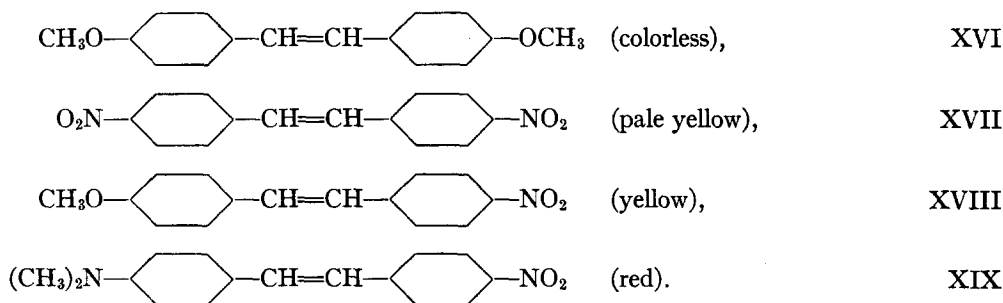
where λ_1 , is in angstrom units, V_0 is in electron volts.

If we put V_0 equal to 2.00 ev, i.e., a value double that proposed for the anhydro bases XIVa, XIVb, we can calculate λ_1 for various values of j' . The results are given in Table I, column 4, and are in satisfactory agreement with the experimental values.

All the same, we can see from the manner in which the calculated and experimental values compare, that V_0 is not absolutely constant, but that it decreases slightly as we increase the length of the chain, i.e., increase j' .^o This tends to show that in the case of a polyene containing a large number of conjugated double bonds, the C—C "double bonds" are less double bond in character, and the "single bonds" correspondingly more double bond in character than those of, say, butadiene. We thus agree with Lennard-Jones,¹⁶ Pauling and Sherman,¹⁷ Coulson,¹⁸ Penney,¹⁹ and Mulliken,²⁰ who also point out that the character of the two kinds of bonds in polyenes becomes more and more alike as the number of conjugated double bonds is increased.

The particular case of the light absorption of the polyenes has been subject to a number of theoretical considerations by various authors. The best results are those of W. Kuhn.²¹ His model replaces the polyene chain by a series of coupled linear oscillators. Each oscillator corresponds to a double bond of the conjugated system. For the wave-length λ_1 of the first absorption maximum he finds the expression:

$$\lambda_1 = \frac{a}{[1 - b \cos(\pi/[j'+1])]^{\frac{1}{2}}}, \quad (15)$$



^o If in each case we calculate V_0 from Eq. (14) using the observed value of λ_1 , we obtain $V_0 = 2.55$ ev, 2.26 ev, 2.06 ev, 1.92 ev, 1.89 ev for $j = 2, 4, 6, 12, 15$, respectively.

¹⁶ J. E. Lennard-Jones, Proc. Roy. Soc. London (A) **158**, 280 (1937).

¹⁷ L. Pauling and J. Sherman, J. Chem. Phys. **1**, 679 (1933).

¹⁸ C. A. Coulson, Proc. Roy. Soc. London (A) **169**, 413 (1939); J. Chem. Phys. **7**, 1069 (1939).

¹⁹ W. S. Penney, Proc. Roy. Soc. London (A) **158**, 306 (1937).

²⁰ R. S. Mulliken, J. Chem. Phys. **7**, 364, 570 (1939).

²¹ W. Kuhn, Helv. Chim. Acta **31**, 1780 (1948).

²² G. N. Lewis and M. Calvin, Chem. Rev. **25**, 237 (1939); G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941), p. 165.

²³ E. Hückel, Zeits. f. Physik **70**, 204 (1931); **76**, 628 (1932); Zeits. f. Elektrochemie **43**, 752 (1937); R. S. Mulliken, J. Chem. Phys. **7**, 364, 570 (1939); Rev. Mod. Phys. **14**, 265 (1942); Th. Förster, Zeits. f. physik. Chemie (B) **47**, 245 (1940).

²⁴ O. N. Witt, Ber. d. D. chem. Ges. **9**, 522 (1876); **21**, 321 (1888).

²⁵ W. Dilthey and R. Wizinger, J. prakt. Chem. (2) **118**, 321 (1928); R. Wizinger, J. prakt. Chem. **157**, 1940 (1941).

where a and b are constants. The values of the two parameters a and b have to be found from the positions of the absorption maxima of *two* representatives of the polyene series. Let us, according to W. Kuhn, put $a = 1.57 \times 10^4 \text{ \AA}$, $b = 0.922$. We obtain from Eq. (15) results for λ_1 , which agree with the experimentally observed values about as well as those obtained from Eq. (14) when the *single* experimentally to be determined parameter, V_0 , is made equal to 2.00 ev.

The model used by W. Kuhn is in part the same as the one used by Lewis and Calvin²² whose quantitative treatment, however, was based on assumptions which do not seem justified. Other authors have used the bond orbital and the molecular orbital methods.²³ These have led to quite satisfactory expressions for the intensity of the absorption band of the polyenes, but the results for the positions of these bands do not agree with experiment.

5. The Classical Color Theory of Witt on the Basis of the Electron Gas Model

According to the theory of Witt²⁴ as extended by Dilthey and Wizinger,²⁵ a dye molecule will, in general, have these three parts:

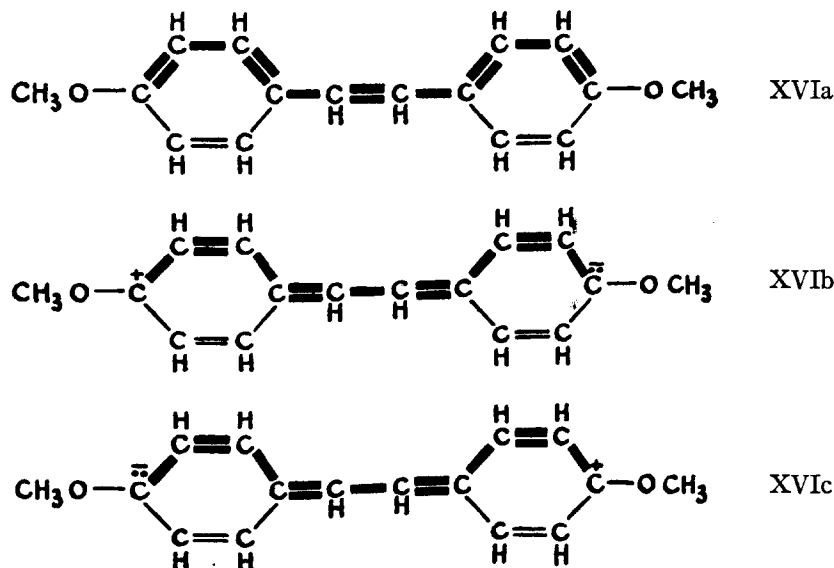
1. A system containing aromatic nuclei, or a chain of conjugated double bonds: the *chromophor*.
2. An electron-donating group like CH_3- , $\text{HO}-$, $\text{H}_2\text{N}-$, $\text{CH}_3\text{O}-$, $\text{R}_2\text{N}-$; the *auxochrom*.
3. An electron-accepting group like $-\text{CN}$, $-\text{NO}$, $-\text{NO}_2$: the *antiauxochrom*.

As typical examples we will consider the following stilbene derivatives:

The first two compounds, of which the first has no anti-auxochrom, and the second no auxochrom, are colorless and pale yellow, respectively. Only the other two compounds, which possess all three of the above parts, have strong yellow and red color, respectively.²⁶

These things can be explained on the basis of the electron gas model in the following manner.^p

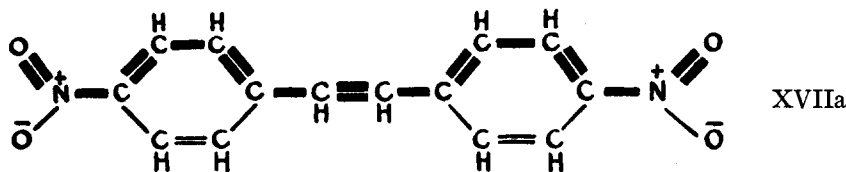
In the case of the colorless compound XVI we have a polyene-like system because here too the reference structure XVIa



contributes more to the normal state than such limiting structures as XVIb, XVIc formed by a changing over of double and single bonds. The first absorption band of this compound will then be expected approximately, where that of the corresponding polyene with five conjugated double bonds is to be found, i.e., at about 3500A

in the ultraviolet. Hence, it is understandable that this compound should be colorless.

Also in the case of the pale yellow compound XVII do we have a polyene-like system. Here, however, we have a chain of seven conjugated double bonds.

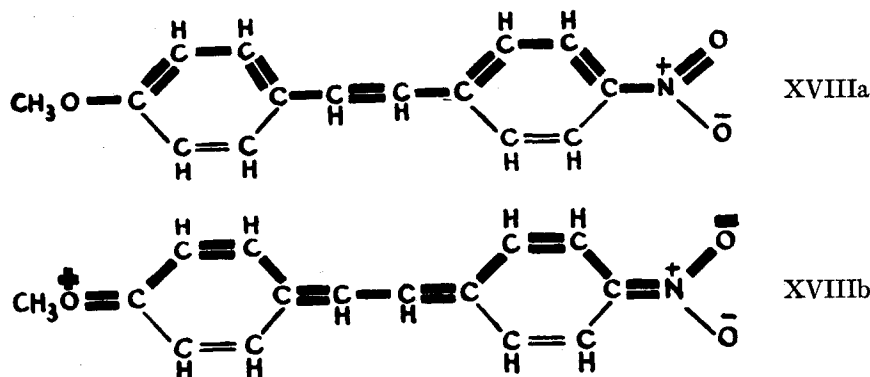


From Table I we can see that the first absorption band is to be expected near 3900A, i.e., just within the visible part of the spectrum and the pale yellow color is explained.

In case of the colored compound XVIII the reference structure XVIIIa is of comparable importance to the dipolar structure XVIIIb which arises from the reference structure by the double and single bonds in the chain changing over. The stability of the limiting structure XVIIIb arises from the fact that the electron donating methoxyl group (the auxochrom) is positively charged, while the electron-accepting nitro group (the antiauxochrom) is negatively charged. This condition is similar to that of the merocyanines XIIIa, XIIIb, and the other polymethine dyes. Thus, the presence of both

auxochrom and antiauxochrom changes the otherwise polyene-like chromophor system into a cyanine-like system. This brings about a shift of the absorption band to longer wave-lengths as has already been discussed. The observed strong color of the compound XVIII is thus very understandable.

^p The fact that dye molecules can as a rule be represented as resonating between two or more valency structures of comparable importance has already been recognized by B. Eistert and F. Arndt [see B. Eistert, *Angew. Chem.* **49**, 33 (1936), *Ber. d. D. Chem. Ges.* **69**, 2395 (1936), *Tautomerie und Mesomerie* (Enke, Stuttgart, 1938)] and independently by C. R. Bury, *J. Am. Chem. Soc.* **57**, 2115 (1935). An investigation of the empirical connection between resonance and color is in particular due to G. Schwarzenbach (reference 14). For qualitative theories of the cause of light absorption by dyes, see Pauling (reference h), Lewis and Calvin (reference 22).



The maximum shift that an auxochrom-antiauxochrom combination can cause would be achieved when the dipolar structure and the reference structure contribute each just 50 percent to the normal state.

This can be brought about by a suitable combination of the electron-donating property of the auxochrom and the electron-accepting tendency of the antiauxochrom, and is just realized in the case of the merocyanines XIIIa, XIIIb. In the case of the stilbene dye XVIII, however, the reference structure XVIIIa is markedly more predominant than the dipolar structure XVIIIb, as the absorption band is still found at far shorter wavelengths than would be expected on the basis of the free-electron gas model.

In the compound XIX the dipolar structure contributes relatively more than that of the dye XVIII just discussed. The dye XIX arises from XVIII when the auxochrom $-\text{OCH}_3$ is replaced by the stronger electron donor $-\text{NH}_2$, which thus enhances the im-

portance of the dipolar structure. It would then be expected that the absorption band of XIX will lie at longer wave-lengths than that of XVIII. This is also the case, as is shown by their red and yellow colors, respectively.

We have seen that a one-dimensional electron gas model leads to a quantitative explanation of the color of simple dye molecules. The success of the model in giving qualitative information about complex cases allows us to hope that a more general theory will be established on this basis which very likely would also be able to explain the color of inorganic complexes such as Prussian blue and molybdenum blue.

Acknowledgments: The author is grateful to Alexander Silberberg for his help in the preparation of the manuscript, to Professor Werner Kuhn for his interest in this work, and to the Ciba-Stiftung and Jacques-Brodbeck-Sandreuter-Stiftung for a grant.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 12 DECEMBER, 1949

The Kinetics of Heterogeneous Atom and Radical Reactions. I. The Recombination of Hydrogen Atoms on Surfaces

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(Received February 28, 1949)

The data on the kinetics of the recombination of hydrogen atoms on various types of surfaces are analyzed in the light of the theory of absolute reaction rates. Expressions are derived for the recombination coefficient and the first-order rate constant, enabling these quantities to be calculated on the basis of postulated mechanisms. It is shown that the experimental activation energies are consistent with estimates using either Hirschfelder's rule or an expression utilizing the experimental "desorption temperature." For the reaction on dry oxides and dry glass good agreement is found assuming that reaction occurs between a gas-phase hydrogen

atom and an adsorbed hydrogen atom, the adsorption being of the van der Waals type at low temperatures and chemisorption at higher ones. The mechanism of surface poisoning by water vapor is shown to be not due to the necessity for desorbing the water molecule: in the high temperature region it is due to an increase in activation energy, the mechanism being $\text{S}-\text{OH}+\text{H}\rightarrow\text{S}-\text{O}+\text{H}_2$; in the low temperature region to a decrease in the number of active centers, the reaction being between a gaseous atom and a van der Waals adsorbed hydrogen atom above the water layer.

INTRODUCTION

THERE have now accumulated sufficient data on heterogeneous atomic and free radical recombinations to permit an analysis of the kinetics and a

discussion of possible reaction mechanisms. The work up to 1941 has been reviewed by L. von Müffling,¹ and an important investigation since then has been carried

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¹ L. von Müffling, in G. M. Schwab's *Handbuch der Katalyse* (Verlag Julius Springer, Berlin, 1943), Vol. VI, p. 94.