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

HANS KUHN
Institute of Physical Chemistry of the University of Basel, Basel, Switzerland
(Received February 21, 1949).

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

Recently it was shown that the position of the absorption maxima of symmetrical polymethines has a close relation to the structure of the molecule. The \( \varepsilon \)-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 \( \varepsilon \)-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

\[
\lambda_1 = \frac{8mc}{h} \left( \frac{1}{N(N+1)} \right),
\]

where \( L \) is the length of the polymethine zig-zag chain, \( N \), the number of \( \varepsilon \)-electrons, \( m \), the mass of the electron, \( c \), the velocity of light, \( h \), Planck's universal constant. Good agreement with experimental results for \( \lambda_1 \) is obtained by the use of this equation.

The problem of porphyrine and phthalocyanine compounds can also be treated with the basis of a free-electron gas model. We treat the \( \varepsilon \)-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 polynynes and related compounds (Carotenes, unsymmetrical cyanines and oxonoles, mercocyanines, 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 \( \varepsilon \)-electrons are considered placed in a one-dimensional potential containing a sine curve periodical.

The wave-length \( \lambda_1 \) is expressed by

\[
\lambda_1 = \frac{1}{N} \left[ 1 + \frac{1}{N(N+1)} \right]^{-1} \cdot \frac{8mc}{h},
\]

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 polynynes 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.

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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 Sklar and Förster 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. 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

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5. Very recently J. R. Platt, *J. Chem. Phys.* 17, 484 (1949), has used a free-electron gas model for treating the absorption of polycycenes 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. Baylis, *J. Chem. Phys.* 16, 287 (1948), has treated the absorption of polyesenes 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.
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 \( \sigma \)-bonds. Each carbon atom of the chain and the two nitrogen atoms at the ends are the center of three such \( \sigma \)-bonds as indicated by the lines in Fig. 1(a).

To form the \( \sigma \)-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 (\( \pi \)-electrons) are attracted by the positively charged carbon and nitrogen atoms, but are repelled by the electrons forming the \( \sigma \)-bonds. Due to the influence of the above electrostatic attractions and repulsions, the \( \pi \)-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 \( \pi \)-electrons of the electron gas, which is thereby brought into a state of excitation.

2. Quantitative Treatment

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

\[
\lambda = \frac{hc}{\Delta E},
\]

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 \( \pi \)-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 \( \pi \)-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 \( \pi \)-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).\(^*\)

\[\text{Fig. 2. According to the model the } \pi \text{electrons can only move along and in the direction of the polymethine zig-zag chain of length } L. \text{ The potential energy along the length } L \text{ is considered constant.}\]

\[\text{\(^*\) 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 \text{ 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).}\]
With these assumptions it is easy to set up and solve the Schrödinger equation for the \( \pi \)-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 \( \pi \)-electrons of the \( \pi \)-electron gas can coexist 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 \( \pi \)-electrons making up the gas (in the case of the dye 1a, 1b, \( N \) 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, \( \Delta E_i \), between level No. \( N/2 \) and the next highest one we obtain, on account of the assumptions made, the relation

\[
\Delta E_i = \frac{(h^2/8mL^2)}{N+1},
\]

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

\[
\lambda = \frac{hc}{\Delta E_i} = \frac{8mcL^2}{h(N+1)}.
\]

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

For the special case of a polyethylene chain where every bond in the chain has a \textit{trans}-configuration (like the chain represented in Figs. 1 and 2) the oscillator strength is given by

\[
f_i = \frac{8\cos^2(\beta/2) \cdot N^2(N+2)^2}{3\pi^2(1+2N+2)}.
\]

where 180° - \( \beta \) is the valency angle between successive chain links. If the polyethylene chain does not exhibit \textit{trans}-configuration at every bond, but if at some, or even all links, the \textit{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

\[
f_{A \rightarrow B} = \frac{8m^2}{3\hbar^2} \Delta E_{A \rightarrow B} \{ |X_{A \rightarrow B}|^2 + |Y_{A \rightarrow B}|^2 + |Z_{A \rightarrow B}|^2 \},
\]

where \( X_{A \rightarrow B} = \int \psi^*_{A} \psi_{B} \cdot x dx \),

\[
Y_{A \rightarrow B} = \int \psi^*_{A} \psi_{B} \cdot y dy,
\]

\[
Z_{A \rightarrow B} = \int \psi^*_{A} \psi_{B} \cdot z dz,
\]

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 \( xy \) coordinate system. The symbol \( dx \) is used to represent the volume element \( dx \cdot dy \cdot dz \) in space, and the integrals are to be taken over the whole space.

Here we are concerned with the transition of a \( \pi \)-electron of the polyethylene 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 \( \Delta E_i \) 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:

\[
\psi_{N/2} = (2/L)^{1/2} \sin((x/L)/N/2),
\]

\[
\psi_{N/2+1} = (2/L)^{1/2} \sin((x/L)(N/2+1)),
\]

where the variable \( x \) 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 \( xy \) coordinate system is now so placed relative to the molecule that the origin is at one end of the chain and the \( x \) axis coincides with the direction of the chain as shown in Fig. 2. Consequently,

\[
x = x \cos(\beta/2).
\]

Formula (4.2) suitably applied to these conditions transforms to

\[
Y_{N/2 \rightarrow N/2+1} = \int_{-L/2}^{L/2} \psi_{N/2} \cdot \psi_{N/2+1} \cdot dx.
\]

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

\[
Y_{N/2 \rightarrow N/2+1} = (2L^3/4) \left( \cos^2(\beta/2) \right) \left( N(N+2)/(N+1)^2 \right).
\]

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 \( f_{N/2 \rightarrow N/2+1} \)

\[
f_{N/2 \rightarrow N/2+1} = \frac{4}{3\pi^2} \cos^2(\beta/2) \left( N(N+2)^2/(N+1)^2 \right).
\]

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 $f_{N, N+1}$ in Eq. (4.10), i.e., the value of $f_1$ is as in Eq. (4).

The value of $f_{A, B}$ 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 oriented parallel to each other 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

$$f_{A, B} = \frac{(8\pi^2\hbar^2)}{R} | \Delta E_{A, B} | X_{A, B}. \tag{4.11}$$

Similarly,

$$f_{A, B} = \frac{(8\pi^2\hbar^2)}{R} | \Delta E_{A, B} | Y_{A, B}. \tag{4.12}$$

$$f_{A, B} = \frac{(8\pi^2\hbar^2)}{R} | \Delta E_{A, B} | Z_{A, B}. \tag{4.13}$$

In the case of a polymethylene chain with an all-trans-configuration, we have from Eq. (4.9) etc., that $X_{N, N+1} \neq 0$; $Y_{N, N+1} = Z_{N, N+1} = 0$. Hence, it follows from Eqs. (4.11), (4.12), and (4.13) that $f_{A, B} \neq 0$. 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 molecule will be most strongly absorbed while light whose electric vector is perpendicular to these axes will not be absorbed at all.

Beyond the first absorption band we expect further though weaker bands at shorter wavelength which are caused by a $\pi$-electron jumping, say, from energy level No. ($\left\lceil N/2 \right\rceil +1$), or to No. ($\left\lfloor N/2 \right\rfloor$), or, say, from level No. $N/2$ to level No. $\left\lceil N/2 \right\rceil +1$, or to No. $\left\lceil N/2 \right\rceil +2$ 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 polymethylene chain is found from the known bond distances; and $N$, the number of $\pi$-electrons of the electron gas, results directly from the structural formula.

In the case of the dye $I_a$, $I_b$ we find for $L$ from Fig. 2,

$$L = 8l, \tag{5}$$

where $l$ is the bond length of the chain elements. $L$ equals 1.39X$10^{-8}$ cm, which according to Pauling\(^9\) 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,

$$\lambda_1 = 4530A \quad \lambda_1 = 1.86 \quad \text{theoretical.}$$

For this dye Brooker\(^4\) obtained the values,

$$\lambda_1 = 4430A \quad f_1 = 1.2 \quad \text{experimental},$$

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

$$\begin{align*}
\text{H}_2\text{C}_2 & \quad \text{Ia} \\
\text{H}_2\text{C}_2 & \quad \text{Ib}
\end{align*}$$

As in the case of the dye $I_a$, $I_b$ we have a polymethylene 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. (3) we find the following expression for $L$, the length of the polymethylene chain (see Fig. 2),

$$L = (2j+2)l, \tag{6}$$

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

$$N = 2j+2. \tag{7}$$


\(^4\) The result given for the wave-length of the absorption maximum refers to the dye $I_a$, $I_b$; 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 $I_a$, $I_b$ only in that the two thiazolium nuclei

in the two thiazolium nuclei

\(^\text{Similar conclusions have been derived on the basis of the molecular and bond orbital methods. See Mulliken, reference 20.}\)

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

\[
\lambda = \frac{(2j+2)^2}{2j+3} \text{ (angstroms).} \tag{8}
\]

In Fig. 4 the dotted lines show the absorption maxima found experimentally by Brooker 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 maxima calculated on the basis of the bond orbital and molecular orbital methods, respectively, by using the equations of Herzfeld and Sklar.

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.

**Oxanole dyes:**

\[
C_6H_5-N-O-C \quad \text{C} \quad O = C - N \quad C_6H_5 \quad \text{IIIa}
\]

**Michler’s hydrol blue and derivatives:**

\[
\begin{align*}
\text{Va} & \quad \text{IVa} \\
\text{Vb} & \quad \text{IVb}
\end{align*}
\]

**Cyanine dyes:**

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 \( \delta = 20 \text{ kcal./mole} \) (arrow No. 3) was found from resonance energies using the same source as above.

The value of these parameters deduced by introducing the experimental value of \( \lambda_1 \) of the dye considered in Herzfeld and Sklar's equations are as follows: \( \alpha = 210 \text{ kcal./mole}, \delta = 31 \text{ kcal./mole} \).

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 polymethylene chain, the potential energy of the \( \pi \)-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 \( (1/\ell) \) over its value given by Eq. (6) in the absence of these nuclei. We then write \( L = (2j+2+1)/\ell \). More generally, \( L = (2j+2+\alpha)/\ell \) and thus:

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

where \( \alpha \) is a constant for each series of symmetrical polymethines, depending upon the nature of neighboring substituting groups. \( \alpha \) 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 treatment 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. 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 polyvinyl ethers 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.

B. PORPHYRINES AND SIMILAR COMPOUNDS

In the case of the porphyrines and the phthalo-cyanines 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.

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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 \( \pi \)-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 \( \pi \)-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 alternate decrease and increase as the electron approaches and moves away from 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 potential has been worked out by Morse. He showed that here the levels group themselves into bands. Each band contains \((2j+1)\) 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 \( \pi \)-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 higher 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.

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

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\[ ^* \] 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 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.

\[ ^{12} \] P. M. Morse, Phys. Rev. 35, 1310 (1930).

\[ ^{1} \] The same applies in the case of radical-like colored compounds such as Wurst’s red, Tschitschibabin hydrocarbon, quinhydrone, the oxidized reduction product of quinhydrone, and similar substances. Here too the levels of the first energy band are 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.
compounds. Let us, for example, consider the dye with the cation:

![Dye structure](image)

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, Brooker 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 \( \pi \)-electron gas along the chain. If we lead a \( \pi \)-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 \( \pi \)-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 \( \pi \)-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
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 Morse\R{14} we obtain, in good approximation,

\begin{equation}
\Delta E_i = \frac{\hbar^2}{8mL^2}(N+1)+V_{0}\left(1-\frac{1}{N}\right),
\end{equation}

where \(\Delta E_i\) 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 \(\pi\)-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 band\R{19}

\begin{equation}
\lambda_1 = \frac{1}{(V_{0}/hc)(1-1/N)+((h/8mc)([N+1]/L^2)^2)}.
\end{equation}

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

\begin{equation}
\lambda_1 = \frac{1.23 \times 10^4}{19.3[(2j+3)/(2j+2)^2]+V_{0}[1-1/(2j+2)^2]}.
\end{equation}

where \(\lambda_1\) is in angstrom units, \(V_{0}\) is in electron volts.

Figure 9 illustrates the dependence according to Eq. (11) of \(\lambda_1\) 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 \(\Delta \lambda_{1;\ldots} a\) as we move up step by step (increasing \(j\)) in a particular series. \(\Delta \lambda_{1;\ldots} a\) can in practice be considered constant for these series. In the case of dyes typified by the unsymmetrical polymethines, the amount \(\Delta \lambda_{1;\ldots} a\) 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 \(\Delta \lambda_{1;\ldots} a\) 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 Schwarzenbach\R{14} and Brooker\R{14} 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 VIIa and VIIb. This can be regarded as a hybrid of the two dyes

---

For the two symmetrical dyes \( V_0 = 0 \) we obtain from Eqs. (8) or (11) a theoretical result, \( \lambda_{\text{theor}} = 4530 \text{A} \). In good agreement with this we have, according to Brooker\(^{11}\) the experimental value \( \lambda_{\text{exp}} = 4450 \text{A} \) for the dye IXa, IXb; and \( \lambda_{\text{exp}} = 4490 \text{A} \) for the dye IXa, IXb. For the unsymmetrical dye VIIIa, VIIIb, on the other hand, we find\(^{11}\) \( \lambda_{\text{exp}} = 4170 \text{A} \), 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 \( \lambda_i \) 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 $\lambda_{\text{theor}} = 5790 \text{Å}$. This is in satisfactory agreement with the experimental results $\lambda_{\text{exp}} = 5910 \text{Å}$ (dye XIA, XIB), and $\lambda_{\text{exp}} = 5750 \text{Å}$ (dye XIIA, XIIIB). For the unsymmetrical cyanine Xa, Xb the largely differing value $\lambda_{\text{exp}} = 5020 \text{Å}$ is found.\(^{11}\) Using this result to determine $V_a$ from Eq. (11), we find $V_a = 0.37 \text{ eV}$, 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 Brooker\(^{11}\) 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 shows\(^{11}\) that the two limiting structures XIIIa and XIIIb take equal shares and that the polymethylene 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.**

<table>
<thead>
<tr>
<th>Polyene</th>
<th>$\lambda_{\text{A}}$</th>
<th>$\lambda_{\text{A}}$ calculated from Eq. (14) for $V_a = 2.00 \text{ eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene</td>
<td>2</td>
<td>2170</td>
</tr>
<tr>
<td>Hexatriene</td>
<td>3</td>
<td>2000</td>
</tr>
<tr>
<td>Octatetraene</td>
<td>4</td>
<td>3020</td>
</tr>
<tr>
<td>Azoraphene</td>
<td>5</td>
<td>3460</td>
</tr>
<tr>
<td>Anhydro Vitamin A</td>
<td>6</td>
<td>3690</td>
</tr>
<tr>
<td>(\beta)-Carotene</td>
<td>11</td>
<td>4310</td>
</tr>
<tr>
<td>Dehydro-(\beta)-Carotene</td>
<td>12</td>
<td>4750</td>
</tr>
<tr>
<td>Dehydrolycopene</td>
<td>15</td>
<td>5040</td>
</tr>
</tbody>
</table>

\(^{1}\)In changing over from structure XIVa to structure XIVb energy must be expended in the separation of the opposing electric charges.
placement $\Delta \lambda_{j-1, j+1}$ as the polymethylene chain grows longer, i.e., as we increase $j$.

The experimentally determined 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 Brookil) 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 $\lambda_1$-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.\(^1\)

**Polyenes**

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

$$
H_2C\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}=\overset{\text{--}}{\text{CH}_3},
$$

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.,

$$
H_2C\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}=\overset{\text{--}}{\text{C}}H_3,
$$

XVb

and

$$
H_2C\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}\overset{\text{--}}{\text{C}}=\overset{\text{--}}{\text{C}}H_3,
$$

XVc

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 $\Delta \lambda_{j-1, j+1}$ with increasing $j$ in the case of the anhydro bases of the cyanines.

In Table 3, column 3, we have collected the experimentally determined maxima\(^2\) 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 $\lambda_1$ from Eq. (3) which assumes a free $\pi$-electron gas we obtain 20300A, while the experimental result, $\lambda_1 = 5040A$, is four times smaller. To consider the $\pi$-electron gas of a polyene as a free-electron gas for a quantitative treatment as has recently been attempted by Bayliss\(^4\) would thus not seem permissible.

As in the preceding cases we consider the $\pi$-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 $L$.

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

From measurements by Schomaker and Pauling\(^3\) 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 $\pi$-electrons,

$$
N = 2j'.
$$

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 $\lambda_1$ 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.

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.

\(^1\) V. Schomaker and L. Pauling, J. Am. Chem. Soc. 61, 1769 (1939).

\(^2\) P. Karrer and E. Jucker, Carotinoides (Verlag Birkhäuser, Basel, 1948). The result for Averophen (the hydrocarboxyl of fundamental importance in Vitamin A) is taken from P. Karrer and J. Bensa, 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. Koferl of Firma Hofman LaRoche Basel.
Substituting (12) and (13) in (10) and using the above values for $l_1$ and $l_4$, we obtain the expression
\[
\lambda_1 = \frac{1.23 \times 10^4}{18.8 (2j'+1) + V_0 (1 - (2j'-1)^{-1})},
\]
where $\lambda_1$, 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 $\lambda_1$ 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 $j'$.* 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 $\lambda_1$ of the first absorption maximum he finds the expression:
\[
\lambda_1 = \frac{a}{\left[1 - b \cos(\pi/2j'+1)\right]^{1/2}}
\]
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 $a = 1.57 \times 10^4 A$, $b = 0.922$. We obtain from Eq. (15) results for $\lambda_1$, 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 for 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$_2$–, HO–, H$_2$N–, CH$_3$O–, R$_n$N–; the auxochrome.
3. An electron-accepting group like –CN, –NO, –NO$_2$: the antiauxochrome.

As typical examples we will consider the following stilbene derivatives:

\[
\begin{align*}
&\text{CH}_3\text{O--} \quad \text{CH=CH--} \quad \text{OCH}_3 \quad (\text{colorless}), \\
&\text{O} \quad \text{N} \quad \text{CH=CH--} \quad \text{NO}_2 \quad (\text{pale yellow}), \\
&\text{CH}_3\text{O--} \quad \text{CH=CH--} \quad \text{NO}_2 \quad (\text{yellow}), \\
&(\text{CH}_3)_2\text{N--} \quad \text{CH=CH--} \quad \text{NO}_2 \quad (\text{red}).
\end{align*}
\]

* If in each case we calculate $V_0$ from Eq. (14) using the observed value of $\lambda_1$, 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.
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).
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.\footnote{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, 2295 (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 b), Lewis and Calvin (reference 22).}

These things can be explained on the basis of the electron gas model in the following manner.\footnote{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 XVIIb, 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.
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 —OCH₃ is replaced by the stronger electron donator —NH₂, which thus enhances the importance 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.