

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

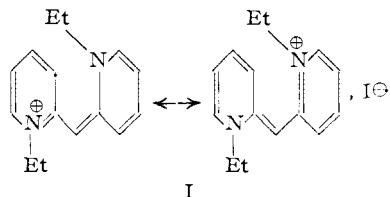
Electronic Spectra of Pyridocyanine Dyes with Assignments of Transitions¹BY GERALD S. LEVINSON, WILLIAM T. SIMPSON AND WALDO CURTIS²

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The electronic spectra of 2,2'- and 4,4'-pyridocyanine dyes have been investigated. There are absorptions at *ca.* 490, 360 and 260 $m\mu$ for both the 2,2'- and 4,4'-, which are assigned, respectively, as long axis, short axis and (probably) long axis polarized. The dye 1,1'-diethyl-2,2'-pyridocyanine iodide has been found to exist as the unsymmetrical isomer, and at low temperatures to aggregate into an ion pair and a dimer of ion pairs. The dimer has a triplet-singlet emission with peaks at 600 and 650 $m\mu$.

Introduction

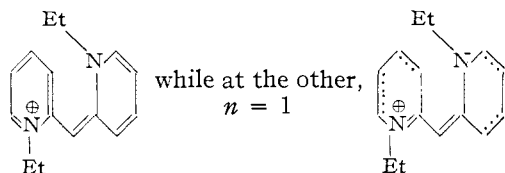
When this research was begun, the aim was mainly to obtain the positions and intensities of the electronic transitions in the visible and quartz ultraviolet for the dye 1,1'-diethyl-2,2'-pyridocyanine iodide³ (called dye I). (The Kekulé resonance in



the pyridinium rings is not shown.) One reason for studying this dye was that it is but a single step up in complexity as compared with the family of straight chain dyes



for which the wave length of absorption varies linearly with chain length. The step is significant because it no longer becomes possible to define a chain length. At one extreme, the effective chain length corresponds to $n = 5$



This means that empirical correlations between chain length and color are ruled out; some sort of interpretation guided by quantum theory is called for.

In the course of the investigation of dye I, it was found that certain chemical effects had to be understood before the spectroscopic investigation could be considered reasonably complete.⁴

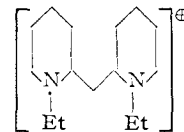
In the first place, it was found necessary to decide which of the plausible isomers was in preponderance, the one given above or the symmetrical one.

(1) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-375. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Eastman Kodak Pre-doctoral Fellow, 1950-1951.

(3) The dye was synthesized by the method of L. G. S. Brooker and G. H. Keyes, *THIS JOURNAL*, **57**, 2490 (1935).

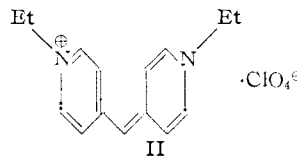
(4) In this connection, see S. E. Sheppard, *Revs. Mod. Phys.*, **14**, 303 (1942).



Second, it was found that aggregation, while not observed in dilute methanol solutions at room temperature, becomes very marked at liquid-nitrogen temperatures.

Isomerism.⁵—In the absorption spectrum of dye I there are strong peaks at 486 and 357 $m\mu$ (Fig. 1). It is believed these represent transitions to the first two singlet excited states. The polarization of the second transition (357 band) relative to the first was determined using the method of polarized fluorescence, and was found to be positive, though less so than the first transition. If the symmetrical isomer predominates, as was anticipated from a superficial consideration of steric hindrance, this positive polarization can only mean that the directions of oscillation of charge for the two transitions are intrinsically the same, and in all probability along the long axis. However, the theoretical treatments all favor having the first two transitions, respectively, long axis and short axis polarized.

Turning to the closely related substance 1,1'-diethyl-4,4'-pyridocyanine perchlorate⁶ (dye II)



we again find two peaks in the absorption spectrum, one at 505 $m\mu$ and one at 372 $m\mu$ (Fig. 1), corresponding to those found for dye I at 486 and 357. This time the peak at 372 is markedly weaker than for dye I. There is only one isomer possible for dye II: it has to be symmetric. Although we tried and were unable to measure the polarization by fluorescence experiments, still the natural conclusion is that the 372 band of dye II represents a short axis polarized transition, because of its low intensity compared to the corresponding band of dye I. The band in dye I may be considered to have gained its strength (and positive polarization) through borrowing from the strong first band. This borrowing

(5) Work on isomerism in cyanine dyes has been reported by C. Scheibe, *Z. Angew. Chem.*, **52**, 631 (1939); *Z. Elektrochem.*, **47**, 73 (1941); L. G. S. Brooker, F. L. White, R. H. Spague, S. G. Dent, Jr., and G. Van Zandt, *Chem. Revs.*, **41**, 325 (1947), and L. G. S. Brooker, F. L. White, D. W. Heseltine, G. H. Keyes, S. G. Dent, Jr., and V. Van Lare, *J. Phot. Sci.*, **1**, 173 (1953).

(6) We are indebted to Dr. L. G. S. Brooker of the Eastman Kodak Co. for sending us this dye.

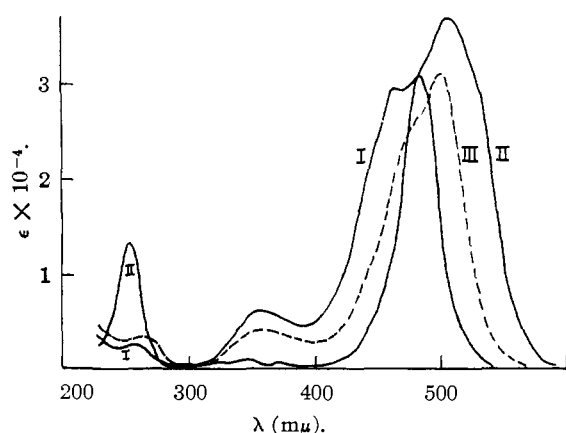
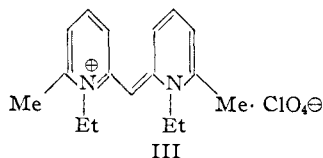


Fig. 1.—Room temperature absorptions of 2,2'-pyridocyanine (dye I), 4,4'-pyridocyanine (dye II), and crowded 2,2'-pyridocyanine (dye III) in methyl alcohol.

could only be induced by departure from symmetry. On this basis it is concluded that dye I exists as the unsymmetrical isomer.

The polarized fluorescence measurements on dye I, interpreted in conformity with our findings on aggregation at low temperatures (see below) might be explained another way, by assuming that the predominant monomeric species at low temperatures is an ion pair consisting of the symmetrical dye cation bonded unsymmetrically to the anion. The lack of symmetry would be considered as producing the borrowing referred to above. If this were the case, however, the room temperature absorptions in a region of concentration for which Beer's law is obeyed would show the 357 band as weak (as for dye II), and the band would strengthen markedly as ion pair formation develops on cooling. Effects of this nature were sought but not found. Thus the evidence favors our first conclusion, that for dye I the unsymmetrical isomer predominates.

In attempting to test this conclusion directly, we synthesized dyes designed to be forced sterically into the symmetrical configuration. The best example found was 1,1'-diethyl-6,6'-dimethyl-2,2'-pyridocyanine perchlorate, called dye III.⁷



The spectrum of this substance (Fig. 1) shows a considerable reduction in the height and area of the 357 band as compared with the corresponding band of dye I (the curve in Fig. 1 is dotted because the values on the ordinate are not quantitative. Instead, the height is made equal to that for dye I in the 486 region.). The reduction in the relative

(7) The method of reference 3 was used in the synthesis. The condensation was carried out between 2,6-lutidinium ethiodide and 2-methyl-6-iodopyridinium ethiodide in propyl alcohol with 2.1 moles of triethylamine. The iodopyridinium salt was prepared by heating 1 mole of 2-methyl-6-bromopyridine with 4 moles of ethyl iodide in a sealed tube at 100° for three days. The 2-methyl-6-bromopyridine was prepared by Mr. F. Bell under the supervision of Dr. A. G. Anderson.

intensity of this band is interpreted as indicating that an appreciable fraction of the dye molecules is now in the symmetrical configuration. Notwithstanding, polarized fluorescence experiments on dye III showed that the 357 region is still positive. Even if the dye were all present as the symmetrical isomer, ion pair formation at the temperatures used for the polarized fluorescence measurements would have to be reckoned with as possibly influencing the polarization direction.

The reason why the unsymmetrical isomer of dye I is the more stable is probably that for this isomer the local permanent dipoles in the pyridine rings are lined up more favorably, as has been suggested to us by Professor J. R. Platt.

Aggregation.—Efforts to determine a unique emission spectrum of dye I were at first unsatisfactory, and the analysis of the difficulties led finally to the discovery that there were two separate species present, each with its own absorption and emission spectrum.

Absorption spectra at two initial concentrations of dye I at 77°K in a rigid glass⁸ are shown in Fig. 2.

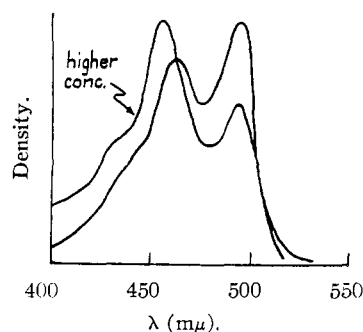


Fig. 2.—Absorption spectra at 77°K. of dye I taken at two different initial concentrations. Solvent is isopropyl alcohol-isopentane mixture.

The dependence on concentration shows aggregation. If pairs of curves such as those in Fig. 2 are worked up by scaling the ordinates to be the same at 495 $m\mu$ and subtracting, then a spectrum is obtained substantially like the one in Fig. 3 marked as belonging to species Y, where Y is the species which grows as the concentration is increased. This process is based on the assumption that Y does not absorb appreciably at 495, and the fact that pairs of curves corresponding to various concentrations all give the same curve for Y is taken as effectively proving the assumption. A curve for a second species, X, was not so easily found because there is no useful wave length where X does not absorb. However, the ratio of optical densities at 495 and 455 was plotted against the optical density at 495 as abscissa for various concentrations. The resulting curve was extrapolated to the value of the abscissa equal to zero, to determine the value of the ratio of infinite dilution. This gave the ratio of densities at 495 and 455 for the X component of the mixture. From this information together with the derived spectrum of Y, and using the absorption obtained with the least concentration of dye, a curve for pure X was constructed (Fig. 3).

The degree of polymerization could unequivocally be obtained from a typical law of mass action plot⁹ if it were not for the fact that the solutions be-

(8) All rigid solutions used were made by dissolving the dye in a mixture of 3 parts of isopropyl alcohol and 7 parts of isopentane, by volume.

(9) The concentration of X can be determined from the composite spectrum at 495 $m\mu$ and the concentration of Y by subtraction. Beer's law is, of course, assumed for the components.

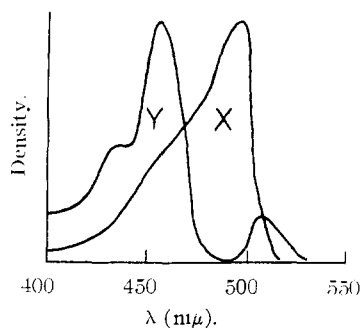
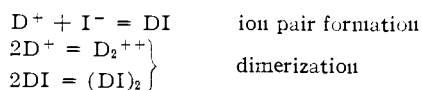


Fig. 3.—Absorptions derived from curves like those in Fig. 2, for species X and Y.

come rigid on approaching (but prior to) 77°K., where the absorption measurements are made. The actual result of a mass action study was to give an order of polymerization equal to the integer two within experimental error. The closeness to two is taken as indicating that the equilibria turned out to be all measured at the same effective temperature. The possible aggregation processes of order two are



where D^+ refers to the dye cation.

A comparison of the spectrum of Y with that for X leads to the conclusion that the process is one of dimerization rather than ion-pair formation, because of the symmetrical splitting into two separate energy levels (Y spectrum) on either side of the monomer first-excited level (X spectrum). The quantum mechanical treatment of this effect is given in the Appendix along with some further consideration of the experimental results.

The experiments have all been repeated using the dye perchlorate instead of the iodide. The half dimerization point is reached at a much lower concentration, and the split between the peaks (Y) is noticeably greater than for the iodide. This means that the anion must be involved in the dimer (and also rules out enhanced singlet-triplet absorption as an explanation of the first absorption). Moreover, since the order of polymerization is only two, the monomeric species (X) has to be the ion pair.

The driving force for the dimerization reaction is essentially the difference between two heats of ion-pair formation. The greater stability of the dimer is to be attributed to the fact that the resonance in the dye cation puts approximately one-half of a positive charge on each ring. By bringing two dye cations together to form a sandwich (see Fig. 7) an arrangement is obtained which allows each fully charged iodide anion to be adjacent to two half charges (one half for each dye cation). In contrast, for the monomeric ion pair the negative iodide can only be adjacent to a full positive charge by polarizing the dye, at the expense of the resonance stabilization of the ground state.

Emission Spectra.¹⁰—The pattern of the emission spectra is simple in its broad outlines, once

(10) The spectra were obtained either photoelectrically or photographically. The exciting light was suitably modified using combina-

the existence of two species is realized. The dimer emits predominantly if not completely in the red, with peaks at *ca.* 600 and 650 $m\mu$. The monomer emits mainly normal fluorescence in the green, following the mirror image rule. Thus changing the excitation wave length from a region of comparatively high monomer absorption (470 $m\mu$) to one of comparatively high dimer absorption (435 $m\mu$) produces an increase in emission in the red at the expense of the emission in the green. The same effect is observed if the wave length of excitation is kept constant but samples having different dye concentrations are examined (Fig. 4). The red emission is greater for a more concentrated sample because the proportion of dimer is greater.

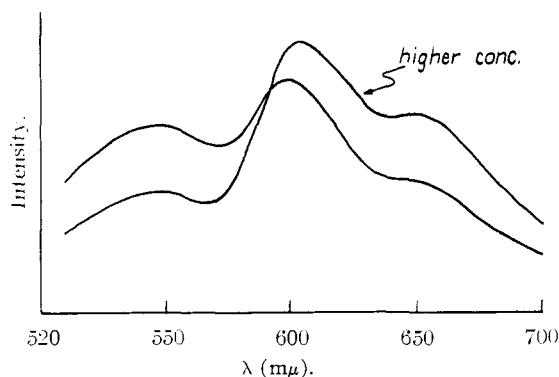


Fig. 4.—Emission spectra of dye I taken at two different initial concentrations (in isopropyl alcohol-isopentane glass at 77°K.).

Using a high concentration and keeping the excitation as much as possible in the dimer absorption region gives an emission spectrum which is approximately that for the pure dimer. From experiments of this type it was found that dimer emission in the green is at least an order of magnitude weaker than in the red.

To see whether or not there is any red emission from the monomer, measurements were carried out using very dilute solutions. However, the results are inconclusive because it was not found possible to lower the dimer concentration by dilution and still have a sufficient monomer concentration to give an emission with measurable intensity. There was little or no change in shape of the red emission on dilution, so if the monomer emits, it is with virtually the same band shape as that of the dimer. This would not be considered unlikely. The reason is that the shape of the red emission in simultaneous emission experiments is the same as that seen through a phosphoroscope (Fig. 5) so the emission is considered to be triplet-singlet. The dimer triplet-singlet emission spectrum would be expected to be virtually identical with the monomer spectrum because the resonance force coupling disappears after the inter-system crossing into the triplet state.

Examination of the emission curves for dilute solutions allows us to say that if the monomer positions of Corning filters, or a monochromator. Photoelectric detection was with a Photovolt Multiplier Photometer unit adapted to monitor the output of an infrared sensitive photomultiplier tube (Dumont Type K 1292). All spectra were recorded at 77°K. in the isopropyl alcohol, isopentane glass described above.

phoresces at all, the intensity is no more than about one-third the fluorescent intensity. Thus we see that the inter-system crossing probability is considerably higher for the dimer. The crossing rate is governed by the competition between the intrinsic crossing process and fluorescent emission. Fluorescent emission for the dimer would be from the low energy state (510 band in Fig. 3), which is only weakly absorbing. The corresponding smallness in spontaneous emission probability coupled with the closeness of this state to the triplet state may account for the greater probability of crossing and hence phosphorescent emission.¹¹

The emission in the red is always polarized negatively. If the polarization direction were simply determined by mixing with singlet states of the dye cation it could be inferred that the negative polarization would have to involve an out-of-plane singlet-singlet transition. The alternative is ruled out because the in-plane directions (\parallel and \perp) are not strongly differentiated by the spin-orbit coupling, so the mixing would be with the closest levels, resulting in long-axis (hence positive) polarization. It was suggested by Dr. D. S. McClure that the existence of neighboring iodide ions might complicate this interpretation. What could be involved, say, is mixing with a charge-transfer transition polarized in the direction of a line joining iodide to nitrogen (see Fig. 7).

Energies, Intensities and Assignments.—The spectra of the 2,2'- and 4,4'-pyridocyanines in the visible and quartz ultraviolet are much alike (Fig. 1). In addition to the bands around 490 and 360, there is a band at about 260 $m\mu$. Absorption is stronger in the 360 region than in the 260 region for the 2,2'-dye, though for the 4,4'-dye this order of intensity is reversed. The transition moment lengths are given in Table I together with the positions of the long wave length peaks.

TABLE I
TRANSITION MOMENT LENGTHS^a AND LOCATION OF FIRST PEAKS FOR THE 2,2'- AND 4,4'-PYRIDOCYANINES^b

| 2,2' (Dye I) | | 4,4' (Dye II) | |
|-----------------|------------------|-----------------|------------------|
| $\lambda(m\mu)$ | $q(\text{\AA.})$ | $\lambda(m\mu)$ | $q(\text{\AA.})$ |
| 486 | 1.40 | 505 | 1.50 |
| 357 | 0.66 | 372 | 0.27 |
| 260 | 0.35 | 254 | 0.72 |

^a Calculated from the areas using the formula $q^2 = -1.09 \times 10^{-18} \int \epsilon d \log \lambda$ (here q is in cm. and ϵ is the molar extinction coefficient). ^b The intensities for the 4,4'-dye were obtained by Mr. R. Lund.

The emission spectrum of dye I is typical in that there is fluorescence from the lowest energy excited singlet, represented by the 486 band in absorption; and, also, phosphorescence at longer wave lengths. The 0,0 value for the singlet-singlet transition is estimated to be $1.9_8 \times 10^4 \text{ cm.}^{-1}$ and for the singlet-triplet, $1.7_2 \times 10^4 \text{ cm.}^{-1}$.

The first singlet-singlet transition is assigned as long axis polarized from the observation that the transition moment length depends directly on the physical chain lengths of members of vinylogous series of cyanine dyes. The ion of dye II has a

(11) We have learned from Professor M. Kasha that phosphorescence seems to predominate over fluorescence in a variety of cases where the concentration or other conditions are such as to favor aggregation.

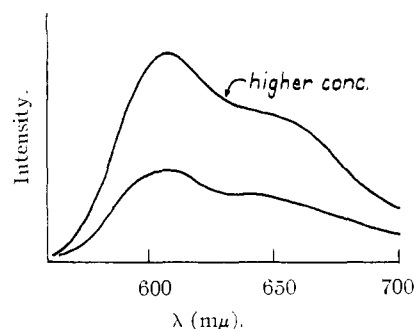


Fig. 5.—Phosphorescence emission spectra of dye I at two different initial concentrations (in isopropyl alcohol-isopentane glass at 77°K.).

plane of symmetry perpendicular to the plane of the molecule, so the wave functions and in-plane transitions may be described by reference to the following simple character table

| | E | σ |
|-------------------|---|----------|
| A (\perp) | 1 | 1 |
| B (\parallel) | 1 | -1 |

The ground state is almost certainly totally symmetric so the long wave length transition described as "long axis" (and denoted as \parallel) is assigned as $A \rightarrow B$. Because of the markedly lower intensity, which increases after an unsymmetrical perturbation, the next transition is presumed to be $A \rightarrow A(\perp)$. The transition at 254 $m\mu$ is tentatively assigned as $A \rightarrow B$ because of the pattern of alternating intensity behavior for dyes II and III as compared with dye I (Fig. 1).

The point of view adopted with regard to dye I is that there is a close correspondence between its levels and the levels for dye II, and that as explained above the intensity changes are caused by the asymmetry (in the placement of the nitrogen atoms) considered as a perturbation. Thus the increase in the 357 region for dye I is attributed to mixing with the adjacent $A \rightarrow B$ transition at 486 and (with the above assignment) to a lesser extent with the one at 260. It is consistent with this interpretation that these essentially long axis transitions are reduced in intensity as compared to those in the symmetrical dye II. In fact, there seems to be something very close to conservation of intensity operative. The extra intensity in the 357 region for dye I is taken as $0.66^2 - 0.27^2$, the difference between the squares of the transition moment lengths. It is 0.36 \AA.^2 . This is balanced by the extra intensity in the 505 region for dye II, $1.50^2 - 1.40^2$ or 0.31 \AA.^2 .

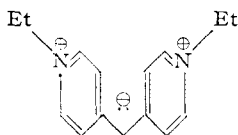
Theoretical Interpretation.—Referring to the structural formula for the straight chain dyes in the Introduction, the 4,4'-dye has a chain length characterized by $n = 3$. Consistent with this it absorbs at around 500 $m\mu$, in accord with our expectation based on counting 100 $m\mu$ for each pair of π electrons in conjugation. The second transition for a simple straight chain dye with $n = 3$ comes, however, at 305 $m\mu$, compared with 372 $m\mu$ for the pyridocyanine. As noted in the Introduction, for the 2,2'-dye a chain length cannot be unambiguously selected, but considering the placement of

the nitrogen atoms one might expect an effective chain length shorter than for the 4,4'-dye.

The extremely close matching of the transition energies for dyes I and II comes, therefore, as a surprise. It is an even greater surprise that the intensities of the first transitions for the two dyes are so similar (the ratio is 0.87).

Thus the nitrogens are not very important in determining the spectrum. This result makes it seem reasonable to base our further theoretical consideration of the pyridocyanines on models in which the nitrogens are treated like carbons. At this point the avenues open for interpretation are a molecular orbital approach or an approach using valence bond structures. The most fruitful procedure for dealing with cyanine dye spectra appears to be to abandon the idea of finding a uniquely simple and effective scheme, and to use the various contemporary approximate theories in their full variety.¹² Such a procedure has been used throughout the course of the present research, but it would be impractical to go into too much detail here. Nonetheless, we shall go on to consider the pyridocyanines according to first an orbital and then a structures approach.

According to the Hückel theory, virtually the same pattern of orbital energies is obtained as for benzene; though there is an extra non-bonding orbital, and all the levels except the non-bonding one are doubled. The non-bonding orbital exists roughly speaking because of structures like

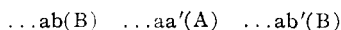


The energy level pattern is shown in Fig. 6. Symmetries of orbitals are given by lower case letters, and of states and configurations by capitals; in each case using species as shown in the character table in the last section.

The ground configuration has symmetry A and may be denoted by the product of species of the two highest energy electrons.



The first excited configuration is threefold degenerate



Allowing for the nitrogens by changing α 's does split the degeneracy but gives the wrong result; namely, that for the 4,4'-dye the first transition would be $a^2 \rightarrow ab(\parallel)$, but for the 2,2'-dye it would be $a^2 \rightarrow aa'(\perp)$! This is analogous to the situation involving pyridine and benzene, where the degenerate configurations obtained on the assumption of an all-carbon model have to be allowed to interact first before the hetero atom is taken into account.

If we allow the configurations to interact here, we find the upper levels ordered



simply by virtue of the "repulsion" between the B configurations. The first transition is now given

(12) This is illustrated in the recent paper on dyes of J. R. Platt, *J. Chem. Phys.*, **25**, 80 (1956).

as $A \rightarrow B$, in agreement with experiment, but only after going to a higher order of approximation. This may be compared with the situation encountered using structures, where resonance between structures must be considered before a reasonable description of the ground state emerges.

Using the Hückel theory before configurational interaction, we can calculate the center of gravity of the triad of absorptions, say, in terms of the center of gravity of the benzene tetrad (average absorption at 210 $m\mu$). Using the orbital energies for the two cases, we find for the dye triad a wave length

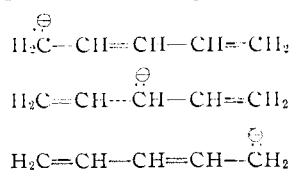
$$210 m\mu \frac{2.133}{1.333} = 337 m\mu$$

which agrees with what is observed (the average of the six transition energies listed in Table I corresponds to absorption at 346 $m\mu$).

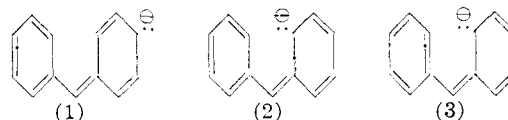
The transition moment length for one of the $A \rightarrow B$ transitions is 1.9 Å. and for the other, 0.4 Å. These values fit the values in Table I reasonably well when it is remembered that configuration interaction is involved. The transition moment length for the $A \rightarrow A(\perp)$ transition is calculated to be 0.6 Å., which is too high.

The A. O. coefficients squared in that b orbital which best characterizes the first B state (that is, with transition moment length 1.9 Å.) are larger at the 4,4'-positions than at the 2,2'-positions. Moreover, the non-bonding (a) orbital does not discriminate between the 2- or 4-positions. Thus putting in nitrogen atoms at the 4,4'-positions would, according to first-order perturbation theory, make the transition energy for the intense first transition somewhat smaller than for the 2,2'-dye, as observed.

If we want to emphasize calculating the position of the first transition, a method using structures proves to be more satisfactory. The basic interaction is considered to be very similar to what occurs in allyl anion, so that the straight chain dye with $n = 1$ would be treated using wave functions corresponding to the following three structures¹³



For the pyridocyanines there are a large number of interactions of allylic type, and there is the Kekulé interaction in the pyridinium rings as well. The allylic interaction is illustrated by the first two structures



The magnitude of the allylic interaction matrix element is taken so as to give correctly the color of the $n = 2$ dye (λ 409 $m\mu$). Interaction between functions, illustrated by the second and third

(13) The method is described by W. T. Simpson, *THIS JOURNAL*, **73**, 5359 (1951).

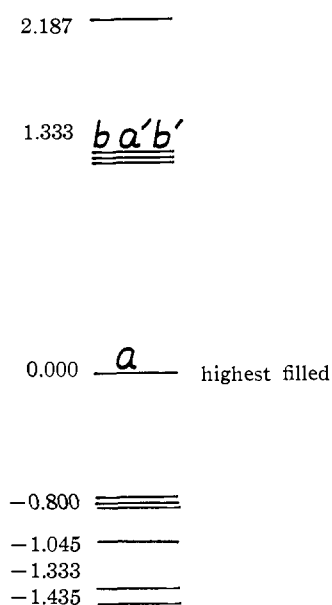


Fig. 6.—Diagram of energies of L.C.A.O. M.O.'s according to Hückel theory. Energies are in units of $|\gamma|$; and highest two levels (+4.000 and +5.076) have been omitted.

structures, is taken so as to put the $A_{1g} \rightarrow B_{2u}$ transition in benzene at 260 $m\mu$. If the charge moves more than two carbon atoms the interaction is set equal to zero, as it is also when there are multiple interactions. In addition, the wave functions are assumed to be orthogonal. The upper corner of the secular equation for the pyridocyanine corresponding to the structures as numbered above would for example, be

$$\begin{array}{c|ccc} & 1 & 2 & 3 \\ \hline 1 & -\lambda & G & 0 \\ 2 & G & -\lambda & K \\ 3 & 0 & K & -\lambda \end{array}$$

where G is the allyl anion resonance parameter and K is the Kekulé resonance parameter. The ratio $K/G = 0.787$.

The first few energies in units of G and the calculated absorption wave lengths are given in Table II where it will be seen that the calculated wave length of the first transition falls very nicely between the $n = 2$ and $n = 3$ dye colors, as observed.

TABLE II

TERM VALUES IN UNITS OF G AND POSITIONS OF THE PEAKS AS CALCULATED USING STRUCTURES

| | Chain dyes | | | Pyridocyanine |
|--------------------------------|------------|---------|---------|--------------------|
| | $n = 1$ | $n = 2$ | $n = 3$ | |
| E_1 | 1.414 | 1.618 | 1.732 | 3.047 |
| E_2 | 0 | 0.618 | 1.000 | 2.201 |
| E_3 | -1.414 | -0.618 | 0 | 1.696 ^b |
| $\lambda(E_2 - E_1)$, $m\mu$ | 289 | (409) | 559 | 470 |
| λ (obsd.) ^a | 309 | 409 | 511 | 486-505 |
| $\lambda(E_3 - E_1)$ | | | | 330 (double) |
| λ (obsd.) | | | | 360 and 260 |

^a W. T. Simpson, *J. Chem. Phys.*, 16, 1124 (1948).
^b Doubly degenerate.

The transition moment length for the first ($A \rightarrow B$) transition is calculated to be 1.90 Å., the same as for the most intense transition in the first

triad according to the Hückel theory. The third energy level obtained using structures is accidentally degenerate, with absorption at 330 $m\mu$ and species A and B. The transition moment lengths to these two states are, respectively, 0.25 Å. (short axis polarized) and 0.14 Å. (long axis polarized). The transition moment lengths agree with what is observed for the 4,4'-dye (Table I) if the absorption at 372 $m\mu$ is assigned as $A \rightarrow A$, and if it is assumed that the actual absorptions at 254 and 505 correspond (after some mixing has taken place) to the first two $A \rightarrow B$ transitions calculated to come at 470 and 330.

Appendix

We shall start by reviewing the theory of the splitting of the monomer levels upon formation of the dimer.¹⁴ It is assumed that the molecular planes of the dye cations are parallel in the dimer, forming a sandwich. One possible arrangement is as shown in Fig. 7.

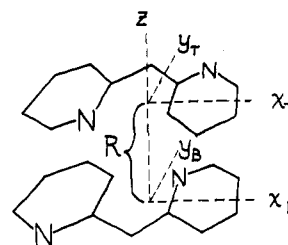


Fig. 7.—One of two possible structures for dimer of dye I. Location of each anion would be in a plane between the two dye cations, as close to a pair of nitrogen atoms as possible.

Neglecting interaction between the monomeric parts the electronic wave functions for the ground state and the (doubly degenerate) first-excited state would be in the form of products

$$\psi_T \psi_B \\ \psi_T^\dagger \psi_B, \psi_T \psi_B^\dagger$$

where T and B refer to "top" and "bottom" molecules, and the dagger denotes electronic excitation, in the present example corresponding to the 486 band of the monomer. The electrostatic interaction in the dipole approximation is the sum of the static coulomb energy, which can be disregarded, and the potential

$$V = (-2\sum z_T z_B + \sum x_T z_B + \sum y_T z_B) e^2 / R^3$$

Here, for example, $\sum z_T$ means a sum over the z components of the electrons in the top molecule, and x , y and z are referred to origins in the respective molecules, as shown in Fig. 7.

(14) An assumption necessary in order that the theory have the simple form outlined here is that the vibrational parts of the wave functions for the dimer excited states can be factored from the electronic parts, which leads to what is called strong coupling. The appropriateness of this assumption is judged by evaluating the terms in the coupling inequality (see W. T. Simpson and D. L. Peterson, *J. Chem. Phys.*, 25, 588 (1957)). The monomer band width for the absorption at 486 $m\mu$, $\Delta \approx 3000 \text{ cm.}^{-1}$ while the splitting for the iodide is actually less, $2\nu \approx 2300 \text{ cm.}^{-1}$; and for the perchlorate more, $2\nu \approx 4800 \text{ cm.}^{-1}$. According to this the perchlorate dimer is in the strong coupling range $2\nu/\Delta > 1$, and the iodide is in the intermediate coupling range. The theory in this Appendix is a strong coupling theory, but even so seems to apply fairly well to the iodide.

Only terms of the type

$$\int \psi_T^\dagger \psi_B V \psi_T \psi_B^\dagger d\tau_T d\tau_B$$

are considered important. That is, the permanent moments, like

$$e \int \psi_T \Sigma x_T \psi_T d\tau_T$$

are taken as zero. The first-order energy correction for the ground state is therefore zero. The correct wave functions for the degenerate manifold are

$$\psi_{\pm} = 2^{-1/2}(\psi_T^\dagger \psi_B \pm \psi_T \psi_B^\dagger)$$

The expectation value of V for these functions does not involve the term

$$-2\Sigma z_T z_B$$

because the transition moments for the monomeric component species are in-plane. What is left is actually the dot product of the respective transition moments, each referred to its own coordinate frame

$$W_{\pm} = \pm \vec{m}_T \cdot \vec{m}_B / R^3$$

where the x component, say, of m_T is

$$(m_T)_x = e \int \psi_T \Sigma x_T \psi_T^\dagger d\tau_T$$

The transition moment for the dimer absorption is

$$\vec{m}_{\pm} = e \int \psi_T \psi_B [\vec{i}(\Sigma x_T + \Sigma x_B) + \vec{j}(\Sigma y_T + \Sigma y_B)] 2^{-1/2}(\psi_T^\dagger \psi_B \pm \psi_T \psi_B^\dagger) d\tau_T d\tau_B = 2^{-1/2}(\vec{m}_T \pm \vec{m}_B)$$

To illustrate the use of these formulas, let us now assume that the nitrogen atoms in the molecules are in fact oriented as shown in Fig. 7. We would then have

$$\vec{m}_T = -\vec{m}_B$$

Substituting in the formula for the energy we find that the lower energy state is W_+

$$+ m_T \cdot (-m_T) / R^3$$

with the corresponding wave function ψ_+ . The transition moment from the ground state (long wave length component of the doublet) is

$$2^{-1/2}(m_T + (-m_T)) = 0$$

The transition moment to the state with wave

function ψ_- , and energy

$$W_- = + m_T^2 / R^3$$

is $2^{-1/2} m_T$, leading to an intensity proportional to the square, $2 m_T^2$ which is twice the intensity for a single molecule.

Even if the orientations had been switched so as to put the nitrogen atoms directly on top of one another, giving

$$\vec{m}_T = \vec{m}_B$$

the same physical result would have been obtained, although the phases in the wave functions would be reversed. The physical result depends on having the transition moments parallel. The fact that experimentally the long wave length component (species Y in Fig. 3) is much the weaker tells us that if a sandwich configuration is correct then the transition moments of the individual dye cations must indeed be virtually parallel.

The dimer split is, of course, $W_- - W_+$ or

$$2 |m_T|^2 / R^3$$

From this we may obtain R by using $|m_T|$ from Table I and the observed splittings for iodide and perchlorate, respectively, 2300 and 4800 cm^{-1} . This gives for the iodide $R = 5.8 \text{ \AA}$., and for the perchlorate $R = 4.5 \text{ \AA}$.

The dipole approximation introduces some error (It would give a calculated split which is too high by *ca.* $1/3$. Thus we should use $\sim 4/3$ the observed splits, which would reduce the calculated R by 10%.) Also, taking the splitting as the energy difference between the peaks results in uncertainty. Even so the values obtained are certainly reasonable. The usual distance between centers for un-charged aromatic systems on top of each other is 3.4 \AA . Considering the fact that the dye cations are charged and that this charge cannot be neutralized perfectly by the anions, it seems as if the cations in the perchlorate dimer are virtually in contact. In the iodide it appears that the dye cations actually are separated to a degree by the iodide ions entering as "filling" to the sandwich. If the iodide ions were completely inside the sandwich, R would be 7.7 \AA ., based on an iodide ion diameter of 4.3 \AA .

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Chemorheological Study of Polyurethan Elastomers¹

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Two series of polyurethan elastomers were prepared which contained (a) predominantly urethan linkages and (b) equal numbers of urethan and substituted urea or biuret groups. The chemorheology of these samples was investigated by stress relaxation experiments. It was found that the urethan linkages underwent scission at a rate one-tenth that of the combined rate of the substituted urea and biuret groups.

Introduction

The chemorheology of polyurethan elastomers based on polyester and polyether chains has re-

(1) This article is based upon a dissertation submitted by Paul C. Colodny in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(2) Thiokol Chemical Corporation Fellow 1955-1957.

cently been investigated by Offenbach and Tobolsky.³ Polyester rubbers cured with benzoyl peroxide had been studied previously.⁴ From these works it was concluded that neither the scission of

(3) J. A. Offenbach and A. V. Tobolsky, *J. Colloid Sci.*, **11**, 39 (1956).

(4) R. D. Andrews, Ph.D. Thesis, Princeton University, 1948.