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Multiple Charge-transfer Bands of the Pyrene-Tetracyanoethylene Complex

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The polarized absorption spectra of the single crystal of the pyrene-tetracyanoethylene complex have been observed by means of a microspectrophotometer. It is shown that two absorption bands, at 12700 cm^{-1} and 20000 cm^{-1} respectively, are polarized along the *c*-axis, the direction connecting the molecular center of the donor and that of the acceptor; hence, both have been assigned to the charge-transfer bands. The interactions of 32 possible charge-transfer states with the no-bond state are discussed in terms of the simple molecular orbital theory, and their contributions to the energy of the complex formation are compared with each other. It is revealed that the interactions of higher charge-transfer states are relatively important and can not be neglected compared with that of the lowest charge-transfer state, and that the appearance of the multiple charge-transfer bands is a natural consequence of such a configurational interaction. It is also suggested that the ratio of the intensities of the first and the second charge-transfer bands may be a parameter that offers information on the orientation of the donor molecule to the acceptor molecule. A probable model is proposed for the structure of the pyrene-tetracyanoethylene complex formed in the solution.

Some charge-transfer complexes show two or three charge-transfer bands in their absorption spectra. The appearance of such multiplet charge-transfer bands has been ascribed to the difference between the donor and acceptor orbitals associated with the charge transfer.[1-4] Briegleb, Czekalla and Reuss[5] have shown that the energy difference between the first charge-transfer band and the second one is approximately equal to the excitation energy of the donor cation in the cases of the chloranil complexes and the tetracyanoethylene (TCNE) complexes which involve polycyclic

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[1] L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).

[2] A. Bier, *Rec. Trav. Chim. Pay-Bas*, **75**, 866 (1956).

[3] R. E. Merrifield and W. D. Philips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[4] A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **81**, 558 (1960).

[5] G. Briegleb, J. Czekalla and G. Reuss, *Z. Physik. Chem. N. F.*, **30**, 316 (1961).

aromatic hydrocarbons as the electron donor. Thus, the second charge-transfer bands in these cases can be assigned to the excitation associated with the charge transfer from the second highest occupied orbital of the donor to the lowest vacant orbital of the acceptor.

This interpretation, however, raises a question about the configuration of the complex. It is generally believed that a donor molecule takes an orientation relative to an acceptor molecule so as to give a maximum overlapping between the highest occupied orbital of the donor and the lowest vacant orbital of the acceptor. Such a structure is most favorable for the appearance of the first charge-transfer band, but it is not necessarily favorable for the second one since the symmetry of the second highest occupied orbital is usually different from that of the highest occupied orbital. In the case of the naphthalene-TCNE complex, for example, the first charge-transfer band should appear strongly when the molecules are stacked face-to-face, with their molecular centers directly over each other and with the central double bond of TCNE parallel to the long axis of naphthalene. However, the second charge-transfer band should be symmetry forbidden in this configuration. A similar situation may be expected also in the case of the pyrene-TCNE complex.

With these things in mind, Gott and Maish⁶⁾ suggested the presence of isomers which are different in the mutual orientations of the symmetry axes of the donor and acceptor. The presence of such orientational isomers has also been assumed by Zweig⁷⁾ as an explanation of the multiple charge-transfer bands of TCNE complexes of substituted benzenes.

In a previous paper,⁸⁾ we have shown, for several TCNE complexes, that the absorption bands corresponding to the first and second charge-transfer bands in the solution spectra appear in the absorption spectra of crystalline powders observed by means of the KBr pellet method. However, the possibility that the second absorption band found in a spectrum of crystalline powder is not a charge-transfer band, but a band associated with the excitation of the donor or acceptor, has not been conclusively ruled out. This point should be clarified by means of the observation of the polarized absorption spectra of the crystals.

In the present paper, the polarized absorption spectra of the crystal of the pyrene-TCNE complex will be shown in an attempt to prove that the multiple charge-transfer bands do really appear in the crystalline state as well as in the solution; then the interpretation of these bands will be discussed in detail in order to elucidate the general features of the multiple charge-transfer bands.

Experimental

Pyrene was purified by the successive application of recrystallization from a xylene solution, alumina column chromatography, and finally sublimation in vacuo. The purification of TCNE was accomplished by the sublimation in vacuo after the repetition of the recrystallization from a chlorobenzene solution. For the observation of the absorption spectrum of the complex crystal, minute single crystals of a lath shape, a few microns in width and in length and less than one micron thick, were prepared from a carbon tetrachloride solution.

The polarized absorption spectra were measured by means of a microspectrophotometer, a modification of the Olympus Model MSP-A-IV microspectrophotometer. An Xe-lamp of 500 W. was used as the light source. Although the technique of microspectrophotometry has been applied by other investigators to the observation of the spectra of organic crystals in the visible and ultraviolet regions, little has been done in the near infrared region because of the difficulty of finding a suitable detector. In the present experiment we have used a RCA 7102 photomultiplier tube as the detector in this region; it enables us to observe the absorption spectrum up to 1200 mμ.

Results and Discussion

(1) The Absorption Spectra and the Crystal Structure.—The visible absorption spectrum of a carbon tetrachloride solution of the pyrene-TCNE complex is shown in Fig. 1. The two broad bands at 13700 cm^{-1} and 19700 cm^{-1} are the first and the second charge-transfer bands respectively. The intensity ratio of these two bands remains constant over a wide temperature range. The oscillator strength of the first charge-transfer band is about 0.02.

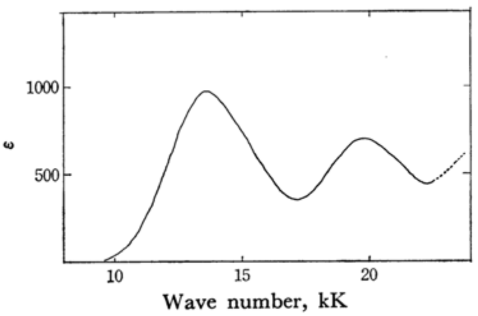

Fig. 1. The charge-transfer bands of pyrene-TCNE complex in carbon tetrachloride.

According to the results of the X-ray analysis of the crystal structure,⁹⁾ the crystal of the pyrene-TCNE complex has a monoclinic unit cell with

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6) J. R. Gott and W. G. Maish, *J. Chem. Phys.*, **39**, 2229 (1963).

7) A. Zweig, *Tetrahedron Letters*, **1964**, 89.

8) H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962).

9) H. Kuroda, I. Ikemoto and H. Akamatu, This Bulletin, **39**, 547 (1966).

the lattice constants of $a=14.58$ Å, $b=7.34$ Å, $c=8.09$ Å and $\beta=92.4°$, and belongs to the $P2_1/a$ space group. Two pyrene and two TCNE molecules are contained in each unit cell. Pyrene and TCNE molecules are stacked alternately along the *c*-axis, their molecular planes parallel to each other so as to give a large overlap between their molecular orbitals. The crystals grown from a solution are either of lath-shape or are prisms elongated along the *c*-axis. In every case, the developed face is a (100) plane. Therefore, the *b*- and *c*-polarized spectra were observed in the direction perpendicular to the *bc*-plane with extremely thin crystals. The direction of the *b*-axis was determined by an examination with a polarizing microscope. The observed spectra are shown in Fig. 2.

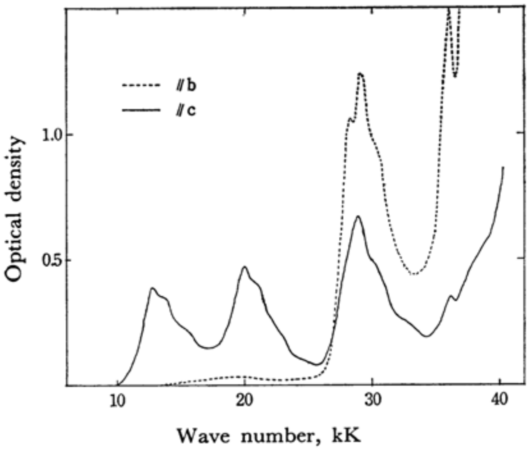

Fig. 2. The polarized absorption spectra of the crystal of pyrene-TCNE complex.

As can clearly be seen in Fig. 2, there are two absorption bands that are markedly polarized along the *c*-axis. The first band has the absorption maximum at 12700 cm^{-1}, and the second one, at 20000 cm^{-1}. No absorption band corresponding to the first one can be found in the *b*-polarized spectrum, but there is a very weak absorption with a maximum around 19000 cm^{-1}, which seems to correspond to the 20000 cm^{-1} band in the *c*-polarized spectrum. The third band in the *c*-polarized spectrum appears in the region of 25000—35000 cm^{-1}, and the fourth begins from 35000 cm^{-1}. These bands are stronger in the *b*-polarized spectrum in contrast to the first and the second bands. Each band seems to have vibrational structures. The position of the peaks and the polarization ratio—the ratio of the integrated optical density of a band in the *c*-polarized spectrum to that in the *b*-polarized spectrum—are summarized in Table I.

The projection of the crystal structure along the *a*-axis onto the *bc* plane is shown in Fig. 3.

TABLE I. POLARIZATION RATIO AND POSITIONS OF PEAKS

Band	Polarization ratio of the band	Wave numbers of peaks cm^{-1}	
		b-polarized	*c*-polarized
I	>20		12700* 14000 15600
II	10	19500	20000* 21300
III	0.5	28900*	28400 29200* 31000
IV	0.2	>35000	>35000

* The maximum of the band.

It can readily be seen from this structure that, according to the oriented gas model, the short-axis polarized absorption of pyrene should be strongly polarized along the b-axis, while the long-axis polarized absorption may be exprected to show a polarization ratio of about unity. In any case, a large polarization ratio can hardly be expected for the local-excitation band. On the other hand, a charge-transfer excitation may be expected to be polarized along the *c*-axis, the direction connecting the centers of the pyrene and TCNE molecules stacked face-to-face. Thus, we can conclude that both the first and second absorption bands are charge-transfer bands, while the others are associated with the local excitations.

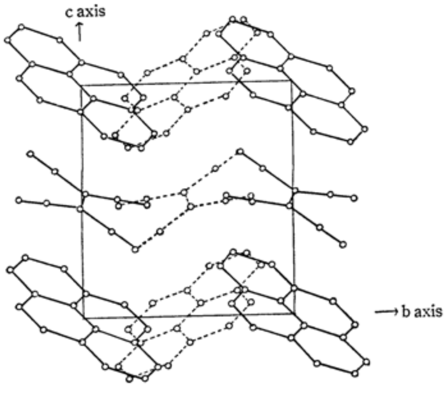

Fig. 3. The projection of the crystal structure of pyrene-TCNE complex along the *a*-axis on the *bc* plane.

The fact that the first band is exclusively polarized along the *c*-axis indicates that it is a pure charge-transfer band. The polarization ratio is a little lower for the second band. This could be due to mixing between the charge-transfer state and a local-excited state. Even if this is the case, however, the contribution of the local-excited state should be quite small in order to give the observed polarization ratio. In the discussion below, therefore, we shall treat both of these absorption bands as pure charge-transfer bands, neglecting completely the interaction with any local excitation. The separation between the main peaks of the first and second charge-transfer bands is 7300 cm^{-1}, which approximately corresponds to the difference between the orbital energy of the highest occupied orbital and that of the second highest occupied orbital. It is most reasonable to presume that the first band is associated with a charge transfer from the highest occupied orbital of pyrene to the lowest vacant orbital of TCNE, and the second one, to that from the second highest occupied orbital. Interestingly, the integrated optical density is nearly the same for these two absorption bands in spite of the difference in the symmetry properties of these two molecular orbitals. The ratio of the integrated optical density of the first band to that of the second one is 0.94 in the c-polarized spectrum, and 1.3 in the solution spectrum. The significance of this ratio will be discussed later.

(2) Charge-transfer Interaction.—Since the experimental results described above indicate unambiguously that the first and second charge-transfer bands appear not only in the solution spectrum but also in the absorption spectrum of the crystal, where we can exclude the possibility of the presence of orientational isomers, the explanation for their appearance has to be found in the nature of the charge-transfer interaction between pyrene and TNCE, without assuming any orientational isomers. For the sake of simplicity, we shall consider here the interaction in a pair, a pyrene molecule and a TCNE molecule, stacked face-to-face as they are in the crystal, instead of the interaction in the crystalline state.

As is well known, the wave function of the ground state of a loosely-bounded molecular complex, or a weak complex, can be expressed as follows:

$$\Phi_{\mathrm{N}} = a\phi_0(\mathrm{D}\cdot\mathrm{A}) + b\phi_1(\mathrm{D}^+\cdot\mathrm{A}^-) \qquad (1)$$

where $\phi_0(\mathrm{D{\cdot}A})$ and $\phi_1(\mathrm{D^+{\cdot}A^-})$ are the wave function of the no-bond structure and that of the dative structure respectively. Usually it is assumed that the wave function of the dative structure is satisfactorily expressed by the wave function of the lowest charge-transfer state where an electron has been transferred from the highest occupied orbital of the donor to the lowest vacant orbital of the acceptor, while the interactions of all the other, higher charge-transfer states are negligible. This approximation has been widely applied with success in the discussions of the charge-transfer bands, the dipole moment, and so on.[10] It can easily be seen, however, that the appearance of the second charge-transfer band can not be understood in terms of this approximation. We have to take into account the second chage-transfer state in which the donating orbital is the second highest occupied orbital of the donor. The energies of the Hückel orbitals of pyrene and TCNE are schematically shown in Fig. 4.* The molecular orbitals are numbered in the way shown in this figure.

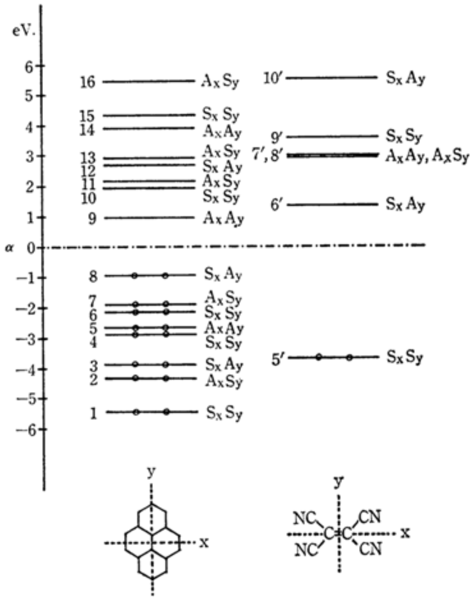

Fig. 4. The orbitals of pyrene and TCNE.

There can be a number of different charge-transfer states. In principle, all of them may interact with the no-bond state, and more or less contribute to the stabilization of the complex. The wave function of the ground state can be expressed generally as follows:

$$\Phi_{\mathrm{N}} = a_0^0\phi_0(\mathrm{D}\cdot\mathrm{A}) + \sum_i\sum_j b_{i\,j}^0\phi_{ij}(\mathrm{D}^+\cdot\mathrm{A}^-) + \sum_k\sum_l c_{k\,l}^0\phi'_{kl}(\mathrm{D}^-\cdot\mathrm{A}^+) \qquad (2)$$

In Eq. 2, $\phi_{ij}(\mathrm{D^+{\cdot}A^-})$ is the wave function of a charge-transfer state where an electron has been transferred from the ith orbital of pyrene to the jth orbital of TCNE; $\phi'_{kl}(\mathrm{D^-{\cdot}A^+})$ is that of a state where an electron has been transferred from the lth orbital of TCNE to the kth orbital of pyrene, and a_0^0, $b_{i\,j}^0$ and $c_{k\,l}^0$ are the coefficients, generally $|a_0^0|\simeq 1$, $|b_{i\,j}^0|\ll 1$, $|c_{k\,l}^0|\ll 1$, for a weak complex such as pyrene-TCNE.

The energy of the ground state can be given by Eq. 3, using the approximation of the second-order perturbation theory:

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10) See, for example, G. Briegleb, "Elektron-donator-acceptor-Komplexe" Springer-Varlay, Berlin, (**1961**).

* The value of $\beta_{\mathrm{C-C}}$ is assumed to be 2.16 eV.

$$\begin{aligned} W_{\mathrm{N}} = W_0 - \{&\sum_i\sum_j [H(0,ij) \\ &- W_0S(0,ij)]^2/(W_{ij}-W_0) \\ &+ \sum_k\sum_l [H'(0,kl) \\ &- W_0S'(0,kl)]^2/(W'_{kl}-W_0)\} \end{aligned} \tag{3}$$

where $H(0,ij)=\langle\phi_0|H|\phi_{ij}\rangle$, $H'(0,kl)=\langle\phi_0|H|\phi'_{kl}\rangle$, $S(0,ij)=\langle\phi_0\mid\phi_{ij}\rangle$ and $S'(0,kl)=\langle\phi_0\mid\phi'_{kl}\rangle$, and where W_0, W_{ij} and W'_{kl} are the energies of the ϕ_0,ϕ_{ij} and ϕ'_{kl} states respectively. If the wave functions of the complex are expressed in terms of the molecular orbitals of the donor and the acceptor, $S(0,ij)$ will be approximately equal to $\sqrt{2}\cdot S_{ij}$, where S_{ij} is the overlap integral between the donating and the accepting orbitals. Furthermore, it is possible to assume that $H(0,ij)$ is approximately proportional to $S(0,ij)$, and hence to S_{ij} also. Thus we can assume that $H(0,ij)-W_0S(0,ij)=-KS_{ij}$, where K is a constant. By using such approximations, Eq. 3 can be simplified to:

$$\begin{aligned} W_{\mathrm{N}} = W_0 - K^2\{&\sum_i\sum_j S_{ij}^2/(W_{ij}-W_0) \\ &+ \sum_k\sum_l S'^2_{kl}/(W'_{kl}-W_0)\} \end{aligned} \tag{4}$$

Therefore, the relative contribution of the interaction of a charge-transfer state, ϕ_{ij}, to the binding energy, $\Delta W=W_0-W_{\mathrm{N}}$, can be determined by comparing the values of $S_{ij}^2/(W_{ij}-W_0)$.

We have calculated S_{ij} as well as $S_{ij}^2/(W_{ij}-W_0)$ for a pair, a pyrene molecule and a TCNE molecule, stacked in the same way as they are in the crystal structure (Fig. 5). The distance between their molecular planes was taken to be 3.32 Å, the value determined by crystal structure analysis.

We have assumed the Hückel orbitals for the molecular orbitals of pyrene and TCNE, and the Slater functions with the orbital exponents of 1.64 and 2.13 a. u. for the 2p atomic orbitals of carbon and nitrogen respectively. It is known that a Slater function is not satisfactory for the tail of the atomic orbital, and it gives a markedly underestimated value in the calculation of an intermolecular integral.[11] In effect, the overlap integrals calculated in the present study will become nearly three times as large if the SCF atomic orbitals given by Roothaan, Clementi and Yoshimine[12] are used instead of the Slater orbitals. The use of a smaller orbital exponent has been recommended for the calculation of intermolecular integrals.[13] It can be shown, however, that the value of the overlap integral obtained by using SCF atomic orbitals is approximately proportional to the one obtained by using a Slater orbital for a given separation between the molecular planes of the donor and the acceptor which are stacked parallel to each other. Therefore, no essential difference is expected to occur in the estimation of the relative contributions of various charge-transfer states, even if SCF atomic orbitals are used, while the value of K is dependent on the atomic orbitals assumed. When Slater atomic orbitals are used, the value of K should be taken as 10—20 eV. in order to effect an agreement between the calculated binding energy and the observed one which is a few kcal./mol. The value of $W_{ij}-W_0$ was taken as equal to the energies of the first and second charge-transfer bands for the lowest charge-transfer state and the second one respectively. The values for the other states were estimated by using these values and the orbital energies.

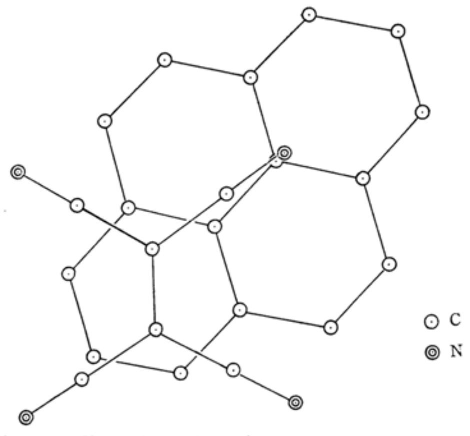

Fig. 5. The orientation of a pyrene molecule relative to the neighboring TCNE molecule in the crystal structure.

In Table II, the calculated values of S_{ij} and $S_{ij}^2/(W_{ij}-W_0)$ are given for 32 different charge-transfer states.* The charge-transfer states where the accepting orbitals are the 9′ orbital and the 10′ orbital of TCNE, and those where the donating orbitals are the 1′—4′ orbitals of TCNE, are omitted in this table because their contributions to ΔW are negligibly small. Generally, the lowest charge-transfer state is expected to play the most important role in the charge-transfer interaction. In the present case, this is the state where the donating orbital is the 8 orbital of pyrene and where the accepting one is the 6′ orbital of TCNE; we shall denote this state as [8→6′]. According to Table II, however, we have to give up such a preconception. The contribution of the lowest charge-transfer state to ΔW is by no means predominant in comparison with those of the other charge-transfer states. It can cover only 16 per cent of ΔW, while the contribution from the second charge-transfer state, [7→6′], is 19 per cent, and those

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11) J. L. Katz, S. A. Rice, S. Choi and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963).

12) E. Clementi, C. C. Roothaan and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).

13) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

* The overlap intergral was calculated by means of an PC-2 electronic computer, at University of Tokyo Data Processing Centre.

TABLE II (a). [$D^+\cdot A^-$] STATES

Donating orbital	Accepting orbital TCNE MO (j)					
	6′		7′		8′	
Pyrene MO (i)	S_{ij} ($\times 10^{-2}$)	$S^2_{ij}/W_{ij}-W_0$ ($\times 10^{-4}$)	S_{ij} ($\times 10^{-2}$)	$S^2_{ij}/W_{ij}-W_0$ ($\times 10^{-2}$)	S_{ij} ($\times 10^{-2}$)	$S^2_{ij}/W_{ij}-W_0$ ($\times 10^{-4}$)
8	+0.93487	0.585	+0.62951	0.127	+0.08169	0.002
7	−1.30721	0.703	+0.85602	0.180	+0.30725	0.023
6	+0.21919	0.018	−0.42038	0.041	+0.50695	0.059
5	−1.29369	0.519	−1.03604	0.221	−0.01051	0.000
4	+1.33335	0.517	−0.98549	0.192	+0.06040	0.001
3	+1.07578	0.262	+0.80119	0.106	+0.03828	0.000
2	−0.23324	0.011	+0.15216	0.004	−0.14353	0.003
1	−0.40761	0.028	+0.42446	0.024	−0.05253	0.000

TABLE II (b). [$D^-\cdot A^+$] STATES

Accepting orbital	Donating orbital TCNE MO (l) 5′	
Pyrene MO (k)	S_{kl} ($\times 10^{-2}$)	$S^2_{kl}/W'_{kl}-W_0$ ($\times 10^{-4}$)
9	+0.21450	0.012
10	−0.26484	0.015
11	−0.53416	0.056
12	−0.17488	0.005
13	+0.03297	0.000
14	+0.07066	0.001
15	+0.05639	0.000
16	+0.02223	0.000

from the [5→6′] and [4→6′] states are both 14 per cent. It is thus revealed that the second charge-transfer state, as well as some of the much higher charge-transfer states, should be taken into account in discussions of the electronic states of the complex.

(3) **The Intensities of the Charge-transfer Bands.**—Corresponding to the expression of the wave function of the ground state given in Eq. 2, we can describe the wave function of a charge-transfer excited state associated with an electron transfer from the *m*th orbital of the donor to the *n*th orbital of the acceptor, as follows:

$$\Phi_{\mathrm{E}}(mn) = a_0^{mn}\phi_0(\mathrm{D}\cdot\mathrm{A}) + b_{mn}^{mn}\phi_{mn}(\mathrm{D}^+\cdot\mathrm{A}^-) + \sum_{i\neq m}\sum_{j\neq n} b_{ij}^{mn}\phi_{ij}(\mathrm{D}^+\cdot\mathrm{A}^-) + \sum_{k}\sum_{l} c_{kl}^{mn}\phi'_{kl}(\mathrm{D}^-\cdot\mathrm{A}^+) \qquad (5)$$

where $|a_0^{mn}|$, $|b_{ij}^{mn}|$ $(i\neq m,\ j\neq n)$, $|c_{kl}^{mn}|\ll 1$ and $|b_{mn}^{mn}|\simeq 1$. The transition moment of the charge-transfer excitation, $\Phi_{\mathrm{E}}\leftarrow\Phi_{\mathrm{N}}$, can then be approximately expressed by Eq. 6, neglecting all small terms and assuming that the dipole moment is zero in the no-bond state. The values of a_0^0 and b_{mn}^{mn} are taken as unity.

$$\mu(0, mn) = \langle\Phi_{\mathrm{N}}|\mu|\Phi_{\mathrm{E}}\rangle \simeq b_{mn}^0\langle\phi_{mn}|\mu|\phi_{mn}\rangle + \langle\phi_0|\mu|\phi_{mn}\rangle \qquad (6)$$

where μ is the operator of the dipole moment. The dipole moment of the charge-transfer state, $\langle\phi_{mn}|\mu|\phi_{mn}\rangle$, is nearly the same for all the charge-transfer states; we shall denote it as μ_{CT}. We can also presume that the $\langle\phi_0|\mu|\phi_{mn}\rangle$ integral is roughly equal to $[S(0, mn)/2]\cdot\langle\phi_{mn}|\mu|\phi_{mn}\rangle$, according to Mulliken's approximation. Thus the following equations can be given for the transition moment:

$$\mu(0, mn) \simeq [b_{mn}^0 + S(0, mn)/2]\cdot\mu_{\mathrm{CT}} \qquad (7)$$

thus:

$$\mu(0, mn) \simeq [K/(W_{mn} - W_0) + 1/\sqrt{2}\,]\cdot S_{mn}\cdot\mu_{\mathrm{CT}} \qquad (8)$$

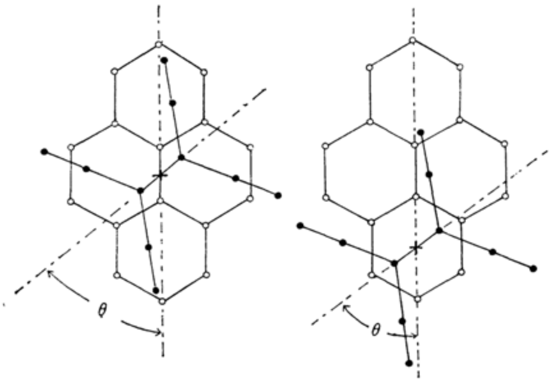
The ratio of the oscillator strength of the first charge-transfer band to that of the second one, f_1/f_2, can be roughly estimated by using Eq. 8. We obtained 0.8 for this ratio, assuming that $K\simeq 10$ eV. Since the observed value is 0.94 in the crystal spectrum and 1.3 in the solution spectrum, the agreement between the observed and the theoretical ratios seems satisfactory for such a rough approximation as we have made here.

We can predict that two charge-transfer bands associated with the charge-transfer states, [5→6′] and [4→6′], can be observed in the 25000—30000 cm^{-1} region with an oscillator strength comparable to the first charge-transfer band. The third band in the *c*-polarized spectrum could be due to these absorptions. The pyrene molecule has, however, $^1\mathrm{L_a}$ and $^1\mathrm{L_b}$ bands in this region. Therefore, we have to consider in this case the mixing of the local-excited states and the charge-transfer states. This problem will not be treated in this paper.

(4) **The Charge-transfer Bands and the Structure of the Complex.**—Hitherto we have assumed the orientation of the pyrene molecule to the TCNE molecule to be as it is in the crystal. However, the orientation could be different from this for the complex in solution. In the crystalline state, molecules would be arranged first of all in such a way that the crystal structure fulfills the condition of the closest packing. This leaves the possibility that molecules take an orientation

that is unfavorable for the charge-transfer interaction. On the other hand, molecules are supposed to take the most favorable orientation when they form a complex in a solution. It is worthwhile, therefore, to evaluate the binding energy associated with the charge-transfer interaction for various different orientations in order to ascertain the most stable structure.

Apparently the binding energy becomes quite small when the donor and acceptor molecules are not in close contact. We can safely ignore such a case, however, and can assume that the molecules are stacked face-to-face, so as to result in a large overlapping between their molecular orbitals. Then we have two variables; the one is the position of the symmetry center of TCNE relative to that of pyrene, and the other is the relative orientation of their molecular axes. We have made our calculation on the relative values of the binding energy, $\Delta W/K^2$, for the following two cases: [Model A], in which the symmetry centers are directly over each other (Fig. 6a), and [Model B], in which the relative positions of the centers are exactly the same as they are in the crystal structure (Fig. 6b). For each model, $\Delta W/K^2$ was evaluated by using Eq. 4 as a function of θ, the angle between the symmetry axes of the molecules, taking the 32 charge-transfer states into account. The results are shown in Fig. 7.



(a) Model A (b) Model B

Fig. 6. The models of pyrene-TCNE complex assumed for the calculation.

Interestingly, $\Delta W/K^2$ varies little with θ in either model. The difference between the largest value and the smallest one is less than 20 per cent of the mean value. This means that the rotation of the TCNE molecule around its symmetry axis perpendicular to the molecular plane would have a very low energy variation, less than 0.4 kcal./mol., as far as only the charge-transfer interactions are concerned. Therefore, we shall not be able to tell the value of θ for the most stable structure unless we have detailed information on other intermolecular interactions. This is a rather unexpected result, since we used to consider that the charge-transfer interaction would be the most strongly dependent on relative orientation of the molecules. Secondly, it may be seen in Fig. 7 that the value of $\Delta W/K^2$ is always larger in Model B than in Model A. This suggests that Model B is more acceptable for the stable structure than Model A.

The ratio of the oscillator strength of the first

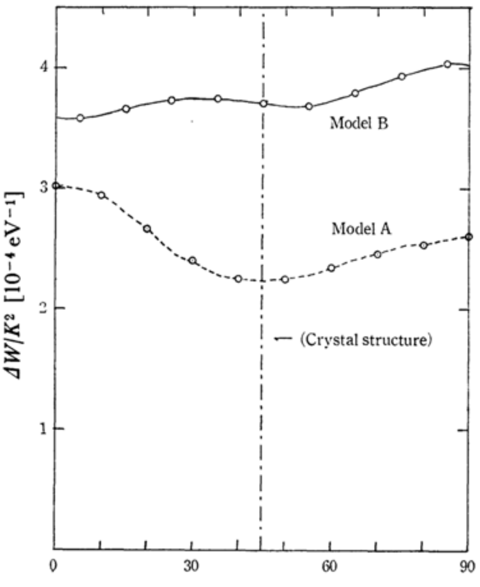


Fig. 7. The dependence of ΔW on the orientation of pyrene to TCNE.

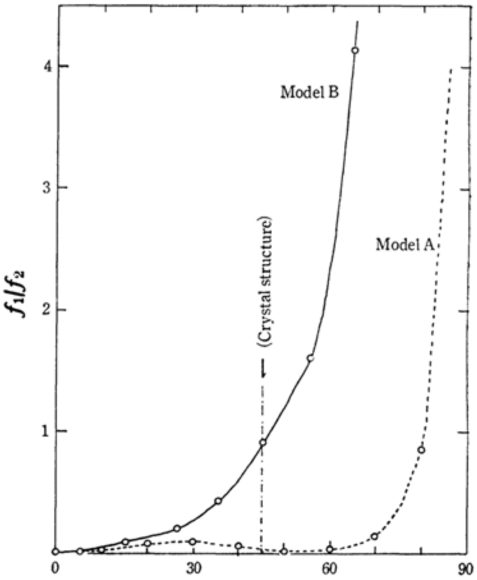


Fig. 8. The relation between the ratio of the oscillator strengths of the charge-transfer bands and orientation of pyrene to TCNE.

charge-transfer band to that of the second one may be theoretically estimated as a function of θ by means of Eq. 8. The results are shown in Fig. 8. It can be seen that the ratio varies markedly, depending on the θ value.

In the case of Model A, the f_1/f_2 ratio is very small except in the θ=80—90° region, where the magnitude of f_2 approaches zero. According to Eq. 8, the value of f_1 is smaller than 0.001 in this model; this is too small compared with the observed value, 0.02. On the other hand, f_1 and f_2 in Model B become comparable to each other in the θ= 40—50° region, where the values of f_1 and f_2 are roughly estimated as 0.01, a value which is in agreement with the observed value. This structure corresponds to the one found in the crystal. Since the binding energy changes little with the θ value, we can not exclude the possibilities that the structures with different θ values co-exist, or that molecules rotate independently around their symmetry axes perpendicular to the molecular plane. In this case the oscillator strength, as well as the f_1/f_2 ratio, will be averaged over different values of θ. In Model A, the average f_1 value will be about 0.0005, and that of f_1/f_2, 0.06. Thus, it is impossible to explain the observed results with this model.

In Model B, however, the average value of f_1 is 0.01, and that of f_1/f_2, 0.9; these values are almost the same as those calculated for the orientation where the value of θ is fixed as 45°. The observed results can be explained well by means of this rotating model. Therefore, the following conclusions can be obtained from the results discussed above; (1) it is difficult to explain either the observed oscillator strengths of the charge-transfer bands or their ratio on the assumption of Model A, and (2) the oscillator strengths and their ratio can be reasonably explained using Model B if we assume either that θ=40—50°, or that the structures with different θ values co-exist with equal probability. In any case, it is Model B that seems more acceptable for the complex in solution.

Summary and Conclusion

We have shown, from the study of the polarized absorption spectra of the crystal of the pyrene-TCNE complex, that the first and second charge-transfer bands can be observed in the crystal spectra. A simple theoretical treatment has proved that the interactions of higher charge-transfer states make significant contributions to the stabilization of the complex. These interactions are by no means negligible; they thus should be taken into account in the discussions of the absorption spectra of the complex. If this has been done properly, the appearance of the multiple charge-transfer bands can be explained. We have pointed out the significance of the relative intensities of the first and the second charge-transfer bands for the purpose of ascertaining the structure of the complex.

We wish also to emphasize another important conclusion that has become clear in the present study. The structure of a charge-transfer complex has often been discussed by considering the symmetry properties of the highest occupied orbital of the donor and the lowest vacant orbital of the acceptor. However, this problem is not so simple. The interaction of the lowest charge-transfer state is not always predominant in the stabilization of the complex. When the interactions of the higher charge-transfer states are taken into account, however, the binding energy due to the charge-transfer interaction becomes rather insensitive to the change in the orientation of the molecular axes of the donor relative to those of the acceptor, provided that their molecular planes are parallel to each other and are in close contact. We can only predict the relative positions of the centers of the molecules in the case of the pyrene-TCNE complex. We have shown that the structure where the molecular centers are directly above each other is not likely to be the most stable structure because, in the first place, the binding energy will be relatively small in this case, and in the second place, the intensities of the observed charge-transfer bands can not be explained using this model. Thus, the relative positions of the centers as they are in the crystal seem to be acceptable also for the complex in solution. Although we have confined our discussion exclusively on the pyrene-TCNE complex, the general features of the conclusions, such as those on the origin of the multiple charge-transfer bands and on the nature of the charge-transfer interaction, can be extended to a number of the weak π-complexes that involve polycyclic aromatic compounds as the electron donors.