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The Charge-transfer Bands in the Crystal Spectra of Molecular Compounds of Tetramethylbenzidine and Those of Benzidine

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The polarized absorption spectra in the 280—1100 mμ region have been observed for the single crystals of eight molecular compounds which involve *N,N,N′,N′*-tetramethylbenzidine and benzidine as the electron donor and *p*-chloranil, TCNQ, 1,3,5-trinitrobenzene, and *p*-benzoquinone as the electron acceptor. The donor and acceptor molecules are not in the ionic states in the ground states of these molecular compounds, in spite of the low ionization potentials of tetramethylbenzidine and benzidine. The observed spectra are composed of absorption bands associated with intramolecular transitions in the constituent molecules and those associated with the charge transfer from the donor to the acceptor. It was found that the polarization of the second charge-transfer band is almost perpendicular to that of the first one in the case of chloranil and TCNQ compounds of benzidine and tetramethylbenzidine. In other cases, the first and second charge-transfer bands were confirmed to be polarized nearly parallel to each other as in a usual charge-transfer molecular compound.

Aromatic amines generally behave as a good π-electron donor. They form solid molecular compounds by the interaction with a variety of π-electron acceptors. These molecular compound crystals have been often found to be an organic semiconductor of relatively good electrical conductivity.[1,2] In a previous paper,[3] we have studied the electronic spectra of single crystals of molecular compounds which are formed by aromatic amines with chloranil. We have shown that a strong donor such as *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) gives a salt-like, solid consisting of the positive ions of donor and the negative ions of acceptor, whereas a "charge transfer" molecular compound, where the constituent molecules are essentially in the non-ionic state, is formed by an aromatic amine of not very strong donor property. The molecular compound of *N,N,N′,N′*-tetramethylbenzidine with chloranil is anomalous in this respect. Although tetramethylbenzidine must be a strong donor with an ionization potential comparable to that of TMPD, this molecular compound has been reported to have a non-ionic structure.[1] Interestingly tetramethylbenzidine forms a non-ionic molecular compound even with a very strong π-electron acceptor such as 7,7,8,8-tetracyanoquinodimethane (TCNQ).[4]

In view of this unusual situation found for the molecular compounds of tetramethylbenzidine, we have attempted to obtain informations concerning the charge-transfer interaction in these molecular compounds by observing the electronic spectra of single crystals. In the present paper, we shall report the polarized absorption spectra in the visible and ultraviolet region observed for the molecular compound crystals which involve tetramethylbenzidine or benzidine as the donor and TCNQ, *p*-chloranil, 1,3,5-trinitrobenzene, and *p*-benzoquinone as the acceptor.

Experimental

Molecular compound crystals were obtained from benzene or carbon tetrachloride solutions containing appropriate amounts of donor and acceptor. The composition of each molecular compound was determined by the elementary analysis of the crystalline powder.

The infrared spectrum was examined on each molecular compound by use of the Nujol-mull method for the purpose to know if the component molecules are in the ionic state or not. The observed infrared spectra of molecular compounds were compared with those of the neutral molecules and ions of the components. We examined also the electron spin resonance absorption. All these results led us to conclude that none of the molecular compounds studied here is an ion-radical salt.

The polarized absorption spectra of single crystals, in the 280—1100 mμ region, were measured with a

1) Y. Matsunaga, *Nature*, **205**, 72 (1965).

2) H. Kuroda, K. Yoshihara and H. Akamatu, This Bulletin, **35**, 1604 (1962).

3) T. Amano, H. Kuroda and H. Akamatu, *ibid.*, **41**, 83 (1968).

4) Y. Matsunaga, Preprint of the 20th annual meeting of the Chemical Society of Japan, 1M 011 (1967).

microspectrophotometer, a modification of OLYMPUS MSP-A-IV. The details of the apparatus and experimental procedures have been already described elsewhere.[5] The measurement was carried out at the room temperature on the developed face of a crystal microscopic size, which have been carefully selected out from a freshly prepared crystalline powder. When we noticed the presence of several different crystal habits, the absorption spectra were observed on each type of crystal. The absorption spectra of the Nujol mulls of crystalline powders were also observed to obtain information concerning the low-energy absorption bands.

Results

The experimental results are shown in Figs. 1—9, where the polarized absorption spectra measured on one typical crystal only are shown for each molecular compound.

(a) Tetramethylbenzidine-Chloranil (1 : 1) Compound. The spectra shown in Fig. 1 indicate the presence of a strong band with an absorption maximum at a wave number below 9 kK. By examining the Nujol-mull spectrum of the crystalline powder, it was found that the maximum of this band is located at 8—9 kK and probably is the lowest-energy electronic band of this molecular compound crystal. This band is exclusively polarized in the direction parallel to one of the edges of a parallel piped crystal, which is denoted "X" in Fig. 1. The next band is found at 18.3 kK, which exhibits a polarization quite different from that of the first band, namely the absorption occurs strongly as the incident light is polarized in the Y-direction, *i. e.* a direction perpendicular to X. The polarization ratio, I_Y/I_X, was found to be about 4. These two bands can not be attributed to any intramolecular transition since the lowest transition is at 32.9 kK ($B_{1u}\leftarrow A_g$, π–π^*) in tetramethylbenzidine and at 27 kK (forbidden π–π^* transition) in chloranil. We shall tentatively assign them as the first and second charge-transfer bands. Seemingly the broad band in the 25—30 kK region is a local excitation band associated mainly with the 32.9 kK transition of tetramethylbenzidine.

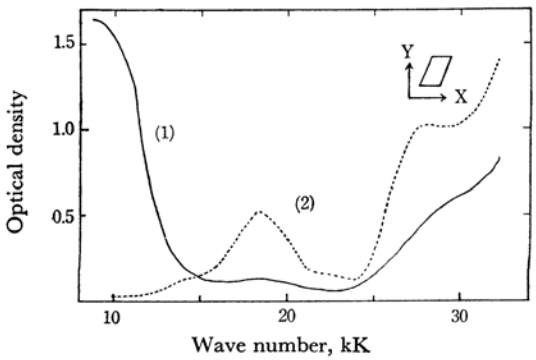

Fig. 1. Absorption spectra of tetramethylbenzidine-chloranil compound.
(1) X-spectrum, (2) Y-spectrum

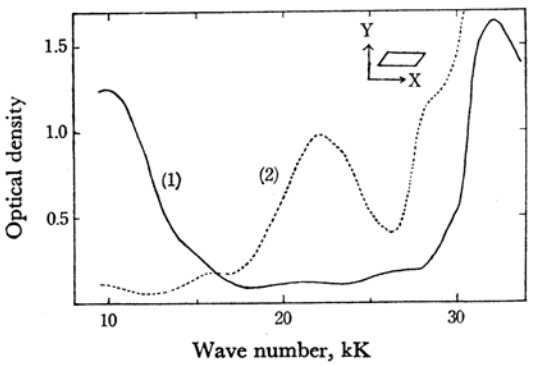

Fig. 2. Absorption spectra of benzidine-chloranil compound.
(1) X-spectrum, (2) Y-spectrum

(b) Benzidine-Chloranil (1 : 1) Compound. The spectra of this molecular compound are similar in many respects to those of the tetramethylbenzidine-chloranil compound. There are two bands in the region where we can expect no band due to intramolecular transition. We assign them as the first and second charge-transfer bands. The maxima of these bands are located respectively at 10 and 22.2 kK. These bands are polarized almost perpendicular to each other as in the tetramethylbenzidine-chloranil compound. A strong peak at 32 kK is probably due to the 35 kK π–π^* transition ($B_{1u}\leftarrow A_g$) of benzidine and/or the 35 kK π–π^* transition ($B_{1u}\leftarrow A_g$) of chloranil. Then we have to consider that these transitions have been shifted to lower energy by about 3 kK in the molecular compound crystal. Presumably a small shoulder at 28 kK is associated with the 27 kK transition (π–π^*, forbidden) of chloranil.

(c) Tetramethylbenzidine-TCNQ (1 : 1) Compound. As is well known, TCNQ is a very

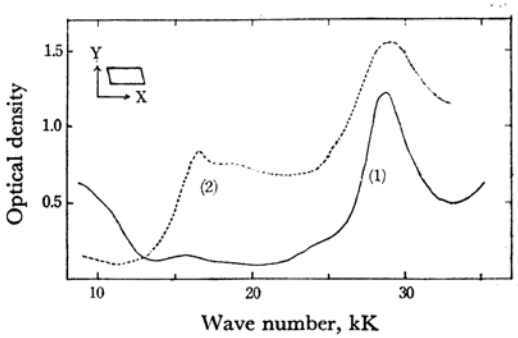

Fig. 3. Absorption spectra of tetramethylbenzidine-TCNQ compound.
(1) X-spectrum, (2) Y-spectrum

5) H. Kuroda, T. Kunii, S. Hiroma and H. Akamatu, *J. Mol. Spectry.*, **22**, 60 (1967).

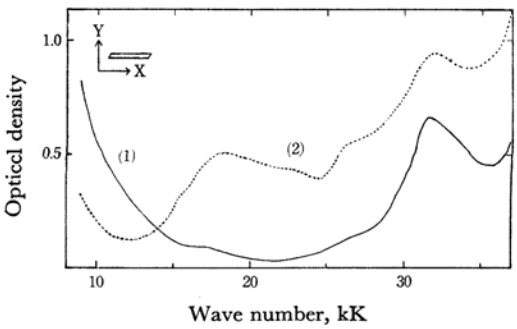

Fig. 4. Absorption spectra of benzidine-TCNQ compound.
(1) X-spectrum, (2) Y-spectrum

strong acceptor, which forms ion-radical salts with a variety of electron donors. In effect, the TMPD-TCNQ compound is composed of $TMPD^+$ ion and $TCNQ^-$ ion, between which there exists a relatively strong charge-transfer interaction.[6] In the case of the tetramethylbenzidine-TCNQ compound, however, all experimental results suggest that the component molecules are essentially in the neutral states. We believe that this molecular compound can be regarded as a non-ionic molecular compound. The high-energy tail of an absorption band can be seen at the low wavenumber limit of the observed spectra shown in Fig. 3. The absorption maximum of this band was found to be located at 7.5 kK in the Nujol-mull spectrum of the powder. The second band is very broad and markedly asymmetric, the maximum of which is located at 16.5 kK. The polarization direction is nearly perpendicular to each other between these two bands. We assign them as the charge-transfer bands. The third band located at about 29 kK is likely to be a local-excitation band associated with the 32.9 kK transition of tetramethylbenzidine. An alternate assignment would be to attribute it to the lowest π–π^* transition of TCNQ (25.3 kK, $B_{1u} \leftarrow A_{1g}$). But the former assignment seems more plausible when we compare the spectrum in this region with that of the benzidine-TCNQ compound.

(d) Benzidine-TCNQ (1 : 1) Compound. Similar to the tetramethylbenzidine-TCNQ compound, we can assign the lowest-energy band at 8 kK and the next band at 18 kK as the first and second charge-transfer bands respectively. In the 25—35 kK region, there is a peak at 32 kK and a shoulder at about 26 kK. It should be noted that the benzidine-chloranil compound also exhibits a strong absorption band at 32 kK while the compound of tetramethylbenzidine with chloranil and that with TCNQ give a band at 29 kK. Therefore the 32 kK band in the benzidine compounds seems to be mainly associated with the intramolecular transition of benzidine, and not due to TCNQ. Presumably the 26 kK shoulder is associated with the 25.3 kK transition of TCNQ.

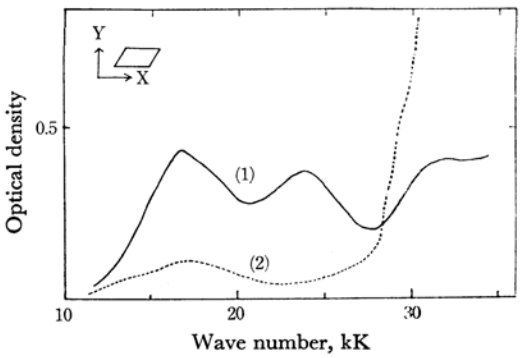

Fig. 5. Absorption spectra of tetramethylbenzidine-trinitrobenzene compound.
(1) X-spectrum, (2) Y-spectrum

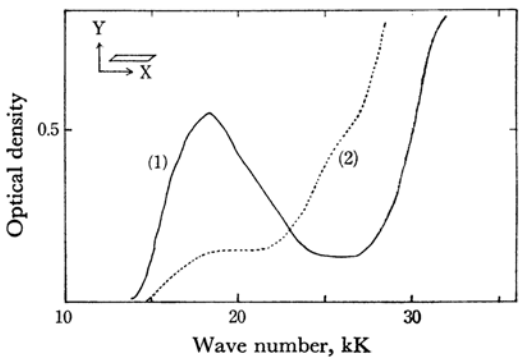

Fig. 6. Absorption spectra of benzidine-trinitrobenzene compound.
(1) X-spectrum, (2) Y-spectrum

(e) Tetramethylbenzidine-Trinitrobenzene (1 : 2) Compound. The two absorption bands, at 16.7 kK and 23.9 kK, can be assigned as the first and second charge-transfer bands. In this case, the polarization is not significantly different between these two charge-transfer bands. In this respect, this molecular compound is markedly different from the chloranil- and TCNQ-compounds mentioned above, but is similar to usual charge-transfer compounds. In order to obtain more precise information concerning the polarization direction, we observed the variation of optical density with the direction of polarization of incident light. The results obtained at the wavenumbers corresponding to the absorption maxima of the two charge-transfer bands are shown in Fig. 7, which indicates that the principal axis of absorption is slightly different between the two bands.

(f) Benzidine-Trinitrobenzene (1 : 1) Compound. The orientation of a trinitrobenzene molecule relative to a benzidine molecule in the

6) H. Kuroda, S. Hiroma and H. Akamatu, This Bulletin, **41**, 2855 (1968).

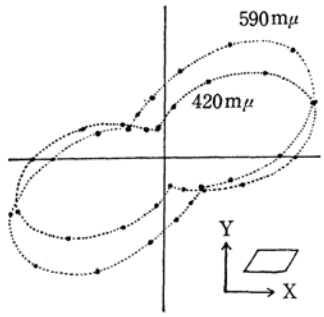

Fig. 7. Variation of optical density with the direction of polarization of incident light, measured for tetramethylbenzidine-trinitrobenzene compound.

crystal of this molecular compound has been reported to be as follows by Wallwork[7]: The benzidine and trinitrobenzene molecules are alternately stacked face-to-face on each other along a crystal axis, but the molecular center of trinitrobenzene is shifted sideway from the position where it would be directly over that of benzidine. In this sence, the arrangement of molecules in this molecular compound is analogous to those in a typical charge-transfer compound. This compound can be obtained in the form of a needle crystal, the elongated axis of which corresponds probably to the direction of the alternate stacking of donor and acceptor molecules. As shown in Fig. 6, we denoted this elongated direction as "X". The absorption band found at 18.3 kK is strongly polarized along the X-direction. This can be assigned as the first charge-transfer band. The second charge-transfer band is not clearly observed. In the Y-polarized spectrum, there is a weak shoulder around 26 kK, which might be due to the second charge-transfer band. If this is the case, we have to consider that there is a significant difference in the polarization direction between the first and second charge-transfer bands. But it is also possible that this 26 kK shoulder is

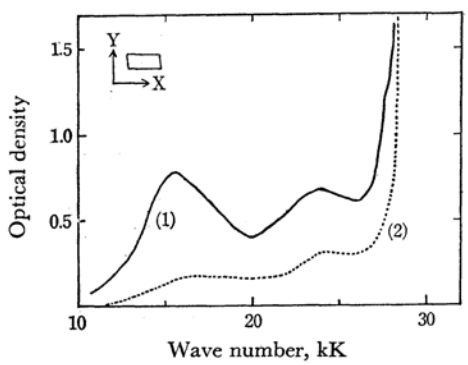

Fig. 8. Absorption spectra of tetramethylbenzidine-*p*-benzoquinone compound.
(1) X-spectrum, (2) Y-spectrum

7) S. C. Wallwork, *J. Chem. Soc.*, **1961**, 494.

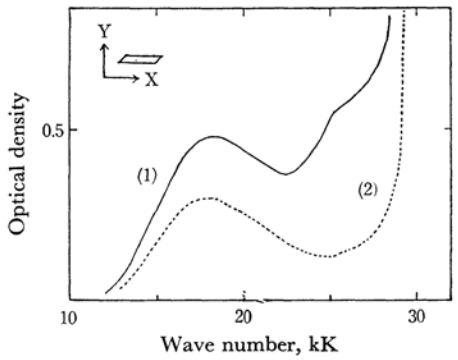

Fig. 9. Absorption spectra of benzidine-*p*-benzoquinone compound.
(1) X-spectrum, (2) Y-spectrum

associated with a local excitation, not with the charge transfer.

(g) Tetramethylbenzidine-*p*-Benzoquinone (1 : 2) Compound. The 15.6 kK and 23.8 kK bands in Fig. 8 can be assigned as the first and second charge-transfer bands respectively. The polarization direction is not appreciably different between these bands. The mole ratio of donor to acceptor is found to be 1 : 2. In these respects, the general situation seems to be similar to the tetramethylbenzidine-trinitrobenzene compound.

(h) Benzidine-*p*-Benzoquinone (2 : 1) Compound. Although the molecular size of benzidine is almost twice that of *p*-benzoquinone, the mole ratio was found to be 1 : 2. This fact seems to suggest that this molecular compound possesses some peculiar crystal structure. The 18kK band in Fig. 9 can be regarded as the first charge-transfer band. The polarization ratio I_X/I_Y is about 1.7 in this band. Presumably a weak shoulder at about 25 kK in the X-polarized spectrum corresponds to the second charge-transfer band.

Discussion

As we have shown above, most of the solid molecular compounds of tetramethylbenzidine and benzidine exhibit two absorption bands in the region where we can expect no local excitation band. We have tentatively assgin them as the first and second charge-transfer bands. The energies of these bands are plotted in Figs. 10 and 11 against the electron affinity of acceptor.*1 These plots clearly demonstrate that the excitation energies are, in fact, almost linearly dependent of the electron affinity of acceptor as expected for a band associated with the charge transfer from a donor molecule to an acceptor molecule.

In solution, tetramethylbenzidine and benzidine

*1 We have adopted here the values of electron affinity which have been proposed by Briegleb.[8]

8) G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

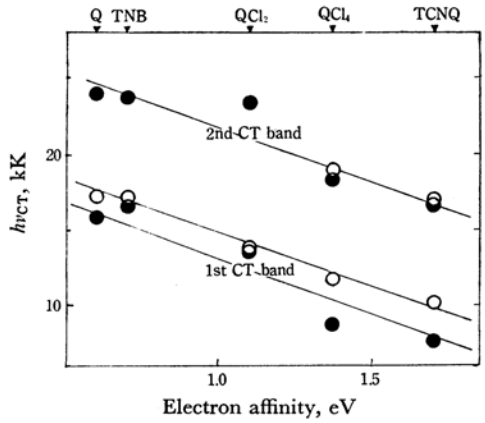

Fig. 10. Energy of charge transfer excitation and electron affinity of acceptor for tetramethylbenzidine compounds.
The acceptor is indicated at the top of the figure.*
○ solution, ● crystal

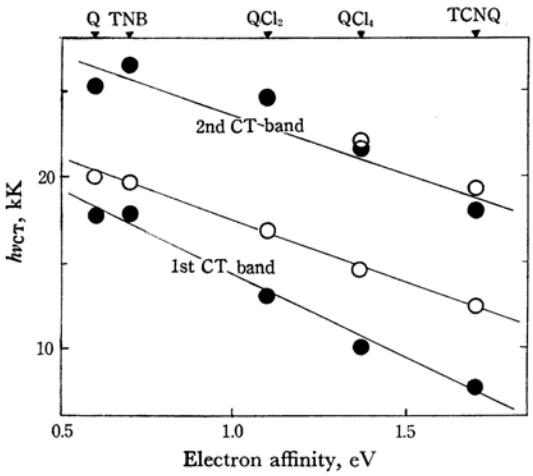

Fig. 11. Energy of charge transfer excitation and electron affinity of acceptor for benzidine compounds.*
○ solution, ● crystal

form molecular complexes with π-electron acceptor, in which the donor and acceptor molecules are in face-to-face contact with each other. The energies of the charge-transfer bands observed for these complexes are also plotted in Figs. 10 and 11. The first charge-transfer band of a molecular compound crystal is a little lower in energy compared with the corresponding band of the molecular complex formed in solution. The energy of the second charge-transfer band of a molecular compound crystal, however, nearly coincides with that of the corresponding band of the complex in solution.

* The following abbreviations are used; Q: *p*-benzoquinone, TNB: 1,3,5-trinitrobenzene, QCl_2: 2,5-dichloro-*p*-benzoquinone and QCl_4: chloranil.

As is well known, there is a simple relation between the ionization potential, I, of the donor and the energy of the charge-transfer band, $h\nu_{CT}$, of the 1 : 1 complex which is formed in solution between a donor molecule and an acceptor molecule. Briegleb and Czekalla have proposed the following empirical equation for a series of chloranil complexes.[9]

$$h\nu_{CT} = I - 5.7 + 0.44/(I-5.7) \quad [\text{eV}] \qquad (1)$$

We have reexamined the relation, and found that the energy of a charge-transfer band of a chloranil complex can be well expressed as follows.

$$h\nu_{CT} = 0.87I - 4.46 \quad [\text{eV}] \qquad (2)$$

We have calculated the self-consistent-field molecular orbitals (SCF-MO's) for the π-conjugated systems in benzidine and tetramethylbenzidine by the variable-β modification of Pariser-Parr-Pople method.*2 The energy and symmetry of the calculated SCF-MO are given in Table 1.

Table 1. Energies of SCF MO's of benzidine and tetramethylbenzidine

Level	Symmetry*	Orbital energy (eV)		
		Benzidine	Tetramethylbenzidine	
1	b_{3u}	−13.56	−13.46	occupied
2	b_{2g}	−13.29	−13.15	
3	b_{3u}	−12.14	−11.95	
4	b_{2g}	−10.97	−10.75	
5	a_u	− 9.90	− 9.85	
6	b_{1g}	− 9.86	− 9.81	
7	b_{3u}	− 9.15	− 8.88	
8	b_{2g}	− 8.05	− 7.84	
9	b_{3u}	− 1.19	− 1.11	unoccupied
10	a_u	− 0.63	− 0.57	
11	b_{1g}	− 0.58	− 0.52	
12	b_{2g}	0.35	0.42	
13	b_{3u}	2.01	2.07	
14	b_{2g}	2.85	2.92	

* The long axis of benzidine molecule is taken as Z axis.

From these calculations, we can predict the ionization potential as 7.0 and 6.8 eV respectively in benzidine and tetramethylbenzidine.[10] Substituting these values in Eq. (1) as well as in Eq. (2), we estimated the energy of the first charge-transfer band for the chloranil complexes of these amines. The energy of the second charge-transfer

9) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

*2 The procedures of SCF-MO calculation are described elsewhere.[10] The calculation was carried out by using HITAC 5020E at the computer center of The University of Tokyo.

10) T. L. Kunii and H. Kuroda, *Theoret. Chim. Acta*, **11**, 97 (1968).

band was estimated by assuming that its energy difference from the first band is equal to the separation between the highest occupied and second highest occupied orbitals of donor. The results are given in Table 2, which are in satisfactory agreement with the observations. Therefore we can conclude that, in the case of these complexes in solution, the first and second charge-transfer bands are associated respectively with the charge transfer from the highest occupied orbital of donor to the lowest vacant orbital of acceptor and that from the second highest occupied orbital of donor.

TABLE 2. CALCULATED AND OBSERVED FREQUENCIES OF THE FIRST AND SECOND CHARGE-TRANSFER BANDS OF BENZIDINE AND TETRAMETHYLBENZIDINE COMPLEXES WITH CHLORANIL IN SOLUTION (kK)

	Calcd		Obsd
	by Eq. (1)	by Eq. (2)	
Benzidine-Chloranil			
First CT band	13.2	13.2	14.2
Second CT band	22.1	22.0	22.0
Tetramethylbenzidine-Chloranil			
First CT band	12.1	11.8	11.7
Second CT band	20.4	20.2	19.7

In the molecular compound crystal, the electronic processes responsible for the charge-transfer bands could be different from those in the 1 : 1 complex in solution since a donor molecule is surrounded by several acceptor molecules in the crystal state. In this case, the charge transfer could take place from a donor molecule not only to the nearest acceptor molecule but also to the second nearest acceptor molecules or others. However, we can safely conclude that the first charge-transfer band of the crystal is associated with the charge transfer from the highest occupied orbital of donor molecule to the lowest vacant orbital of the nearest acceptor molecule since its excitation energy is a little lower than the first charge-transfer band of the corresponding complex formed in solution.

The situation is a little complicated in the second charge-transfer band. In the crystal of a typical charge-transfer compound, the donor and acceptor molecules are alternately stacked along one of the crystal axes. In such a case, an absorption band associated with the charge transfer from a donor molecule to the nearest acceptor molecule should be polarized parallel to this stacking axis unless it is markedly mixed with a local excitation. In effect the observed direction of polarization is in accord with this prediction for the first charge-transfer bands as well as for the second one in a variety of molecular compounds. However, in the molecular compounds of tetramethylbenzidine or benzidine with chloranil and in those with TCNQ, the second charge-transfer band in the crystal spectrum is polarized in the direction almost perpendicular to the polarization direction of the first charge-transfer band. This polarization of the second charge-transfer band could not be explained if we attribute the band to the charge transfer from a donor molecule to the neareast acceptor molecule as in the first charge-transfer band.*3

Presumably the second charge-transfer band is associated with the charge transfer from a donor molecule to the second-nearest acceptor molecule whereas the first one is associated with the charge transfer to the nearest acceptor molecule. If the distance of the second-nearest acceptor molecule from the donor is markedly larger than that of the nearest acceptor molecule, the band due to the charge transfer to the second-nearest acceptor molecule should be of extremely small intensity. This is not the case as can be seen in the spectra shown in Figs. 1—4. We have to consider therefore that the second-nearest acceptor molecule is also in a close contact with the donor molecule.

Then the large energy difference between the first and second charge-transfer bands could not be attributed to the difference in the Coulomb energy term only. A possible explanation would be as follows: the relative orientation of a donor molecule to the nearest acceptor molecule allows the charge transfer from the highest occupied orbital of donor to the lowest vacant orbital of acceptor, but not that from the next occupied orbital of donor, whereas the latter can effectively occur between a donor molecule and the second-nearest acceptor molecule. In other words, the second chrage-transfer band is mainly associated with the charge transfer from the second highest occupied orbital of a donor molecule to the lowest vacant orbital of the second nearest acceptor molecule. Thus the energy difference between the first and second charge-transfer band would be mainly determined by the energy difference between the highest two occupied orbitals of the donor. Anyway, the crystal structure analysis has to be carried out on one of these molecular compounds in order to clarify the validity of the above posturated explanation for the charge-transfer bands. It is now in progress in our laboratory on the tetramethylbenzidine-chloranil (1 : 1) compound.

The polarized crystal spectra of benzidine-TCNQ molecular compound shown in this paper was measured by Mr. S. Hiroma of our laboratory, to whom the authors' thanks are due.

*3 We can exclude the possibility that the first and second bands correspond to the factor group components of a single transition because they are separated from each other as large as 1 eV or more.