Electronic Spectra and Electrical Resistivities of the Molecular Complexes of Benzidine and Its Derivatives

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The electronic structures of about sixty polycrystalline molecular complexes of benzidine and its derivatives have been examined on the basis of the vibrational and electronic spectra. The complexes show a strong tendency to be non-ionic, in spite of the low ionization potentials of the electron donors. Several non-ionic complexes exhibiting resistivities of the order of 10^3—10^5 ohm cm have been found. The optical and electrical properties of the complexes consisting of donor molecules with amino groups and of acceptor molecules with carbonyl groups are distinctly different from those of the others. The first charge-transfer absorption band of the solid complex in the former group appears at an energy considerably lower than that of the corresponding complex in chloroform. Moreover, the activation energy for semiconduction seems to be appreciably reduced by the formation of a hydrogen bond.

On the basis of the electronic and vibrational spectra, it has been established that the crystal charge-transfer complexes can be rather sharply divided into two groups, namely, those having essentially non-bonding ground states (hereafter to be called "non-ionic complexes") and those having dative ground states("ionic complexes").[1-3] In general, an ionic complex may be formed when a donor molecule with a low ionization potential is combined with an acceptor molecule with a high electron affinity. However, one of the present authors has demonstrated that the electrostatic energy of the charged lattice is as important as the energy needed to charge the constituent molecules in governing the formation of an ionic crystal complex.[4] Among the donor compounds examined in our previous paper, tetramethylbenzidine was found to show a very strong tendency to form non-ionic complexes in spite of its low ionization potential, which has been estimated to be as low as 6.8 eV.[5] In connection with this observation, it is noteworthy that most of the noticeably semiconducting quinone complexes are ionic.[6] Furthermore, non-ionic complexes display relatively low resistivities only when the charge-transfer absorptions are located in an exceptionally low-energy region. The tetramethylbenzidine-*p*-chloranil complex, which has a resistivity of 10^7 ohm cm, is known to be such an example. Therefore, one may hope to have a good chance of examining the physical properties of a large number of non-ionic complexes exhibiting charge-transfer absorptions at unusually low energies by studying the crystal complexes of benzidine and its derivatives.

Experimental

Materials. The following five compounds, the ionization potentials of which are supposed to increase in the order of numbering, were used as donors: *N,N,N′,N′*-tetramethylbenzidine (I), *o*-tolidine (II), benzidine (III), *o,o′*-dibromo-*o*-tolidine (IV), and *o,o′*-dichloro-*o*-tolidine (V). The first three compounds were commercially obtained. They were purified by recrystallization and then by sublimation in a vacuum. The last two were prepared by the halogenation of compound II, as has been reported by Schlenk.[7] The fifteen acceptors used in this work were as follows: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (a), tetracyano-*p*-benzoquinodimethane (TCNQ) (b),[8] tetracyanoethylene (TCNE) (c), 2,3-dicyano-*p*-benzoquinone (d),[9] 2,3-dicyano-α-naphthoquinone (e),[10] 9-dicyanomethylene-2,4,7-trinitrofluorene (f), *p*-chloranil (g), 2,5-dichloro-3,6-dibromo-*p*-benzoquinone (h),[11] *p*-bromanil (i),[12] *p*-fluoranil (j), 2,5-dichloro-*p*-benzoquinone (k), 2,3-dichloro-*p*-benzoquinone (l),[13] 2,6-dichloro-*p*-benzoquinone (m), dichloro-*p*-xyloquinone (n),[14] and *s*-trinitrobenzene (TNB) (o). Their electron affinities decrease in approximately the above order. These compounds were obtained from commercial sources unless references are cited.

The molecular complexes were prepared by mixing the component compounds, previously separately dissolved in a hot solvent, usually benzene, chloroform, or dichloroethane. They were crystallized upon cooling or were precipitated immediately. Some ion-radical salts, the vibrational and electronic spectra of which were to be compared with those of the molecular complexes, were also prepared. The oxidation of the donor compounds was carried out with bromine according to the procedure of Hughes and Hush.[15] The acceptor compounds, a, b, d, and f, were reduced with the iodide ion following the methods reported by various workers.[2,16,17]

Measurements. The vibrational spectra of the crystal complexes were determined as Nujol mineral oil mulls with a Jasco IR-G infrared spectrophotometer, and the electronic spectra, with a Beckman DK-2A spectrophotometer with the

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[1] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963).

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[3] K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.*, **1965**, 2079.

[4] Y. Matsunaga, This Bulletin, **42**, 2490 (1969).

[5] T. Amano, H. Kuroda, and H. Akamatu, *ibid.*, **42**, 671 (1969).

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[12] H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).

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[14] E. Carstanjen, *J. Prakt. Chem.*, (2), **23**, 421 (1881).

[15] G. K. Hughes and N. S. Hush, *J. Proc. Roy. Soc. N. S. W.*, **81**, 48 (1947).

[16] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

[17] T. K. Mukherjee and L. A. Levasseur, *J. Org. Chem.*, **30**, 644 (1965).

aid of a reflectance attachment. The procedure in the latter measurements was similar to that described in our previous paper.[18] The charge-transfer absorption spectra were also examined in solution. The solvent used throughout was chloroform, Wako Special Reagent. As the present donor compounds dissolved in chloroform are easily oxidized with air, sample solutions were prepared immediately before measurements by dissolving appropriate amounts of the component compounds.

The resistivities up to 10^8 ohm cm were examined by a voltage-current method employing a cell similar to that designed by LaFlamme.[19] The temperature was adjusted in the range from 20 to 60°C using a heating tape wrapped around the cell and connected to a variable transformer.

Results and Discussion

Characterization of Complexes. The complexes were classified into two groups, namely, non-ionic and ionic complexes, on the basis of the vibrational spectra. This method was described in detail in a previous paper.[2] In short, when the vibrational spectrum of a complex is well approximated by a superposition of the spectra of the component compounds, the complex is considered to be non-ionic. If the spectrum consists of the spectra of the ionized components, namely, D^+ and A^- free-radical ions, the complex is characterized as ionic. The vibrational spectrum of the A^- ion is usually readily distinguishable from that of the A molecule; therefore, it is not difficult to characterize the complexes by this technique. The results of the characterization are presented in Fig. 1. In this diagram the complexes have been arranged by placing the ionization potentials of the donors on the abscissa and the electron affinities of the acceptors on the ordinate. As had been proposed earlier,[4] the energy of the charge-transfer absorption in the TNB complex, X, as determined in a chloroform solution, was taken as a measure of the former quantity, and that in the pyrene complex, Y, as a measure of the latter (see Eq. (1) in next section). The complexes which were found to be non-ionic are indicated by open circles, and those found to be ionic, by shaded circles. The following three, shown by shaded triangles, are of a complicated nature or are unstable: IIb, IIIc, and IIIg; therefore, they could not be well characterized. The complex IIb has a composition different from that calculated for 1 : 1, and it gives a vibrational spectrum which is too complicated to be considered as simply either non-ionic or ionic. A similar phenomenon has been disclosed by Ohmasa *et al.* in a closely related complex, benzidine-TCNQ, IIIb, when solvent molecules are occluded.[20] It has been known for a long time that benzidine forms a very unstable complex with *p*-chloranil.[21] Furthermore, this complex, IIIg, has been reported to be non-stoichiometric.[22]

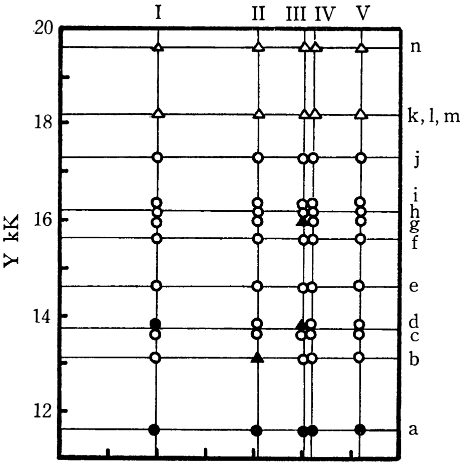

Fig. 1. Electronic structures of molecular complexes as revealed by the vibrational spectra. Non-ionic complexes are indicated by open circles and ionic ones by shaded circles. As to notations I—V, a—o and X and Y, see text.

For the combinations expressed by open triangles, no solid complex could be isolated. As may be seen in Fig. 1, most of the complexes examined in this work are non-ionic. The only exceptions are the DDQ complexes of I—V and the complex Id. These observations are in good accordance with our earlier view that the remarkably strong tendency to be non-ionic found in the tetramethylbenzidine complexes arises from the size and shape of this donor molecule, factors which are unfavorable to strong electrostatic interaction with acceptors.

Electronic Spectra. The energy of the charge-transfer absorption, $h\nu_{CT}$, in a non-ionic, 1 : 1 single complex may be written, as a good approximation:[23]

$$h\nu_{CT} = I_D - A_A - C' , \qquad (1)$$

where I_D is the ionization potential of the donor molecule and where A_A is the electron affinity of the acceptor molecule. The term C', the magnitude of which is known to be relatively insensitive to the kinds of donor and acceptor, arises largely from the electrostatic energy in the dative-bond structure. The complexes on the $Y = -X +$ constant line in Fig. 1 should all exhibit charge-transfer absorptions at nearly the same energy. The values of $h\nu_{CT}$, as estimated by the use of Fig. 1, are equal to:

$$\begin{aligned} & h\nu_{CT}(\mathrm{D \cdot TNB}) + h\nu_{CT}(\mathrm{pyrene \cdot A}) - h\nu_{CT}(\mathrm{pyrene \cdot TNB}) \\ & = I_D - A_A - C'(\mathrm{D \cdot TNB}) - C'(\mathrm{pyrene \cdot A}) \\ & + C'(\mathrm{pyrene \cdot TNB}) \, . \end{aligned} \qquad (2)$$

In Fig. 2, the $h\nu_{CT}$ values observed in chloroform solutions are plotted against the $h\nu_{CT}$ values estimated by the use of Eq. (2). The agreement is generally excellent; this confirms the assumption that the observed low-energy absorption is due to the charge-transfer from the donor molecule to the acceptor molecule. Double charge-transfer absorptions were recorded in

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19) P. M. LaFlamme, *Rev. Sci. Instrum.*, **35**, 1193 (1964).

20) M. Ohmasa, M. Kinoshita, and H. Akamatu, This Bulletin, **42**, 2402 (1969).

21) H. Fecht, *Ber.*, **41**, 2983 (1909).

22) H. Kusakawa and S. Nishizaki, This Bulletin, **38**, 2201 (1965).

23) H. M. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

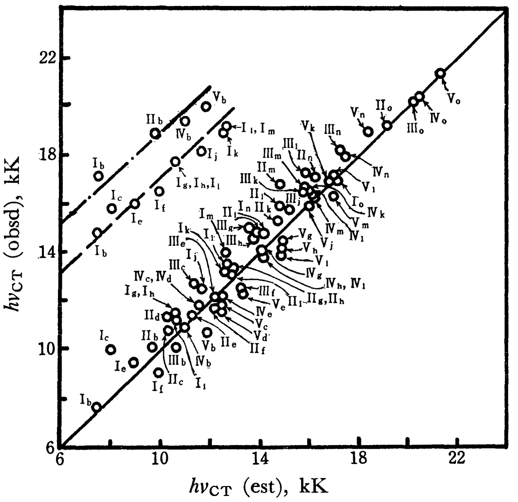

Fig. 2. Comparison between the observed energies of charge-transfer bands measured in solutions and the energies estimated by Fig. 1.

some combinations. The plot of the energy of the second absorption against the above-mentioned estimated $h\nu_{CT}$ values indicates that the second absorptions may be classified into two different classes. As one of them is characteristic of the complexes of tetramethylbenzidine, the absorption is apparently to be assigned to the charge-transfer from the second highest occupied orbital of the donor to the lowest vacant orbital of the acceptor. The absorption bands characteristic of the complexes of TCNQ form the other class. In this instance, the appearance of the second absorption is due to the charge-transfer from the highest occupied orbital of the donor to the second lowest vacant orbital of TCNQ. The average difference of 9.3 kK between the first and second bands in the TCNQ complexes is in agreement with the difference between the first and second transition energies in the TCNQ molecule as calculated by means of the molecular orbital method.[24] The existence of two classes in the second absorptions leads to the appearance of triple charge-transfer bands in the TCNQ complex of tetramethylbenzidine, as is shown in Fig. 3. The first band in the crystal complex is shifted to the low-energy side, and the second and third bands, to the high-energy side, compared to the corresponding bands observed in chloroform. An examination of Fig. 2 indicates that the third band is associated with the second lowest vacant orbital of TCNQ.

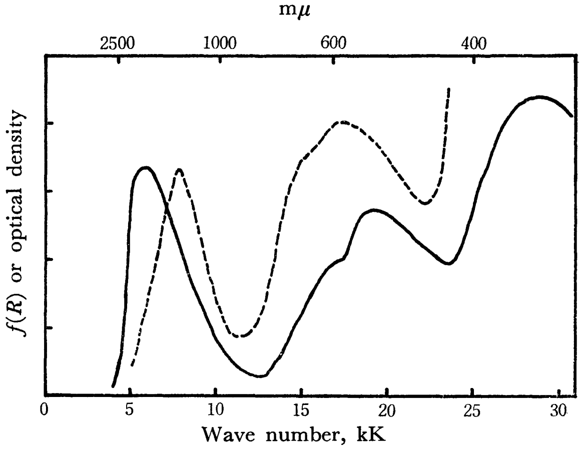

Fig. 3. Electronic spectra of tetramethylbenzidine-TCNQ in the solid state (——) and in a chloroform solution (----).

In Table 1 the energies of the charge-transfer absorptions of the solid complexes are summarized, along with the amounts of the shifts compared to the energies observed for the complexes in chloroform. As was noted in Fig. 1, the complexes with the acceptors, k, l, m, and n, could not be crystallized from the solution. For some of them, the charge-transfer absorptions in the solid phase could be measured with samples made by grinding together mixtures of the solid components. The energies obtained in this way are also presented in Table 1. Amano *et al.* have examined the polarized absorption spectra using single crystals of several complexes of benzidine and its tetramethyl derivative.[5,25] Their compounds include the following seven: Ib, Ig, Io, IIIb, IIIg, IIIk, and IIIo. The results given by Amano, which are cited for the sake of comparison in the footnote in Table 1, are in essential agreement with ours.

The first charge-transfer bands in all the solid complexes but Ij are shifted to the low-energy side if compared with those of the complexes in chloroform. A closer consideration of the amounts of the shifts shows that these non-ionic complexes must be further classified into two subgroups. With the donor I, the shifts are no more than 3.0 kK. Secondly, when the acceptor is not a quinone, the largest shift observed is 2.9 kK in the complexes Ic and IIb. Thus, the red-shifts found in this subgroup are usually small, and they may be explained in terms of a change in the surrounding molecules acting as a dielectric medium or by a change in the relative arrangement of the donor and acceptor molecules.[26,27] The second subgroup comprises complexes of quinones combined with the donors II—V, which bear unsubstituted amino groups. The red-shifts are quite substantial, ranging from 2.7 kK in the complex Vd to 6.0 kK in the complex Vn. In this respect, the complexes with *p*-fluoranil are quite exceptional; even a blue-shift was found in the complex Ij. The presence of amino groups in the donor molecules and carbonyl groups in the acceptor molecules induces the formation of hydrogen bonds in the crystal complexes. As it is a common feature that the donor and acceptor molecules are alternatively stacked, face-to-face, on each other along one of the crystal axes, the donor molecules linked to the acceptor molecules by hydrogen bonds should belong to different stacks. Thus, the effects of the hydrogen-bond formation, if any, must be observable only in the crystal complexes. A large red-shift of the charge-transfer absorption in quinhydrone as a result of the crystal-

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

[27] T. Matsuo and H. Aiga, *ibid.*, **41**, 271 (1968).

Table 1. The energies of charge-transfer absorptions in the solid complexes of benzidine and its derivatives and the amounts of shifts compared to those of the complexes in chloroform (in kK)

A	D				
	I	II	III	IV	V
b	5.9[a] (−1.8)	7.2 (−2.9)	8.0[b] (−2.1)	8.9 (−2.0)	9.1 (−1.6)
	16.9 (+2.1)	17.4	20.0	19.6 (+0.2)	20.0 (0.0)
	19.0 (+1.8)				
c	7.0 (−2.9)	9.8 (−1.1)	11.0 (−1.8)	9.9 (−1.9)	10.0 (−1.9)
	16.0 (+0.6)		24.6	20.5	21.0
d				9.0 (−2.8)	9.1 (−2.7)
				18.2	18.5
e	7.7 (−1.8)	8.0 (−3.4)	9.1 (−3.0)	6.7 (−5.5)	8.4 (−3.9)
	16.3 (+0.3)		20.2	18.7	19.0
f	8.7 (−0.4)	10.3 (−1.5)	11.5 (−1.0)	12.0	12.5
	17.3 (+0.8)		17.0		
g	9.5[c] (−1.9)	9.2 (−4.0)	[d]	9.1 (−5.0)	9.5 (−5.0)
	17.9 (−0.1)	19.7		20.5	20.8
h	8.4 (−3.0)	9.4 (−3.8)	9.8 (−4.8)	9.3 (−4.6)	9.6 (−4.7)
	17.7 (−0.1)	19.7	20.4	20.3	20.7
i	8.4 (−2.9)	9.1 (−4.0)		9.2 (−4.7)	9.9 (−4.3)
	17.5 (−0.3)	19.7		20.5	20.5
j	13.2 (+0.7)	13.9 (−0.9)	9.5[e]	14.5 (−1.2)	14.7 (−1.2)
	20.5 (+2.3)	23.2	20.4	24.1	26.0
k		12.3 (−3.1)	12.0[e] (−4.5)		
		25	25.3		
l	12.0 (−1.3)	12.1 (−3.8)			
	20.2	23			
m	13.3 (−0.2)			11.7 (−4.7)	11.8 (−4.5)
	22.5			22.9	
n	13.3 (−1.5)			13.7 (−4.3)	13.1 (−6.0)
o	16.2[f] (−0.8)	17.6 (−1.6)	19.0[g] (−1.2)	18.2 (−2.2)	19 (−2.3)
	24.0				

a) 7.5 and 16.5, b) 8 and 18, c) 8—9 and 18.3, d) 10 and 22.2, e) 12.5, f) 16.7 and 23.9, g) 18.3 and 26 were reported by Amano, Kuroda, and Akamatu, see Refs. 5 and 25.

lization has also been ascribed to the intermolecular hydrogen bond.[28]

The location of the second charge-transfer bands in the complexes of tetramethylbenzidine is only slightly affected by a change in the state. The nature of these absorptions has been speculated upon by Amano *et al.* on the basis of their measurements of the polarized absorption spectra.[5]

A striking resemblance between the spectra of the ionic DDQ complexes and the solid cation-radical salts derived from the donors should be mentioned. For example, the spectrum of the complex IVa is compared with that of solid *o,o'*-dichloro-*o*-tolidine bromide in Fig. 4. The latter is very similar to those of the solid bromides of benzidine, *o*-tolidine, and tetramethylbenzidine described in our earlier papers.[29,30]

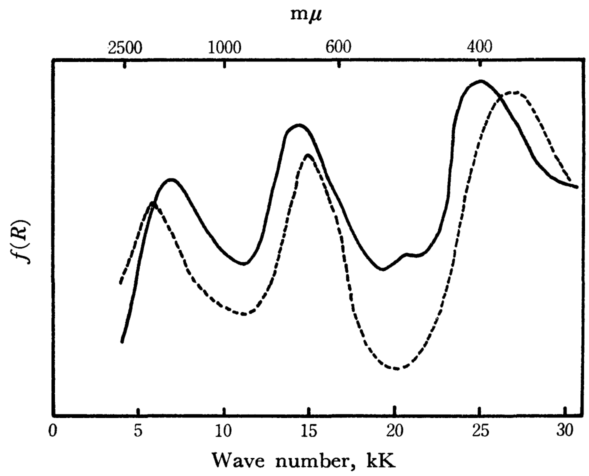

Fig. 4. Diffuse reflection spectra of dichloro-*o*-tolidine-DDQ (——) and dichloro-*o*-tolidine bromide (----).

The electronic spectra of ion-radical salts have been known to depend considerably upon the mode of intermolecular interaction. The spectrum shown in Fig.

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28) T. Amano, H. Kuroda, and H. Akamatu, Preprint of the 21th Annual Meeting of the Chemical Society of Japan, 19222 (1968).

29) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

30) A. Hakusui, Y. Matsunaga, and K. Umehara, *ibid.*, **43**, 709 (1970).

Table 2. Electrical resistivities (in ohm cm) at room temperature and activation energies for semiconduction (in eV) of the solid complexes of benzidine and its derivatives

A	D				
	I	II	III	IV	V
a	6×10^3	1×10^3 [a]	6×10^3	2×10^3	7×10^3
b	2×10^6 0.36	2×10^4	5×10^6 0.38	3×10^6 0.27	2×10^7 0.42
c	2×10^8	8×10^8 0.51 (10^{16}) [b]	2×10^8 0.53 (10^{14} 0.71) [b]	6×10^8 0.43	5×10^7 0.38
d		2×10^3		5×10^4 0.27	8×10^4 0.30
e		2×10^5 0.13	7×10^5 0.31	4×10^7 0.31	1×10^7 0.36
g	9×10^7 0.49 (10^7) [c]	4×10^6 0.20 (4×10^9 0.53) [b]		1×10^8 0.21	6×10^7 0.27
h	3×10^7 0.56	5×10^7 0.39		4×10^7 0.40	7×10^7 0.38
i	1×10^6 0.50 (10^8) [d]	3×10^8		2×10^7 0.30	2×10^7 0.31
j	(10^{12}) [c]				
o	(1×10^{17} 0.81) [e]				

a) The initial value in the measurement because of the slow but steady increase on standing.
b) By Kusakawa and Nishizaki, Ref. 22.
c) By Schwarz, Davies and Dobriansky, Ref. 32.
d) By Matsunaga, Ref. 6.
e) By Kuroda, Yoshihara and Akamatu, Ref. 26.
f) By van der Hoek, Lupinski and Oosterhoff, Ref. 31.

4, which bears no resemblance to either the monomer or dimer spectrum and which is extended into a lower-energy region, is assigned to the cation-radicals in a strong more-than-by-pairs interaction. Consequently, we may conclude that the ionized donor molecules in these DDQ complexes strongly interact with each other. Such an interaction is possible, even if the donor and acceptor molecules are alternately stacked, because of the rather large difference in the size and shape of the component molecules.

Electrical Properties. The electrical resistivities, ρ, at room temperature and the activation energies for semiconduction, E_a, as defined by

$$\rho = \rho_0 \exp(E_a/kT) \qquad (3)$$

are presented in Table 2, along with the values appearing in the literature.[6,22,26,31,32] The ionic DDQ complexes exhibiting resistivities of the order of 10^3 ohm cm are the most conductive ones in the present series of complexes. Nevertheless, it must be noted that the non-ionic complexes can be as conductive as the ionic ones if the component molecules are properly chosen. Their resistivities are continuously distributed from 10^3 ohm cm on upward; one in the order of 10^3, IId, three in the order of 10^4, IIb, IVd, and Vd, and two in the order of 10^5, IIe and IIIe. Thus, the resistivity of a complex seems to be very much determined by the acceptor. The complexes of the acceptors d and e tend to exhibit low resistivities. On the other hand, the TCNE complexes have resistivities of the order of 10^7 or 10^8 ohm cm, and the complexes of the acceptors f and j—o have resistivities higher than our upper limit, 10^8 ohm cm.

The electronic spectra and electrical resistivities in the series of the TCNE complexes and also the TNB complexes have been examined by Kuroda *et al.*[26,33] They have pointed out that $2E_a$, the energy gap if the conduction is intrinsic, is approximately equal to the energy of the charge-transfer absorption in the crystal complex. The empirical relation between these two quantities may be expressed, in general, by this equation:

$$2E_a = h\nu_{\mathrm{CT}}(\text{solid}) - \Delta\,, \qquad (4)$$

where Δ is nearly constant in a series of molecular complexes with a given acceptor if the donor molecules are of the same type. The magnitude of Δ varies within a rather narrow range, *e.g.*, 0.2 eV for the TNB complexes of aromatic amines. In Fig. 5, we plotted twice the activation energy for semiconduction against the energy of the first charge-transfer absorption given in Table 1. The complexes in the first subgroup are indicated by open circles, and those in the second, by shaded circles.

Another result which seems to be the consequence of the hydrogen bonding is clearly demonstrated here; that is, considerable deviations from Eq. (4) are observed with the complexes in the latter subgroup. The direction of the deviation is in accordance with the conclusion by Gravatt and Gross that an extended intermolecular overlap resulting from the hydrogen bonding produces a decrease in the activation energy for semiconduction.[34] However, their resistivities are close to those of the corresponding complexes of

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[31] J. A. van der Hoek, J. H. Lupinski, and L. J. Oosterhoff, *Mol. Phys.*, **3**, 299 (1960).

[32] M. Schwarz, H. W. Davies, and B. J. Dobriansky, *J. Chem. Phys.*, **40**, 3257 (1964).

[33] H. Kuroda, M. Kobayashi, M. Kinoshita, and S. Takemoto, *ibid.*, **36**, 457 (1962).

[34] C. C. Gravatt and P. M. Gross, *ibid.*, **46**, 413 (1967).

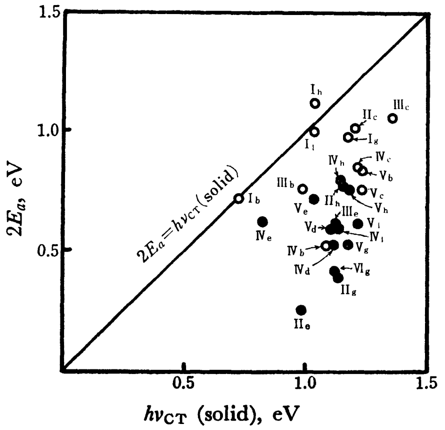

Fig. 5. Plot of twice the activation energy for semiconduction against the energy of the first charge-transfer band in solid complex. As to the meaning of open and shaded circles, see text.

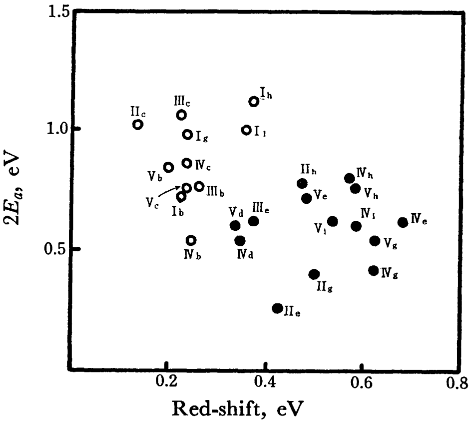

Fig. 6. Classification of molecular complexes on the basis of twice the activation energy for semiconduction and the amount of red-shift in the first charge-transfer band caused by crystallization.

tetramethylbenzidine. The decrease in the activation energy is apparently compensated for by an increase in the preexponential factor in Eq. (4), ρ_0. As the hydrogen bonding causes; (i) a large red-shift in the first charge-transfer band by crystallization and (ii) a substantial decrease in the activation energy for semiconduction, the molecular complexes can be quite distinctly divided into the two subgroups in a diagram such as that shown in Fig. 6. However, the mechanisms involved in these electronic processes are yet unknown.