Semiconductivities and Charge Transfer Spectra of Solid Molecular Complexes of 1, 3, 5-Trinitrobenzene

By Haruo KURODA, Keitaro YOSHIHARA and Hideo AKAMATU

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The solid molecular complexes formed by the interaction of polycyclic aromatic hydrocarbons with halogens are semiconductors of a high electrical conductivity[1]. In such molecular complexes, a charge transfer interaction between the molecules contributes to the solid formation, where halogen molecules behave as electron acceptors, while hydrocarbon molecules behave as electron donors. These solid molecular complexes exhibit a strong electron spin resonance absorption[2,3], which indicates a strong electron transfer from the donor to the acceptor molecules. There are, however, a number of charge transfer complexes which do not show any appreciable electron spin resonance absorption. In such molecular complexes, the intermolecular charge transfer between donor and acceptor molecules is relatively weak in the ground state. In these cases, Mulliken's theory of charge transfer interaction can be successfully applied to a discussion of the electronic state[4]. We shall temporarily call such complexes by the name of "loose molecular complexes". The complexes formed from polycyclic aromatic hydrocarbons, as the donor, and tetracyanoethylene or 1, 3, 5-trinitrobenzene (TNB), as the acceptor, are of this kind.

In a previous paper[5], we have shown, with a series of tetracyanoethylene-complexes, that the energy gap, twice the activation energy for the electrical conduction, determined from the temperature dependence of the electrical resistivity is approximately equal to the energy corresponding to the peak of the charge transfer band in the absorption spectrum of the crystal. In order to explain such a result, we presumed that a charge carrier is produced through a charge transfer from a donor to an acceptor molecule. If this is actually the case, a similar relation will be found with other loose molecular complexes. It seems, therefore, of interest to compare the activation energy for the electrical conduction with the frequency of the charge transfer band observed with such other loose molecular complexes as TNB-complexes.

Experimental

The TNB-complexes, in which the mole ratios of the donors to TNB were 1 : 1, were prepared by cooling hot solutions containing equivalent amounts of the donors and of TNB. The crystals of the complexes usually precipitate as fine needles.

The electrical resistivity of each complex was measured by the D. C. method. A crystalline powder of the complex was packed in a quartz cell, and the resistivity was measured under a compression of 116 kg./cm². The field applied externally for the resistivity measurement was below 2000 V./cm., where the resistivity obeyed Ohm's law. The temperature dependence of the resistivity was studied in a range from room temperature to a little below the melting point.

The visible and ultraviolet absorption spectra of the crystalline powders were measured by means of the KBr-pellet method with a Cary spectrophotometer.

Results

Absorption Spectra. — The absorption spectrum of the solid complex formed between *N, N, N′, N′*-tetramethylbenzidine and TNB is shown in Fig. 1. The absorptions at wavelengths shorter than 500 mμ can be assigned to the excitation of either the donor or the TNB molecules, while the band extending from 500 to 800 mμ is the characteristic absorption band for the complex formation. Almost every

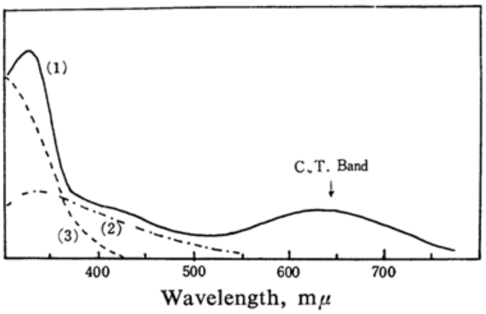

Fig. 1. Absorption spectrum of tetramethylbenzidine-TNB complex in the crystalline state: (1) solid complex, (2) tetramethylbenzidine (solid), (3) TNB (solid).

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1) H. Akamatu, H. Inokuchi and Y. Matsunaga, This Bulletin, 29, 219 (1956).

2) Y. Matsunaga, *J. Chem. Phys.*, 30, 855 (1959).

3) L. S. Singer and J. Kommandeur, ibid., 34, 133 (1961).

4) R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

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

TABLE I. CHARGE TRANSFER SPECTRA OF TNB-COMPLEXES

Donor	Ionization potential of donor eV.	Solution (in CCl_4) $\tilde{\nu}_{max}$ 10^3 cm^{-1}	Crystal $\tilde{\nu}_{max}$ 10^3 cm^{-1}	$\Delta\tilde{\nu}$ ($=\tilde{\nu}$(soln.)$-\tilde{\nu}$(solid)) 10^3 cm^{-1}
Anthracene	7.55[a]	22.5	20.4	2.1
			21.5	1.0
			22.6	−0.1
Phenanthrene	8.03[a]	26.8	24.3	2.5
Pyrene	7.55[b]	22.5	21.5	1.0
Chrysene	7.8[b]	23.3	22.5	0.8
Perylene	7.15[b]	19.6	18.0	1.6
Anthanthrene	(7.1)[c]	18.5	17.9	0.6
Aniline	7.70[d]	25.0	22.7	2.3
Dimethylaniline	7.3[b]	20.9	19.6	1.3
Benzidine		20.0	17.6	3.4
Tetramethylbenzidine		17.1	16.0	1.1
p-Phenylenediamine	7.15[b]	20.0	17.3	2.7
α-Naphthylamine		21.7	20.9	0.8

a) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1958 (1959).
b) D. Brieglebs and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).
c) F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).
d) K. Watanabe and J. R. Mottl, ibid., **26**, 1773 (1957).

solid complex studied here has such a characteristic band, which is always very broad and without any fine structure, the width at half of the intensity maximum being more than 8000 cm^{-1} in wave number. The solid complex of anthracene was found to be an exception in this respect; it showed an absorption band with a fine structure which we shall mention later.

The wavelength at the peak of the characteristic band is given in Table I, together with the wavelength of the charge transfer band observed with the carbon tetrachloride solution of the complex. McGlynn and Boggus[6] have shown that the frequency of the charge transfer band of TNB-complexes of polycyclic aromatic hydrocarbons in solutions is linearly dependent on the ionization potential of the donor. The frequency of the charge transfer band in carbon tetrachloride, $\nu_{C.T.}$(soln.), given in Table I, can be described as:

$$h\nu_{C.T.}(\text{soln.}) = 0.85 I_p - 3.65 \quad [\text{eV.}] \qquad (1)$$

where I_p is the ionization potential of the donor. The relation between the frequency of the characteristic band of the solid complexes, $\nu_{C.T.}$(solid), and the ionization potential of the donor can also be described by a similar equation:

$$h\nu_{C.T.}(\text{solid}) = 0.85 I_p - 3.82 \quad [\text{eV.}] \qquad (2)$$

The regularity mentioned above implies, in the first place, that the characteristic absorption bands observed with the solid complexes are also due to the excitation associated with a charge transfer from the donor to the TNB molecules, and that, in the second place, the energy of the charge transfer excitation is, in the crystalline state, lower by an average of 0.17 eV. than that of the isolated complex in carbon tetrachloride. In other words, we can consider that the charge transfer band shows a red-shift as a result of the crystallization. The magnitude of the red-shift in each complex is given in the last column of Table I.

The absorption spectrum of the solid complex of anthracene-TNB is shown in Fig. 2. The absorption in the wavelength region of 400∼500 mμ is the charge transfer band. In this band we can observe three peaks separated from each other by 1070 cm^{-1}. Lower, Hochstrasser, and Reid[7] have observed the absorption spectrum of a single crystal of

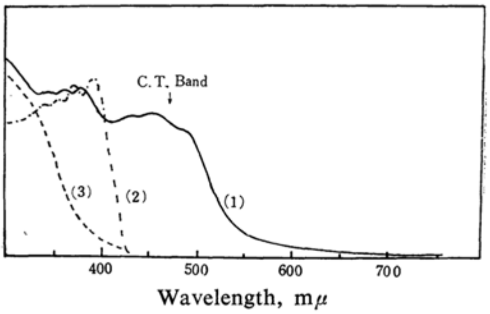

Fig. 2. Absorption spectrum of anthracene-TNB complex in the crystalline state: (1) solid complex, (2) anthracene (solid), (3) TNB (solid).

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[6] S. P. McGlynn and J. D. Boggus, *J. Am. Chem. Soc.*, **80**, 5096 (1958).

[7] S. K. Lower, R. M. Hochstrasser and C. Reid, *Mol. Phys.*, **4**, 162 (1961).

anthracene-TNB at the temperature of liquid nitrogen and have found a similar fine structure in the change transfer band. They assigned the fine structure to the TNB-ring stretching vibration, 1070 cm^{-1}, an intermolecular vibration, 250 cm^{-1}, and their combinations. This fine structure can be observed in the crystalline state only; the charge transfer band in the absorption spectrum of the complex in solution shows no structure.

Electrical Resistivity. — All the TNB-complexes studied here are poor semiconductors, exhibiting an electrical resistivity of $10^{13}\sim10^{20}$ $\Omega\cdot$cm. at room temperature. As is known to be the case for many organic semiconductors, the resistivity is exponentially dependent on the reciprocal of the temperature. A typical example of the temperature dependence is given in Fig. 3. The resistivity can be described, therefore, with the following equation:

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

where E is the activation energy for the electrical conduction, and ρ_0 is a constant. The experimental results are summarized in Table II. It is to be noted that the activation energy required for the electrical conduction

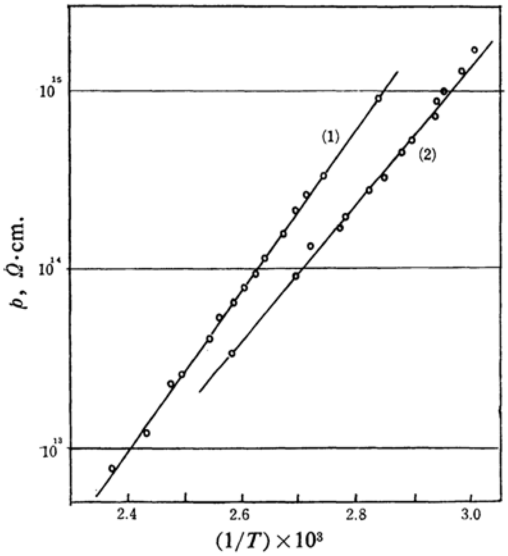

Fig. 3. Temperature dependence of the electrical resistivity: (1) anthracene-TNB, (2) tetramethylbenzidine-TNB.

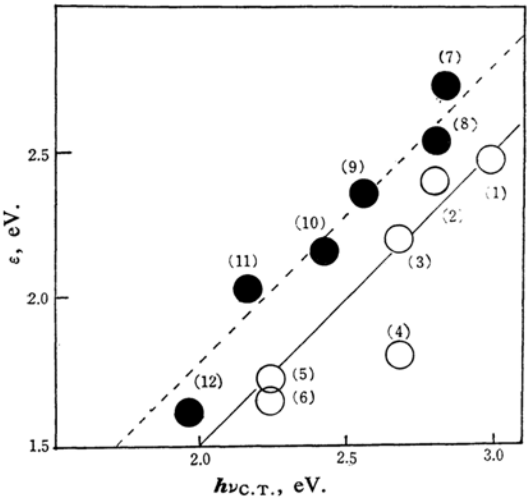

Fig. 4. Energy gap and energy of charge transfer excitation: (1) TNB complexes of phenanthrene, (2) chrysene, (3) pyrene, (4) anthracene, (5) anthanthrene, (6) perylene, (7) p-chloroaniline, (8) aniline, (9) α-naphthylamine, (10) N,N'-dimethylaniline, (11) p-phenylenediamine, (12) N,N,N',N'-tetramethylbenzidine.

—— $\varepsilon=h\nu-0.5$ [eV.]

---- $\varepsilon=h\nu-0.2$ [eV.]

TABLE II. ELECTRICAL RESISTIVITIES OF TNB-COMPLEXES

Donor	$\rho_{(15°C)}$ $\Omega\cdot$cm.	ρ_0 $\Omega\cdot$cm.	Activation energy E eV.	Energy gap ε eV.	Energy of C.T. excitation $h\nu_{C.T.}$ eV.
Anthracene	9×10^{17}	3×10^{1}	0.9	1.8	2.53
Phenanthrene	7×10^{18}	1×10^{-4}	1.24	2.48	3.01
Pyrene	1×10^{20}	2	1.10	2.20	2.66
Chrysene	7×10^{18}	2×10^{-3}	1.20	2.40	2.78
Perylene	1×10^{19}	5×10^{3}	0.83	1.66	2.23
Anthanthrene	1×10^{18}	2×10^{2}	0.86	1.72	2.22
Violanthrene	5×10^{13}	2×10^{3}	0.57	1.14	—
N,N,N',N'-Tetramethylbenzidine	1×10^{17}	2×10^{2}	0.81	1.62	1.98
Aniline	1×10^{17}	4×10^{-7}	1.27	2.54	2.82
p-Phenylenediamine	8×10^{16}	2×10^{2}	1.02	2.04	2.14
p-Chloroaniline	5×10^{13}	5×10^{-12}	1.36	2.72	2.82
N,N-Dimethylaniline	1×10^{16}	7×10^{-4}	1.04	2.08	2.42
α-Naphthylamine	3×10^{7}	1×10^{-4}	1.18	2.36	2.58

is very high in TNB-complexes, being comparable with or even higher than that of the donor hydrocarbons.

In Fig. 4, the energy gap, twice the activation energy for the electrical conduction, is plotted against the energy of the charge transfer excitation as determined from the frequency at the peak of the charge transfer band in the solid state. It can easily be seen in Fig. 4 that there is a very close correlation between these two values. They agree well with each other in the complexes formed with aromatic amines. In hydrocarbon-TNB complexes, the energy gap is a little lower than the energy of the charge transfer excitation, although there is a linear relation between them; it coincides, rather, with the absorption edge.

Discussion

In a previous paper⁵⁾ we have pointed out that, in several solid complexes formed between TCNE and polycyclic aromatic hydrocarbons, the energy gap, ε, determined from the temperature dependence of the electrical resistivity agrees well with the energy of the charge transfer excitation measured from the wavelength at the peak of the charge transfer band. We have confirmed in the present study that these two values are also closely related with each other in many TNB-complexes. We can not say, however, that they exactly equal one other. The relation between them may be expressed in general by the following equation:

$$\varepsilon = h\nu_{\mathrm{C.T.}}(\mathrm{solid}) - \Delta \tag{4}$$

where Δ is nearly constant in a group of molecular complexes with a fixed acceptor if the donors are molecules of a same type. The average value of Δ is -0.1 eV. in polycyclic aromatic hydrocarbon-TCNE complexes, and 0.2 and 0.5 eV. in TNB-complexes of aromatic amines and in those of polycyclic aromatic hydrocarbons respectively.

Although we have compared here the energy gap with the energy corresponding to the absorption maximum, there is no theoretical reason to take that energy figure instead of the energy of the absorption edge, which is lower than the other by about 0.5 eV. in these solid complexes. We can say that, in the molecular complex mentioned above, the energy gap is equal to or a little higher than the energy of the absorption edge.

If we presume that the band model can be applied to the electronic state of the crystal of the molecular complex, and that the absorption spectrum is associated with an excitation of an electron from the highest filled energy band to the conduction band, the experimental results mentioned above can be explained rather simply. In such a case, the highest filled band may be supposed as one formed from the overlapping between the highest filled molecular orbitals of the donor molecules, and the lowest conduction band, from that of the lowest empty molecular orbitals of the acceptors. Therefore, the excitation of an electron from the filled band to the conduction band corresponds to the transfer of an electron from the donor to the acceptor; hence it is a charge transfer. According to this model, the thermal excitation needed to produce the charge carriers will be identical in its nature with the charge transfer excitation in the optical process.

It is questionable, however, whether or not the observed spectrum is actually associated with such a "band-to-band" excitation as has been postulated above. The energy of the charge transfer excitation in a (1:1)-complex formed in solution can be expressed by the following equation, providing the charge transfer interaction is very weak:

$$h\nu_{\mathrm{C.T.}} = I_{\mathrm{p}} - A - (e^2/\overline{R}_{\mathrm{D^+\cdot A^-}}) - \Delta W \tag{5}$$

where I_{p} is the ionization potential of the donor, A, the electron affinity of the acceptor, $\overline{R}_{\mathrm{D^+\cdot A^-}}$, the average distance between the positive and the negative charges in the excited state, and ΔW, the energy difference which is not given by the first three terms of this equation. It can be seen that the Coulomb interaction makes quite a large contribution to determining the magnitude of $h\nu_{\mathrm{C.T.}}$. In the crystal, on the other hand, if the electron excited from a donor molecule is not localized on the neighboring acceptor molecule, but occupies an orbital that is a little more extended over the crystal lattice, a marked decrease in the Coulomb term will result, which decrease will contribute to a blue-shift of the charge transfer band of the crystal from that of the solution. On the other hand, if the excited electron remains localized on the neighboring acceptor molecule, forming an ion pair, and if the surrounding molecules affect it as a dielectric medium, a red-shift is to be expected, since the charge transfer band of the solution is known to make a red-shift, as the refractive index of the medium is higher⁸⁾.

The wavelength of the charge transfer band in the solid complex can be determined by balancing these two opposing effects. The observation that the energy of the charge transfer excitation in the crystalline state is a

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8) J. Czekalla and K.-O. Meyer, *Z. physik. Chem. N. F.*, 27, 185 (1961).

little lower in TNB-complexes than the corresponding energy of a (1 : 1)-complex in carbon tetrachloride, suggest that it is not a delocalized electron, but an neighboring ion pair, that is produced in the crystal by the charge transfer absorption. It has also been suggested by Lower, Hochstrasser and Reid(7), on the basis of their studies of the vibrational structure and of the Davydov splitting of the charge transfer band of a single crystal of anthracene-TNB complex, that the exciton in this crystal is an ion pair localized at a lattice position for a relatively long time.

if the charge transfer state in the crystal is such a one as has been discussed above, the charge carriers may not be produced directly through such an excitation process; consequently, the energy of the charge transfer need not coincide with the energy gap as determined from the electrical conduction. We can imagine a number of electronic states which can contribute to the electrical conduction in a crystal of a loose molecular complex. Let us consider a widely separated ion pair. If the distance between a positively-charged donor molecule and a negatively-charged acceptor molecule is so large that the electrostatic interaction between them is completely negligible, the positive charge can change its position from one donor molecule to another donor molecule without requiring additional energy, or at least, with a small activation energy. The same can be said about the movement of the negative charge on acceptor molecules. Thus, the widely separated ion pair can contribute to the electrical conduction. This will be the lowest conduction state; hence, the energy necessary to produce a widely separated ion pair will be equal to the energy gap. This energy can be estimated by the following energy cycle: a donor molecule is taken out from the crystal to the vacuum, then ionized and returned into the original lattice position, and a similar procedure is true for an acceptor molecule at a lattice position sufficiently separated from the positive ion of the donor. The total work necessary to complete such a process, or the energy gap, can be described as:

$$\varepsilon = I_p - A - (W_p^+ + W_p^-) \qquad (6)$$

where W_p^+ and W_p^- represent the polarization energy arising from the positive and negative ions respectively. On the other hand, the energy required to form a neighboring ion pair in the crystal can be expressed by Eq. 5. Therefore, the relation between the energy gap and the energy of the charge transfer can be expressed as:

$$\varepsilon = h\nu_{\mathrm{C.T.}} - \delta \qquad (7)$$

$$\delta = (W_p^+ + W_p^-) - (e^2/\overline{R}_{D^+\cdot A^-} + \Delta W)$$

If the donors are molecules of a same type in a series of the complex of an acceptor, $(W_p^+ + W_p^-)$ will not change very much. δ will be nearly constant in this case. The value of δ seems to be less than 1 eV. in TNB-complexes. According to this model, ε is not necessarily equal to $h\nu_{\mathrm{C.T.}}$, although it is linearly dependent on the other. The model given above seems to give a probable explanation for the experimental results.

Summary

A series of solid complexes of aromatic hydrocarbons and amines, with 1, 3, 5-trinitrobenzene as the common electron acceptor, were prepared. These complexes were of the loose molecular complex type, and the charge transfer bands were observed with the solid complexes, which showed only small red-shifts from the corresponding bands of the solutions. These solid complexes are poor semiconductors, and the energy gap for the excitation to the conduction state is relatively large, and is nearly coincident with the energy for the charge transfer excitation. From these results, it has been suggested that the charge transfer state in the crystal may not be very different from the corresponding state in the isolated (1 : 1)-complex in the solution. The relation between the charge transfer state and the conduction state has been discussed, and a probable model for the formation of a charge carrier has been suggested.

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo