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Solvent Inclusion Effects on the Structure and Electrical Conductivity of Benzidine-TCNQ Complex

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The solvent-containing modification of benzidine (BD)-tetracyanoquinodimethane (TCNQ) complex is a new type of inclusion compound where solvent molecules are included in the channels of the host lattice formed by hydrogen bonding and charge-transfer interaction between BD and TCNQ. The electrical conductivity at 18 °C is 7×10^{-10} ohm$^{-1}\cdot$cm^{-1} and the activation energy of semiconduction is 0.54 eV in the solvent-free state, but they change to 10^{-4}—10^{-6} ohm$^{-1}\cdot$cm^{-1} and 0.1—0.2 eV, respectively, when an aliphatic solvent is included, and to 10^{-6}—10^{-9} ohm$^{-1}\cdot$cm^{-1} and 0.3—0.5 eV, when benzene or its derivatives is included. By examining the changes of the electrical conductivity and the spin density of BD$\cdot$TCNQ$\cdot$[CH_2Cl_2] system with the pressure change of the ambient dichloromethane vapor, it is concluded that the conductivity of BD$\cdot$TCNQ$\cdot$[CH_2Cl_2] is strongly controlled by the amount of solvent vacancies in the crystal lattice. The correlations between the electrical properties and crystal structures of solvent-containing modifications are discussed.

In the earlier investigations by Ohmasa *et al.*[1] it was first found that the electronic properties of the solid molecular complex between benzidine (BD) and tetracyano-*p*-quinodimethane (TCNQ) were significantly dependent on the solvent used in the preparation of the crystals, and these phenomena were concluded to be due to the solvent inclusion in the crystal lattice of BD$\cdot$TCNQ complex. They reported that dichloromethane, 1,2-dichloroethane, dibromomethane, bromoethane, acetonitrile, nitromethane and acetone were able to be included in BD$\cdot$TCNQ complex, while chloroform and 1,1-dichloroethane were not.

Later, we found that a variety of aromatic solvents such as benzene, chlorobenzene, bromobenzene, toluene, benzonitrile and nitrobenzene can be included in BD$\cdot$TCNQ complex. By carrying out crystal structure analysis on the solvent-free modification as well as on several solvent-containing modifications, we have concluded that the solvent-containing modifications of BD$\cdot$TCNQ complex are to be regarded as a new type of inclusion compound where the hydrogen bonding and charge-transfer interaction between donor and acceptor molecules are playing an important role in the formation of the channeled structure of the host lattice.[2-4]

In the present paper, we report the effects of the solvent inclusion on the electrical conductivity of the BD$\cdot$TCNQ system, and their relations with the crystal structures.

Experimental

The solvent-containing modifications of BD$\cdot$TCNQ complex were obtained by the following procedures; an appropriate amount of benzidine was dissolved in a hot solution which had been almost saturated with TCNQ, and this solution was gradually cooled and kept at room temperature for about one day yielding the crystals of BD$\cdot$TCNQ complex from the solution. The solvent-free modification was prepared by the same method using chloroform as the solvent.

Since the included solvent is gradually lost when a crystal of a solvent-containing modification is kept in the ordinary atmosphere at room temperature, we took out the crystals from their mother solutions immediately before each experiment.

The X-ray diffraction patterns of the powder samples were observed with a diffractometer, Geigerflex. The presence of the included solvent was examined by thermogravimetric analysis (TG) combined with differential scanning calorimetry (DSC), which were carried out with a Rigaku TG-DSC apparatus. The infrared absorption spectra were examined by use of Nujol mull method.

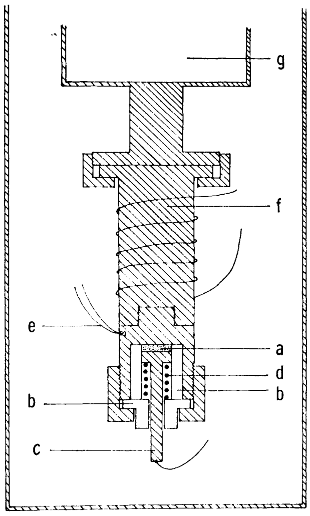

Fig. 1. Apparatus for conductivity measurement: (a) sample, (b) Teflon cylinder, (c) electrode, (d) spring, (e) thermo-couple (Cu-constantan), (f) heat-conductor with a heater, (g) liquid N_2.

The DC conductivity of each modification was measured on a polycrystalline sample by using the apparatus illustrated in Fig. 1. The crystalline powder[5] was packed in the sample cell, and compressed to a polycrystalline disc between the electrodes using a pressure of about 16 kg$\cdot$cm^{-2}. In this way, the sample was tightly sealed in the cell so as to prevent the evolution of the included solvent during the measurement. To minimize the solvent evolution, we carried out the measurement only at lower temperatures. The size of the polycrystalline disc of the sample was measured after the conductivity experiment. Typically, it was about 8 mm in diameter and about 0.5 mm thick. Applying a DC voltage of 1—20 volt between the electrodes, we measured the current through the sample with an electrometer, Takeda Riken TR-8651.

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Results and Discussion

Structural Aspects of Solvent Inclusion. From the examination of the powder X-ray diffraction patterns of various modifications of BD·TCNQ complex, with and without solvent inclusion, we concluded that there are, at least, three different types of crystal lattice for the BD·TCNQ system: The first one (Type I) is the crystal lattice of the solvent-free modification, BD·TCNQ·[n], the second one (Type II) is that of a modification containing an aliphatic solvent, and the third one (Type III) is that of a modification containing an aromatic solvent.

We have carried out the crystal structure analysis on a representative example of each of the above three types; the solvent-free modification, BD·TCNQ·[n], as Type I, the one containing dichloromethane, BD·TCNQ·[CH_2Cl_2], for Type II, and the one containing benzene, BD·TCNQ·[C_6H_6], for Type III. The details of the crystal structure analysis of each modification have been separately reported elsewhere.[2–4] In the crystal of BD·TCNQ·[n],[3] benzidine and TCNQ molecules are alternately stacked on each other to form molecular columns along the c-axis, and those molecular columns are closely packed together without leaving any free space to accommodate solvent molecules.

The crystal structure of BD·TCNQ·[CH_2Cl_2] is reproduced in Fig. 2.[2] Benzidine and TCNQ molecules are alternately stacked on each other to form molecular columns which are almost the same as in BD·TCNQ·[n], but these columns are arranged so as to leave channels running through the crystal along the c-axis, in which solvent molecules are accommodated. There seems to be no specific interaction between the included dichloromethane molecules and the BD·TCNQ host lattice.

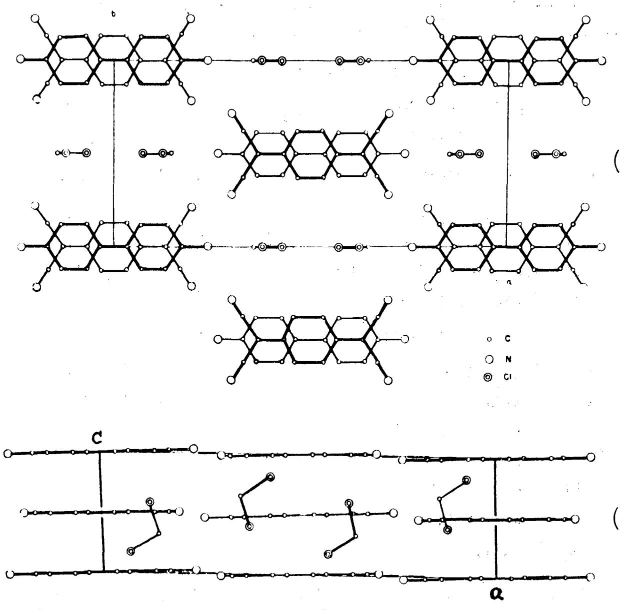

Fig. 2. Crystal structure of BD·TCNQ·[CH_2Cl_2]. (a) projection to the (001) plane, (b) projection to the (010) plane.

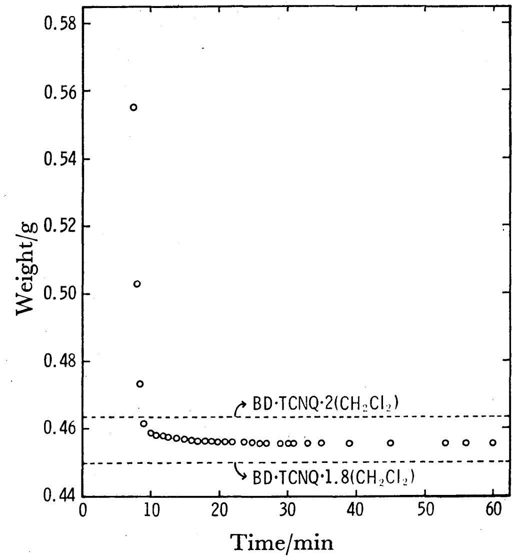

Fig. 3. Weight change of BD·TCNQ·[CH_2Cl_2] powder in the ordinary atmosphere, starting from the state wet with dichloromethane liquid. Note that the weight settles at the value corresponding to BD·TCNQ·1.8 (CH_2Cl_2), and remains the same after that. The mole ratio was calculated from the weight loss of the sample heated in vacuum.

According to the crystal structure, the ideal composition of the BD·TCNQ·[CH_2Cl_2] system is to be BD·TCNQ·2(CH_2Cl_2), but the actual composition was BD·TCNQ·1.8(CH_2Cl_2) under normal conditions. This means that about 10 percent of dichloromethane molecules are missing from the crystal lattice of BD·TCNQ·[CH_2Cl_2] creating the corresponding amount of vacancies at the solvents sites without producing any significant distortion of the host lattice. When the crystalline powder of BD·TCNQ·[CH_2Cl_2], which was wet with an excess dichloromethane, was kept in the ordinary atmosphere, the amount of the included solvent changed with time as shown in Fig. 3. The amount of the included solvent decreased to the value corresponding to BD·TCNQ·1.8(CH_2Cl_2), and thereafter it stayed at the same value for a long period. Further loss of the included solvent took place when the powder was heated to about 60 °C in vacuum, but, in this case, the solvent evolution was accompanied by conversion

TABLE 1. CRYSTAL DATA OF BD·TCNQ

	Space group	a	b	c	β	Z
BD·TCNQ·[n]	C2/m	12.231	12.679	6.477	104.84	2
BD·TCNQ·[CH_2Cl_2]	I2/m	20.892	9.950	6.445	91.92	2
BD·TCNQ·[CH_2ClCH_2Cl]	Immm	10.199	20.765	6.529		2
BD·TCNQ·[CH_2BrCH_2Br]	Immm	10.205	20.785	6.525		2
BD·TCNQ·[C_6H_6]	P2$_1$/m	17.184	9.852	7.680	100.3	2

of the crystals to BD·TCNQ·[n]. Seemingly, BD·TCNQ·1.8(CH_2Cl_2) is the limiting composition for keeping the channeled structure of the host lattice.

The crystal data of other two modifications of Type II are compared in Table 1 with those of BD·TCNQ·[CH_2Cl_2]. Above three modifications are almost isomorphous to each other. In effect, preliminary analyses of the crystal structures of BD·TCNQ·[CH_2ClCH_2Cl] and BD·TCNQ·[CH_2BrCH_2Br] have shown that, in these cases, the host lattice is almost the same as in BD·TCNQ·[CH_2Cl_2]. The amount of included solvent was found to be 1.6 mole per one mole of BD·TCNQ in BD·TCNQ·[CH_2ClCH_2Cl] as well as in BD·TCNQ·[CH_2BrCH_2Br], which is approximately equal to the value that is expected to fill up the channels with dichloroethane or dibromoethane. The analyses of the diffraction patterns have led us to conclude the presence of a considerable disorder as regards the arrangement of solvent molecules in the channels. Seemingly, such a disorder has been inevitably introduced to fill up the channels with the solvent molecules. Although a detailed investigation has not yet been carried out on the crystal structure of other modifications of Type II, we believe that all of them commonly possess the same type of host lattice.

The crystal structure of BD·TCNQ·[C_6H_6]⁴⁾ is different from the structures of the modifications of Type II; The BD·TCNQ column is composed of BD·TCNQ pairs⁶⁾ and one benzene molecule is surrounded by four BD·TCNQ pairs. The amount of the included benzene was found to be one mole per one mole of BD·TCNQ as it is expected from the crystal structure. When a crystal of BD·TCNQ·[C_6H_6] is kept in the ordinary atmosphere at room temperature, the included benzene is gradually lost converting the crystal to the solvent-free modification. There seems to be no stable phase which has some fixed amount of solvent vacancies in this case.

As we have already mentioned, the modifications which contain aromatic solvents, exhibit diffraction patterns similar to that of BD·TCNQ·[C_6H_6], and the mole ratio of included solvent is always one mole per one mole of BD·TCNQ as in BD·TCNQ·[C_6H_6]. Thus, the structure of the host lattice is likely to be essentially the same in all of these cases.

Electrical Conductivities of Solvent-containing Modifications. Although some of the solvent-containing modifications were obtainable as a single crystal sufficiently large for performing the measurement of electrical conductivity, we carried out the measurement exclusively on the compressed polycrystalline samples by the method described in the earlier part of this paper because it is more difficult to prevent a loss of the included solvent during the conductivity measurement when we use a small single crystal.

In Fig. 4, we show the experimental results obtained for three representative modifications. For all modifications, the temperature dependence of electrical conductivity was reproducible between the cooling and heating processes, and the relation between the conductivity σ and the temperature was describable with a single exponential function (Eq. (1)).

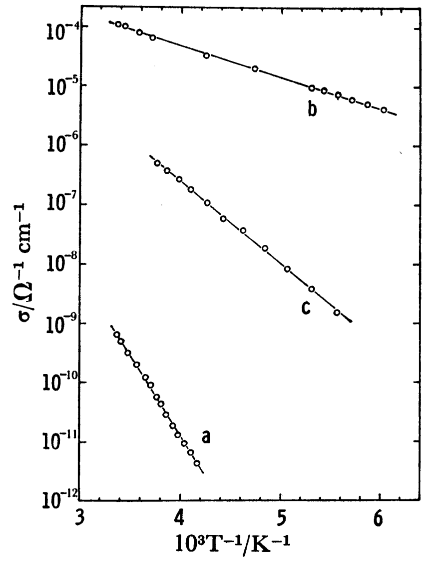

Fig. 4. Temperature dependence of conductivity.
(a) BD·TCNQ·[n], (b) BD·TCNQ·[CH_2Cl_2], and (c) BD·TCNQ·[C_6H_6].

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \qquad (1)$$

These facts imply that we were practically able to avoid the solvent loss during the conductivity measurements.

The electrical conductivities at 18 °C and the activation energies of semiconduction are summarized in Table 2, where the results reported by Ohmasa *et al.*¹⁾ are also included for comparison.

TABLE 2. CONDUCTIVITY DATA OF BD·TCNQ

	Included solvent (mole ratio)	Crystal lattice	σ (18°C) [ohm⁻¹·cm⁻¹]	ΔE [eV]
(1)	solvent-free	I	7×10^{-10}	0.54
(2)	CH_2Cl_2 (1.8)	II	1×10^{-4}	0.11
(3)	C_2H_5Br (1.8)	II	2×10^{-4}	0.12ᵃ⁾
(4)	CH_2ClCH_2Cl (1.6)	II	1×10^{-5}	0.14
(5)	CH_3CN (0.8)	II	1×10^{-5}	0.16ᵃ⁾
(6)	CH_3COCH_3 (0.8)	II	3×10^{-6}	0.21ᵃ⁾
(7)	C_6H_6 (1.0)	III	1×10^{-6}	0.28
(8)	C_6H_5Cl (1.0)	III	3×10^{-7}	0.38
(9)	C_6H_5Br (1.0)	III	1×10^{-7}	0.40
(10)	$C_6H_5CH_3$ (1.0)	III	3×10^{-8}	0.43
(11)	C_6H_5CN (1.0)	III	2×10^{-9}	0.44
(12)	$C_6H_5NO_2$ (1.1)	III	3×10^{-9}	0.50

a) Ref. 1.

First of all, we note that a large increase of conductivity and a marked lowering of activation energy are caused by the solvent inclusion. These changes are most significant in the modifications which have been classified as Type II. In these cases the conductivities at 18 °C are of the order of 10^{-4}—10^{-6} ohm⁻¹·cm⁻¹ and the activation energies are only 0.1—0.2 eV while the former is 10^{-9} ohm⁻¹·cm⁻¹ and the latter is 0.54 eV in the case of BD·TCNQ·[n].

According to Eq. (1), the relation between the conductivity at 18 °C, σ (18 °C), and the activation energy of semiconduction, ΔE (in eV units), can be expressed as follows;

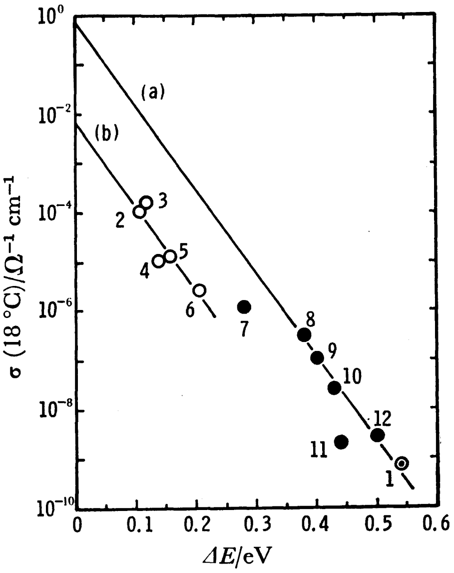

Fig. 5. Plots of the conductivity at 18 °C *versus* the activation energy of semiconduction. (See text for the meanings of lines (a) and (b). Their inclinations corresponds to $-1/kT$ (T=291 K).) Refer Table 2 for the numbering of the systems.

$$\log \sigma\ (18\,^{\circ}\mathrm{C}) = \log \sigma_0 - 17.32\Delta E \tag{2}$$

Therefore, if σ_0 is the same for different modifications, we should have a straight line when we plot log σ (18 °C) versus ΔE. We show the log σ (18 °C) *vs.* ΔE plots in Fig. 5. Interestingly, the plots in the ΔE region of 0.4—0.6 eV are on the line (a) which correspond to σ_0=1 ohm^{-1}·cm^{-1}. These plots are concerned with the modifications of Type III and the solvent-free modification. On the other hand, the plots concerned with the modifications of Type II fall on another line (b) which corresponds to σ_0 of about 10^{-2} ohm^{-1}·cm^{-1}. If we assume that the density of states are of the same order of magnitude as the number of BD·TCNQ units per unit volume, and the mobilities of charge carriers are 10^{-2}—10^{-1} cm^2·V^{-1}·s^{-1} as reported for several charge-transfer complexes,[7—9] σ_0 is expected to be 10^0—10^1 ohm^{-1}·cm^{-1} for the intrinsic semiconduction. Naturally, it is difficult to make a quantitative discussion on σ_0 by using the conductivity data obtained of polycrystalline samples, but we could say that the σ_0 value corresponding to the line (a) is not unreasonable for the intrinsic semiconduction while that corresponding to the line (b) is too small.

The value of activation energy provides another criterion. In the case of a charge-transfer complex, the energy gap (*i.e.*, the energy required for the intrinsic carrier formation) can be estimated by the following relation;

$$\varepsilon = I(\mathrm{D}) - A(\mathrm{A}) - \{P(\mathrm{D}^+) + P(\mathrm{A}^-)\} \tag{3}$$

where I(D) and A(A) are the ionization potential of the donor (D) and the electron affinity of the acceptor (A), respectively, and $P(\mathrm{D}^+)$ and $P(\mathrm{A}^-)$ are the polarization energies associated with the formations of D$^+$ and A$^-$ ions in the crystal, respectively. Ionization potential of benzidine is estimated as 7.15 eV from the charge-transfer band of the benzidine-chloranil complex in solution,[10] and the electron affinity of TCNQ has been reported to be 2.8 eV.[11,12] According to Batley and Lyons,[13] the photoionization threshold of BD·TCNQ complex is at 5.03 eV. Since the ionization potential of TCNQ, 9.6 eV,[14] is more than 2 eV higher than that of benzidine, the photoionization threshold corresponds to the energy for the ionization of a benzidine molecule in the crystal of the complex. This energy can be related to I(D) and $P(\mathrm{D}^+)$ as follows;

$$I(\mathrm{D};\ \text{solid DA}) = I(\mathrm{D}) - P(\mathrm{D}^+) \tag{4}$$

By substituting I(D; solid DA)=5.03 eV and I(D)=7.15 eV into Eq. (4), we obtain $P(\mathrm{D}^+)$=2.12 eV. At present, $P(\mathrm{A}^-)$ can not be experimentally estimated, but one could reasonably assume it as 1.5—2 eV. If we put these figures into Eq. (3), the energy gap is estimated to be less than 1 eV, which is rather smaller than the twice of the activation energy actually observed of the solvent-free modification. Thus it is not unreasonable to consider that the observed conductivity is due to the intrinsic carrier formation in this case.

We may expect two kinds of effects of solvent inclusion on the activation energy of semiconduction in the BD·TCNQ system. The first is the one associated with the formation of hydrogen bonds between benzidine and TCNQ. We have found that the crystal of the molecular complex which has an infinite hydrogen-bonded chain of donor and acceptor as in quinhydrone, generally exhibits a charge-transfer band at an energy lower by 0.4—0.6 eV than the value that is expected simply from the ionization potential of donor and the electron affinity of acceptor.[16] Seemingly, the value of $I(\mathrm{D})-A(\mathrm{A})$ is reduced when a hydrogen-bonded chain or network is formed between donor and acceptor. From this point of view, we can expect that the solvent inclusion of BD·TCNQ complex will cause a decrease of the activation energy of semiconduction, since benzidine and TCNQ molecules are forming hydrogen-bonded networks when solvent molecules are included, while not in the solvent-free state.[17]

The second effect of solvent inclusion is the one associated with a change in the polarization energy term. The values of $P(\mathrm{D}^+)$ and $P(\mathrm{A}^-)$ will naturally be affected by the solvent inclusion. Although it is not easy to quantify this effect we can qualitatively predict that the polarization energy term will be a little smaller in the solvent-containing modifications than in the solvent-free modification. Therefore, this effect of solvent inclusion is likely to cause an increase of activation energy.

Since the above two effects are giving mutually opposite contributions, the solvent inclusion will cause a relatively small change in the intrinsic energy gap. In this sense, the activation energies observed of the modification of Type III are quite understandable, but those observed of the modifications of Type II seem to be too small for the intrinsic carrier formation.

Solvent Vacancies and Electrical Conductivity. As we have already mentioned, the amount of the included solvent can vary within a certain range without changing the structure of the host lattice in the case of the modifications of Type II. This is typically the case in BD·TCNQ·[$\mathrm{CH_2Cl_2}$]. Thus we examined the correlation between the electrical conductivity and the amount of solvent vacancies by varying the pressure of the ambient dichloromethane vapor. For this purpose the crystalline powder of BD·TCNQ·[CH_2Cl_2], still wet with dichloromethane, was packed between two gold-mesh electrodes so as to keep a good contact with the ambient vapor, and put in a glass cell for the conductivity measurement. This cell was connected to the system for controlling the pressure of the dichloromethane vapor. When the vapor pressure was stepwisely varied after the removal of excess dichloromethane, the current changed rather rapidly settling to a new stationary state within 5—10 minutes at each vapor pressure. In Fig. 6, we plotted the observed steady-state current against the vapor pressure of dichloromethane. In the pressure region above 6 mmHg, the steady-state current significantly increased on decreasing the vapor pressure, and conversely, decreased on increasing the vapor pressure, but there appeared an appreciable hysteresis in the current *vs* pressure curve. The current reached a maximum value at about 6 mmHg, and remained at almost the same value at lower vapor pressures. Examining the amounts of included solvent in the powders which have been subjected to the conditions similar to those in the above experiments, we concluded that the results shown in Fig. 6, are giving the conductivity change due to the variation of the composition, BD·TCNQ·x(CH_2Cl_2) in the range of $1.8 \leq x \leq 2$. The experimental results described above, most clearly demonstrate that the electrical conductivity of the BD·TCNQ·[CH_2Cl_2] system is strongly controlled by the amount of solvent vacancies, and the conductivity data obtained under the ordinary condition, where the composition of the sample is BD·TCNQ·1.8(CH_2Cl_2), should be regarded as primarily associated with an extrinsic semiconduction caused by the presence of solvent vacancies.

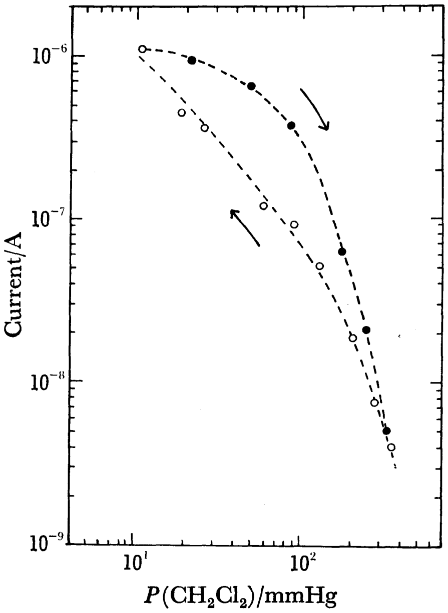

Fig. 6. Dependence of the conductivity of BD·TCNQ·[CH_2Cl_2] on the vapor pressure of dichloromethane in the ambient atmosphere. The current observed at a constant applied field is directly plotted instead of the conductivity.

In this connection, it is interesting to see that the BD·TCNQ·[CH_2Cl_2] system exhibits a strong ESR absorption in the presence of solvent vacancies. It was reported by Ohmasa *et al.*[1] that BD·TCNQ·[CH_2Cl_2] did not exhibit ESR signal when measured with its well-grown crystals immediately after preparation, but gave strong ESR signals when ground to a fine powder. They observed also that a strong ESR signal appeared when a pulverized sample of BD·TCNQ·[n] was exposed to the vapor of dichloromethane.

In order to elucidate the relation between spin centers and solvent vacancies, we examined the ESR signal of BD·TCNQ·[CH_2Cl_2] powder in the dichloromethane vapor. The powder sample, still wet with an excess dichloromethane, was put into the ESR sample tube which had a stopcock and a joint so that it could be connected to the vacuum system for controlling the vapor pressure of dichloromethane. The ESR signal was first observed in the presence an excess dichloromethane, then its change was observed by stepwisely reducing the vapor pressure of the dichloromethane in the sample tube. At each vapor pressure, we waited for about 45 min before the ESR measurement so that the sample had settled in an equilibrium state with the ambient dichloromethane vapor. The results are shown in Fig. 7, in which we have plotted the spin density against the vapor pressure, both in logarithmic scale.

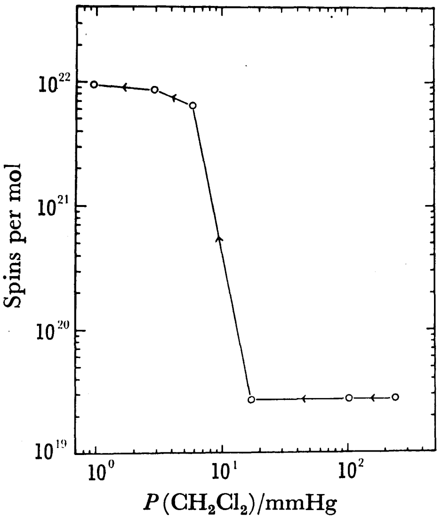

Fig. 7. Dependence of the spin concentration of BD·TCNQ·[CH_2Cl_2] on the vapor pressure of dichloromethane.

Since we had pulverized the crystals, the sample exhibited a weak ESR signal even in the presence of an excess dichloromethane. On driving off the excess dichloromethane, the spin density increased slightly, but after a small initial change it remained almost at a constant magnitude down to 20 mmHg. A steep rise of spin density was observed on decreasing the vapor pressure from 20 mmHg to about 6 mmHg,[15] then the change was leveled off in the lower pressure region. The above data clearly demonstrate that the spin density is closely related to the amount of solvent vacancies. Although benzidine and TCNQ molecules are essentially in non-ionic states when they are at their regular sites, radical ions could be easily formed through electron transfer from benzidine to TCNQ at the crystal sites which possess features favouring ion-formation, since benzidine has a low ionization potential and TCNQ has a very high electron affinity. Seemingly the solvent vacancies are contributing somehow to the creation of such sites in the crystal. If a radical ion of benzidine and/or that of TCNQ are formed in the crystal, they could also contribute as the origins of extrinsic charge carriers. However, it is not possible to find out a direct correlation between the vapor pressure dependence of spin density (Fig. 7) and that of electrical conductivity (Fig. 6). Possibly, this is because the latter is, to some extent, reflecting the properties of the surface regions of crystals, while the former is more related to the bulk properties.

We examined the temperature dependence of magnetic susceptibility on the powder of BD·TCNQ·1.8(CH_2Cl_2) by means of Faraday method. The observed results are shown in Fig. 8. We found that the paramagnetic susceptibility, which was obtained by subtracting the diamagnetic term, $\chi_d = -336 \times 10^{-6}$ emu·mol^{-1}, from the observed molar susceptibility, followed the Curie-Weiss law with the Weiss temperature of about −130K and the Curie constant $C = 0.047$ emu·K. This seems to suggest that the spin centers are not entirely isolated from each other, but are distributed in the state that allows a weak interaction between them.

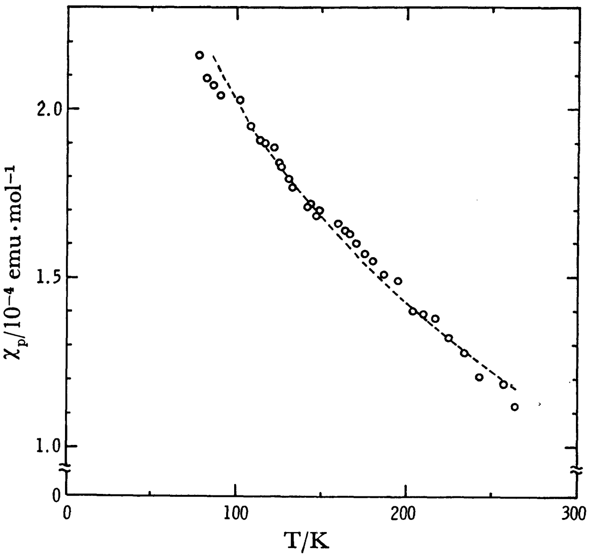

Fig. 8. Temperature dependence of the paramagnetic susceptibility of BD·TCNQ·1.8(CH_2Cl_2).

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5) A freshly prepared crystalline powder was used without grinding to a fine powder, to avoid the loss of the included solvent.

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17) The maximum of the first charge-transfer band is located at 0.81 eV in the case of BD·TCNQ·[CH_2Cl_2] while it is at 0.94 eV in the case of BD·TCNQ·[n].