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Electronic Properties of Benzidine·TCNQ System

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The benzidine·tetracyano-*p*-quinodimethane (TCNQ) system forms two types of charge-transfer complexes; one (I) containes some sort of solvent molecules, while the other (II) does not. The electronic properties of I have been found to be unusual in many respects compared to II which shows the properties expected from those of ordinary charge-transfer complexes. I and II did not exhibit ESR absorption, if they were well-grown crystals. However, when they were pulverized to fine powder, I showed a strong absorption while II did not. The visible range absorption spectra of I and II consisted of three main bands, but all the bands of I were found to be shifted to longer wavelengths compared to those of II. In addition to these bands, two shoulders were found in the spectrum of I. The shoulders were considered to be due to the ion radicals produced from benzidine and TCNQ. The electrical resistivities are again quite different from one another. The resistivity of I was found to be 10^3—10^5 ohm cm at room temperature, the value being dependent on the kind of the solvent molecules included, while that of II was 2×10^9 ohm cm. The activation energy for conduction was smaller for I (0.1—0.2 eV) than for II (0.34 eV).

The electronic properties of charge-transfer complexes of tetracyanoquinodimethane (TCNQ) with a series of aromatic diamines were examined in the previous paper.[1] It was found that the complex of benzidine (BD) with TCNQ which was prepared in dichloromethane showed unusual properties compared with the other complexes studied. The electrical resistivity of the BD·TCNQ complex was very low and its infrared absorption spectrum was not explained either by a superposition of the spectra of ionic components or that of neutral components.

Later study revealed that BD and TCNQ form two types of complexes[2]: one is the complex which contains solvent molecules [BD·TCNQ·S][3] and the other is the complex which does not contain solvent molecules [BD·TCNQ(n)]. The former complex was proved to be a kind of inclusion compound.[4] Preliminary examination has revealed that the electronic properties of these two types of complexes are quite different from each other. It was the BD·TCNQ·S complex which was observed previously to show unusual properties.

Several authors[5-9] have studied the effect of the occluded solvent molecules on the electronic properties of charge-transfer complexes and on the difference in the electronic properties of the complexes which are composed of the same donor and acceptor and are prepared from different solvents. Ottenberg *et al.*[7] studied electrical and ESR properties of the *p*-phenylenediamine·*p*-chloranil complex. They observed no significant effect of entrapped solvent molecules on these properties. Cairns and McGeer[8] prepared diaminodurene·TCNE complex in chloroform and tetrahydrofurane and obtained two types of complexes which have different colors. Among these works, the study on polymorphic forms of diaminopyrene·chloranil system by Matsunaga[5,6] is parti-

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[1] M. Ohmasa, M. Kinoshita, M. Sano, and H. Akamatu, This Bulletin, **41**, 1998 (1968).

[2] M. Ohmasa, M. Kinoshita, and H. Akamatu, *ibid.*, **42**, 2402 (1969).

[3] As for the notation of the complex, see Ref. 4.

[4] M. Ohmasa, M. Kinoshita, and H. Akamatu, This Bulletin, **44**, 391 (1971).

[5] Y. Matsunaga, *Nature*, **211**, 183 (1966).

[6] Y. Matsunaga, *Nippon Kagaku Zasshi*, **89**, 905 (1968).

[7] A. Ottenberg, C. J. Hoffman, and J. Osiecki, *J. Chem. Phys.*, **38**, 1898 (1963).

[8] T. L. Cairns and E. G. McGeer, *Chem. Abstr.*, **62**, 1775f (1965).

[9] M. Batley and L. E. Lyons, *Mol. Cryst.*, **3**, 357 (1968).

cularly interesting. He observed that electronic properties of this complex precipitated from benzene were greatly changed by compressing the sample in the presence of benzene. After the compression, electrical resistivity of the sample was greatly reduced and its infrared absorption spectrum was entirely changed. These facts indicate that the occluded solvent has an important effect on the electronic properties of the diaminopyrene·chloranil system. However, the cause of the effect of the occluded solvent is not clear at present.

The benzidine·TCNQ system is similar to the diaminopyrene·chloranil system in some respects, and is considered to be suited for the study of the effect of the occluded solvent, because both BD·TCNQ(n) and BD·TCNQ·S complexes can be prepared individually, and many kinds of solvents are found to form the BD·TCNQ·S complex. In the present study, the electronic properties of BD·TCNQ·S and BD·TCNQ(n) complexes are described in detail and are compared with each other.

Some of the electronic properties of the complexes of TCNQ with *o*-tolidine, 3,3′-diaminobenzidine and 3,3′-dichlorobenzidine were also examined in brief.

Experimental

Complex Preparation. The BD·TCNQ·S and BD·TCNQ(n) complexes were prepared by the method previously.[4]

Infrared Absorption Measurement. To determine the character of the complex, infrared absorption spectra of the complex and related compounds were examined with a Hitachi infrared spectrophotometer in the range of 4000—400 cm^{-1}. The method of Nujol mull was adopted in the measurement.

ESR Absorption Measurement. Electron spin resonance (ESR) absorptions were measured as described in the previous paper.[1]

Visible and Near Infrared Absorption Measurement. Absorption spectra in the visible and infrared regions were measured for the solid samples using the method of Nujol mull.

Electrical Resistivity. Electrical resistivity of a complex was measured in a form of compressed pellet by a DC-method. Measurements on single crystals were also made for BD·TCNQ·S(CH_2Cl_2) at room temperature.

Results and Discussion

Infrared Absorption Spectra. The infrared absorption spectra of BD·TCNQ(n) and BD·TCNQ·S(CH_3COCH_3) are shown in Fig. 1 together with the spectra of BD, BD bromide, TCNQ and lithium salt of TCNQ. The spectra of the complexes containing other solvent molecules are similar to that of BD·TCNQ·S(CH_3COCH_3) complex except for the bands due to the solvent molecules.

The spectra of TCNQ[10,11] and TCNQ anion radical (lithium salt of TCNQ) are clearly different in the following points. Firstly, the C≡N stretching vibration of TCNQ appears at 2223 cm^{-1} and is very sharp, but the corresponding band of TCNQ anion radical appears at 2203 cm^{-1} and is broadened and split.[1] Secondly, a strong absorption band which is located at 1540 cm^{-1} in TCNQ is considered to be a superposition of the ring C=C stretching mode and the ethylenic C=C stretching mode. In the spectrum of TCNQ anion radical, however, no strong band appears at 1540 cm^{-1} and new bands are located at 1580 cm^{-1} and 1507 cm^{-1}. This is considered to be due to the difference in bond lengths of the ring and ethylenic C=C bonds in TCNQ and its anion radical. Thirdly, a strong absorption band is observed at 1183 cm^{-1} for the anion radical, whereas no strong band is observed for TCNQ in this region.

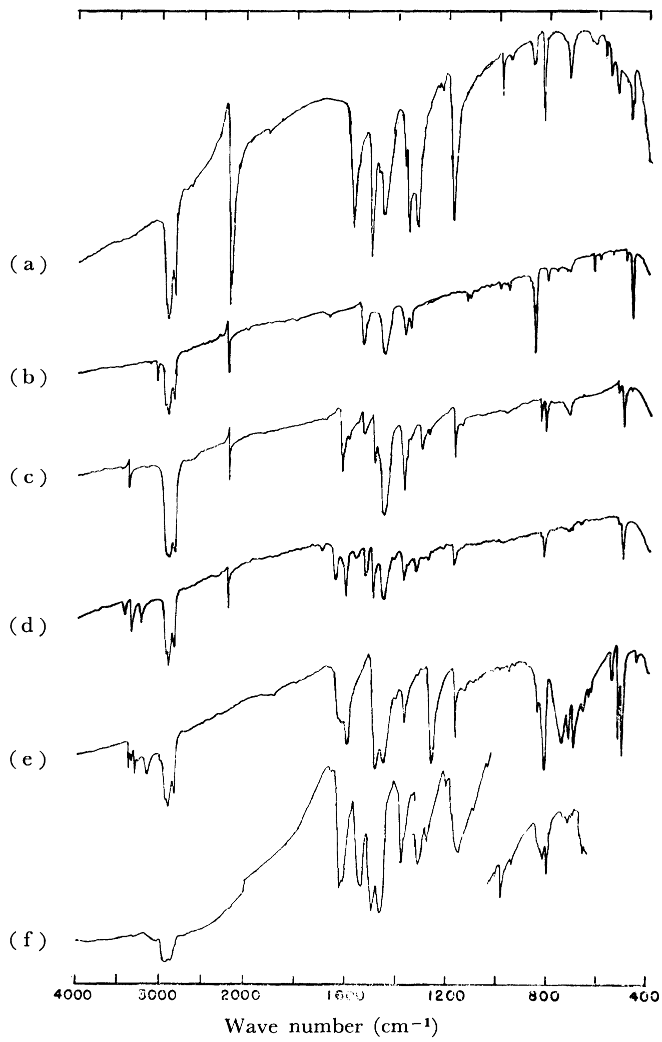

Fig. 1. Infrared absorption spectra of BD·TCNQ complexes and related compounds.
(a) LiTCNQ, (b) TCNQ, (c) BD·TCNQ(*n*), (d) BD·TCNQ·S(CH_3COCH_3), (e) BD, (f) BD·bromide.

The absorption spectra of BD and BD cation radical (BD bromide) are also very different in many respects.[12] In the spectrum of BD cation radical was

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[10] T. Takenaka, Preprint of Symposium on Molecular Electronic States, October, 1969, Fukuoka, Japan.

[11] B. Lunelli and C. Pecile, *J. Chem. Phys.*, **52**, 2375 (1970).

[12] The infrared absorption spectrum of BD is very similar to that of aniline and the vibrational modes were assigned according to the assignments of aniline by Evans.[13]

[13] J. C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).

observed a fairly intense band at 1545 cm^{-1}, but no intense band was observed around this wave number for BD. The ring stretching mode involving considerable C–N stretching appears at 1268 cm^{-1} for neutral BD, but in the spectrum of BD cation radical, no strong absorption is located in this region and a new band appears at 1318 cm^{-1}. The bands at 1176 cm^{-1} and 1140 cm^{-1} for BD are assigned to the in-plane CH bending modes. For BD cation radical, a fairly broad band is located at 1160 cm^{-1}, but the shape of this band is clearly distinguishable from the shape of the CH bending modes.

(a) BD·TCNQ(n) Complex: In the spectrum of BD·TCNQ(n) complex, the C≡N stretching frequency is slightly shifted to lower values compared with that of neutral TCNQ (from 2223 cm^{-1} to 2205 cm^{-1}), but the band is neither broadened nor split. The C=C ring stretching mode of TCNQ of the complex is observed at the same frequency as that of neutral TCNQ. As for the amine part, the ring stretching mode which is located at 1490 cm^{-1} in neutral BD is observed at 1498 cm^{-1} in the complex, and the bands at 1176 cm^{-1} and 1146 cm^{-1} for the complex are found to be clearly resembling in the frequency and in the shape to the in-plane CH bending modes of neutral BD. Furthermore, no band of the complex is found to correspond to the ring stretching band at 1545 cm^{-1} for BD bromide. From these, it is concluded that BD·TCNQ(n) complex is essentially of non-bonding type.

In the ground state, however, the dative structure seems to contribute to somewhat large extent in this complex, because the ring stretching mode involving considerable C–N stretching is shifted to 1308 cm^{-1} in the complex and the position is close to the band at 1318 cm^{-1} for BD bromide.

(b) BD·TCNQ·S(CH_3COCH_3) Complex: In the BD·TCNQ·S(CH_3COCH_3) complex, the C≡N stretching mode of TCNQ appears at 2210 cm^{-1}, and is neither broadened nor split. The fact suggests that the complex is of non-bonding type.

The following observations, however, show fairly large contribution of the dative structure to the ground state of the complex. The C=C stretching bands which appear at 1540 cm^{-1} in neutral TCNQ are shifted to 1528 cm^{-1} in the complex. The band at 1180 cm^{-1} of the complex shows almost the same frequency and shape as the band at 1183 cm^{-1} of lithium salt of TCNQ. In this complex, the in-plane CH bending mode of neutral BD at 1140 cm^{-1} disappears and a shoulder is located at 1160 cm^{-1} where a band of BD bromide lies. The ring stretching mode involving considerable C–N stretching of BD is observed to be shifted to 1330 cm^{-1} and is found to be rather near the band of BD bromide at 1318 cm^{-1}. Moreover, a new band appears in the complex at 1560 cm^{-1}, where no band is observed in the spectra of BD, BD bromide, TCNQ, and lithium salt of TCNQ. This band may correspond to the band at 1545 cm^{-1} of BD bromide or to the band at 1580 cm^{-1} of lithium salt of TCNQ.

From these observations, it is concluded that BD·TCNQ·S(CH_3COCH_3) complex is neither of non-bonding type nor of ionic type and that its electronic character may be considered to lie in the intermediate between the non-bonding and the ionic characters. The same conclusion is also drawn for BD·TCNQ containing other solvent molecules.

For BD·TCDQ·S complexes, the band characteristic of the solvent included is also observable. For example, the C=O stretching mode of acetone is seen at 1705 cm^{-1} in the spectrum of BD·TCNQ·S(CH_3-$COCH_3$).

Magnetic Properties. The magnetic properties of BD·TCNQ·S complexes are very different from those of BD·TCNQ(n) complex. BD·TCNQ(n) is diamagnetic and exhibit no ESR absorption, whether the sample is in the form of crystal or in the form of finely ground powder. The well-grown crystals of BD·TCNQ·S show no (or sometimes very weak) ESR absorption, but when they are ground to fine powder, they exhibit a strong ESR absorption signal. When the pulverized sample of BD·TCNQ(n) is exposed to the vapor of dichloromethane overnight, it becomes to show a strong ESR absorption. The fact is consistent with the observed change in the X-ray diffraction pattern described in Ref. 4.

The unpaired electrons in BD·TCNQ·S are produced by the following three ways. (i) The spin concentration of a crystalline sample of BD·TCNQ·S complex increases greatly when the sample is ground. For example, when the crystals of BD·TCNQ·S(CH_2-Cl_2) were ground in a vacuum at room temperature, the ESR absorption intensity of the sample increased by a factor of 270.

(ii) The spin concentration of freshly prepared samples of BD·TCNQ·S is dependent on conditions of the sample preparation. The sample which was prepared in a concentrated solution of the components and was not composed of well grown crystals showed a larger spin concentration than the complex which was prepared in a dilute solution and was composed of well-grown crystals. The results of the experiments on BD·TCNQ·S (CH_2Cl_2) are shown in Table 1, where relative intensities of the ESR absorption are listed as a measure of spin concentrations.

TABLE 1. RELATION BETWEEN ESR ABSORPTION INTENSITY OF BD·TCNQ·S (CH_2Cl_2) COMPLEX AND THE CONDITION OF ITS PREPARATION

Sample	Initial concentration of components[a)]		Relative intensity of ESR absorption[b)]
1	TCNQ	2.6×10^{-3} mol/l	4.50
	BD	7.6×10^{-3}	
2	TCNQ	2.7×10^{-3}	1.90
	BD	2.5×10^{-3}	
3	TCNQ	9.2×10^{-4}	0.32
	BD	8.3×10^{-4}	

a) These values show the initial concentration of each component in the solution from which the complex is precipitated.

b) ESR absorption intensity is measured within a several hours after filtration of the sample.

(iii) The ESR intensity of BD·TCNQ·S increases gradually when it is exposed to the air.

The facts (i) and (ii) show that the unpaired electrons are produced at the lattice defect and/or on the surface of the crystals.

The temperature dependence of the ESR intensity of BD·TCNQ·S (CH_2Cl_2) is given in Fig. 2. The ESR intensities of both samples, ground and not ground, increase in proportion to $1/T$ as the temperature is lowered down to 77°K. The fact indicates that the interaction between the unpaired electrons is very weak in the complex. The line shape of the ESR absorption, however, is very much narrowed and asymmetric in a vacuum. For example, the width between the points of half maximum of the absorption curve ($\Delta H_{1/2}$) was 1.1G for BD·TCNQ·S (CH_2Cl_2) in a vacuum. The narrow line width seems to be due to the motional narrowing, because the interaction between unpaired electrons is very weak.

The ESR absorption signal is sensitively changed by an introduction of air. In the air, the absorption line is almost symmetric and Lorentzian, whereas it is symmetric in a vacuum. The line width in the air is greater than that in a vacuum. The width $\Delta H_{1/2}$ of BD·TCNQ·S(CH_2Cl_2) is 3.1G in the air. This behavior suggests that the unpaired electron is produced near the surface. The integrated ESR absorption intensity, however, is not affected so sensitively by the introduction of air, although the intensity increases gradually in the air. The value of *g*-factor for BD·TCNQ·S(CH_2Cl_2) is 2.0027±0.0004.

The ESR behavior of the unpaired electrons generated by grinding and by the interaction with the air was identical. Therefore, both kinds of the unpaired electrons are considered to belong to the same paramagnetic species.

Visible and Near Infrared Absorption Spectra. The visible and near infrared absorption spectra of solid BD·TCNQ(n), BD·TCNQ·S (CH_2Cl_2) and BD·TCNQ·S(CH_3CN) complexes are shown in Fig. 3. The absorption peaks for the solutions of BD, BD·bromide,[14] TCNQ,[15] lithium salt of TCNQ[16] and BD·TCNQ complex are also shown in this figure. The spectrum of BD·TCNQ·S(CH_2Cl_2) is essentially identical with that reported by T. Amano *et al.*[17]

These spectra are composed of three main bands. The bands for BD·TCNQ·S complexes, however, are shifted to longer wave lengths compared with those of BD·TCNQ(n) complexes.

The bands of BD·TCNQ(n) at 1300 mμ and 520 mμ are assigned to the first and the second charge-transfer band; respectively, because of the following reasons. Firstly, the solution spectra of both BD and TCNQ[15] show individually no absorption peak in the region longer than 450 mμ. Since BD·TCNQ (n) is essentially of non-bonding type as was described before, these two bands of BD·TCNQ(n) are considered to be charge-transfer bands. Secondly, the positions of these two bands are near to the first and the

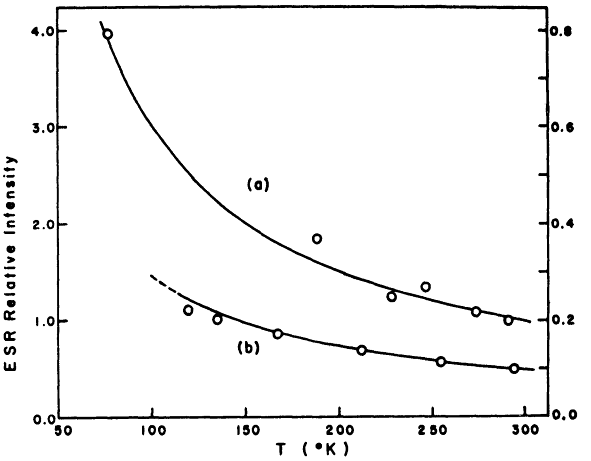

Fig. 2. Plots of relative ESR absorption intensities as a function of temperature for BD·TCNQ·S(CH_2Cl_2); (a) the sample which was ground mechanically, and (b) the sample which was not ground.
The scale for (a) is indicated on the left, while for (b) on the right.

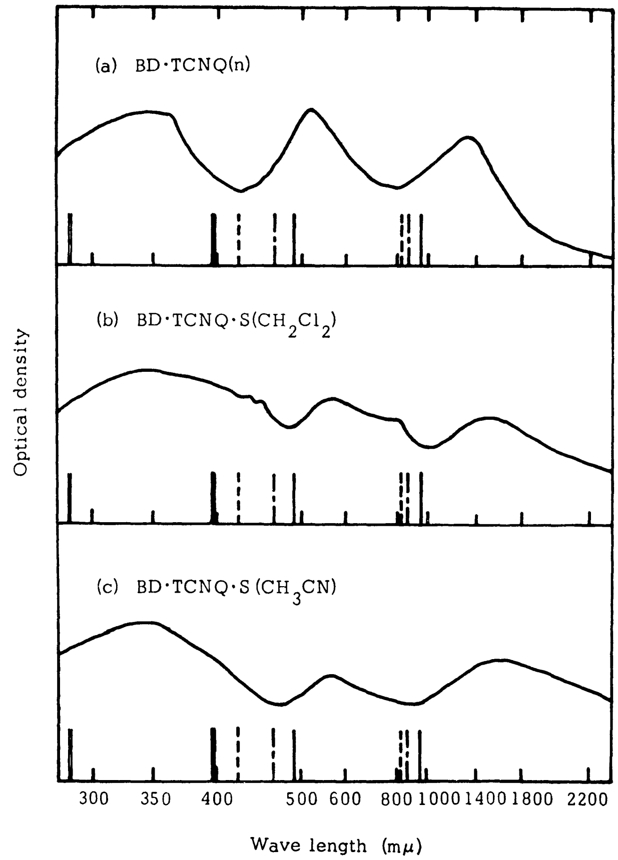

Fig. 3. Visible and near infrared absorption spectra of the solid complexes; (a) BD·TCNQ(*n*), (b) BD·TCNQ·S(CH_2Cl_2), and (c) BD·TCNQ·S(CH_3CN).
In the figure are also shown the positions of absorption peaks for solutions of TCNQ (——), BD (═══), Li^+TCNQ^- (- - -) and BD bromide (—·—), and of charge-transfer absorption maxima of chloroform solution of BD·TCNQ complex (——).

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[14] K. Takemoto, H. Matsusaka, S. Nakayama, K. Suzuki, and Y. Ooshika, This Bulletin, **41**, 764 (1968).

[15] D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 337 (1962).

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

[17] T. Amano, H. Kuroda, and H. Akamatu, This Bulletin, **42**, 671 (1969).

second charge-transfer bands for the solution of BD·TCNQ, respectively. Thirdly, as is shown in Table 2, the difference in the energies for the peaks at 520 mμ and 1300 mμ of BD·TCNQ(n) is nearly equal to the difference in the energies of the second and the first charge-transfer bands for the solution of BD·TCNQ.

The broad band at about 360 mμ for BD·TCNQ(n) considered to be related to the intramolecular transitions of BD and TCNQ.

As is shown in Fig. 3, the three main bands of BD·TCNQ·S complexes are almost independent of the kind of the solvent contained and their peaks are observed at 1500—1600, 550—560 and ~340 mμ. The lowest energy and the second lowest energy transitions can be assigned to the first and the second charge-transfer bands, respectively, because they are near to the first and the second charge-transfer bands of of BD·TCNQ(n), and because the energy difference in the former bands is equal to that in the latter bands (Table 2).

Table 2. Energies of charge-transfer transitions of BD·TCNQ system

	First C-T band[a]	Second C-T band[a]	Difference[b]
Chloroform solution	1.29 eV	2.56 eV	1.27 eV
BD·TCNQ(n)	0.95	2.38	1.43
BD·TCNQ·S (CH_3CN)	0.78	2.22	1.44

a) The energy at the charge-transfer absorption maximum.
b) The energy difference between the second and the first charge-transfer bands.

Besides the three main bands just discussed, the weak absorption bands were observed in the spectra of BD·TCNQ·S complexes. These bands appear at 430 and 820 mμ as shoulders of the main bands, and their wave lengths are very close to those of the absorption peaks of TCNQ anion radical[16] and BD cation radical.[14] The intensity of these weak bands are dependent on the kind of the solvent included. In fact, as is seen in Fig. 3, these bands are clearly observed in BD·TCNQ·S(CH_2Cl_2), but they are very weak and are scarcely observed in BD·TCNQ·S(CH_3CN). On the other hand, the effect of grinding on the ESR intensity is more remarkable in the former complex than in the latter.[18] By considering these facts, it is concluded that the weak bands at 430 and 820 mμ are due to TCNQ anion radical and BD cation radical which are formed at the lattice defects or on the surface.

It may be pertinent to note here that the complex, which was prepared by grinding carefully an equimolar mixture of BD and TCNQ in an agatemortar, showed similar optical and magnetic properties to those of the BD·TCNQ·S complexes, although the complex thus obtained does not contain solvent molecules. For example, a rather intense ESR absorption was observed with this complex, and its infrared absorption spectrum showed the bands characteristic of BD·TCNQ·S complexes, although the bands characteristic of BD·TCNQ(n) complex were very also weakly observable. In Fig. 4 is shown the optical absorption spectrum in the visible and near infrared region for the complex prepared under the dry condition. The location and the shape of the main bands in the spectrum are very similar to those observed in the spectrum of BD·TCNQ·S complexes shown in Fig. 3.

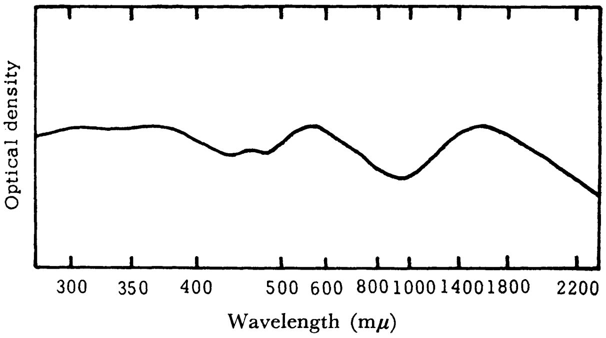

Fig. 4. Optical absorption spectrum of BD·TCNQ complex which was prepared by grinding a mixture of TCNQ and BD powders.

Table 3. Specific resistivities of BD·TCNQ complexes

Solvent included	$\rho_{18^\circ C}$ (Ω·cm)	E (eV)
CH_2Cl_2	7×10^3	0.10
C_2H_5Br	6×10^3	0.12
CH_3CN	7×10^4	0.16
CH_3COCH_3	4×10^5	0.21
no solvent	2×10^9	0.34

Electrical Properties. The electrical resistivities of polycrystalline samples of BD·TCNQ(n) and BD·TCNQ·S complexes were found to follow the equation, $\rho=\rho_0\exp(E/kT)$. The values of E and $\rho_{18^\circ C}$ observed are listed in Table 3. Both E and $\rho_{18^\circ C}$ are lower for BD·TCNQ·S complexes than for BD·TCNQ(n) complex. The resistivities of BD·TCNQ·S complexes are small compared with most of other nonionic molecular complexes.[19,20]

The resistivities of the single crystals of BD·TCNQ·S(CH_2Cl_2) were measured several times. The crystal of the complex was a thin needle and its typical dimension was 2.5 mm × 0.10 mm × 0.06 mm. The resistivity was measured along the long axis at room temperature. The average of the results obtained is 1.4×10^3 Ωcm. This value is several times lower than the value for the polycrystalline sample listed in Table 3.

In order to eliminate the possibility that the observed low resistivity be due to ionic conduction, the following experiment was carried out. A pellet of BD·TCNQ·S(CH_2Cl_2) was pressed at 165 kg/cm² and the

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18) After grinding in an agatemortar, the spin concentration of BD·TCNQ·S(CH_2Cl_2) increased to 6×10^{22} per mole, while that of BD·TCNQ·S(CH_3CN) to 1×10^{22} per mole.

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

20) M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.*, **33**, 868 (1960).

current was run through it at room temperature until the amount of charge passed had exceeded the amount expected from the Faraday's law by 3 times. No significant decrease was observed in conductivity. The conduction was thus concluded to be electronic in character.

Complexes of TCNQ with o-*Tolidine, 3,3′-Diaminobenzidine and 3,3′-Dichlorobenzidine.* The electronic properties of these complexes are dependent on the kind of the donor. Thus, 3,3′-dichlorobenzidine (DCBD) which is the weakest of the three donors gives a diamagnetic complex. DCBD·TCNQ complex does not show any ESR absorption whether the sample is ground or not. This behavior is similar to that of BD·TCNQ(n) complexes.

On the other hand, the complex of 3,3′-diaminobenzidine (DABD), which is the strongest of the three donors, shows a strong ESR absorption. No significant effect of grinding on the ESR absorption intensity was observed. These facts indicate that the complex is ionic in character.

The magnetic properties of the complex of *o*-tolidine (TL) and TCNQ which contains dichloromethane or chloroform are similar to those of BD·TCNQ·S complexes. The spin concentration of the sample of TL·TCNQ·S(CH_2Cl_2) was found to be 8×10^{21} per mole before grinding and was found to increase by 16 times after grinding. The line width (ΔH_{msl}) of a sample was observed to be 0.93 G in vacuo, while it became 1.70G in the air. From these observations, it is concluded that TL·TCNQ·S complexes have a similar electronic character to that of BD·TCNQ·S complex. This conclusion was further supported by the fact that the characteristics of the infrared absorption spectra for the former complexes are very similar to those for the latter.