Two Types of Complexes of *o*-Phenylenediamine with Tetracyanoquinodimethane

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o-Phenylenediamine and tetracyano-*p*-quinodimethane (TCNQ) were shown to form two types of solid complexes with compositions of 1 : 1 and 2 : 1. The 2 : 1 complex is essentially of ionic type, while the 1 : 1 complex is characterized as of non-bonding type from the analysis of its infrared absorption spectrum. It was shown that the difference in type is reflected on the magnetic and electrical properties of these complexes. The ESR absorption or the spin concentration of the 1 : 1 complex changed irreversibly with grinding or heat-treatment (70°C), while no appreciable change was observed in the 2 : 1 complex with these treatments. The electrical resistivity is lower for the 1 : 1 complex than the 2 : 1 complex by a factor of 10^2. From these observations, it is considered that the ground state electronic structure of the 1 : 1 complex is in a similar situation to those of diaminopyrene-chloranil and benzidine-TCNQ complexes.

In a previous paper,[1] the electronic properties of the 2 : 1 complex of *o*-phenylenediamine (*o*-PD) with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) have been discussed as a complex of ionic type. Since then, it was found that the complex of 1 : 1 composition can also be obtained. The ground state character for the 1 : 1 complex was found to be primarily of non-bonding type in contrast to the 2 : 1 complex.

It is of interest to examine and compare the electronic properties of these complexes, since both types can be obtained from the same donor and acceptor. The magnetic and electrical properties of the two complexes were found to differ a great deal from each other.

Experimental

Complex Preparation. *The 2 : 1 Complex*: To a saturated solution of TCNQ in 15 m*l* of dichloromethane was added a solution of 400 mg of *o*-PD in 10 m*l* of dichloromethane at room temperature, and the resulting purple precipitate was collected.

The 1 : 1 Complex: A solution of 610 mg of *o*-PD in 15 m*l* of dichloromethane was added to a solution of 107 mg of TCNQ in 50 m*l* of dichloromethane, and the mixture was cooled to −10°C. Black crystals thus formed were collected.

Measurements. The absorption spectra in the visible and infrared regions, the ESR absorption spectra and the electrical resistivity were measured in a similar manner to that in previous reports[1,2] in which purification of the chemicals was also described.

Results and Discussion

Composition of the Complexes. The chemical composition (donor to acceptor ratio) of the complex was determined from the analysis of the absorption spectra in the UV and visible regions. The results obtained are given in Table 1, the assigned stoichiometric ratios being also listed.

Table 1. The chemical composition of the *o*-PD·TCNQ Complexes

Complex	Composition (Donor : Acceptor) Spectral analysis	Composition (Donor : Acceptor) Assigned stoichiometry
o-PD·TCNQ(1 : 1)	1 : 0.97	1 : 1
o-PD·TCNQ(2 : 1)	1 : 0.47	2 : 1

Characterization of the Complexes. The infrared absorption spectra of both 2 : 1 and 1 : 1 complexes of *o*-PD with TCNQ are shown in Fig. 1, together with the spectra of *o*-PD, TCNQ,[3,4] and lithium salt of TCNQ.

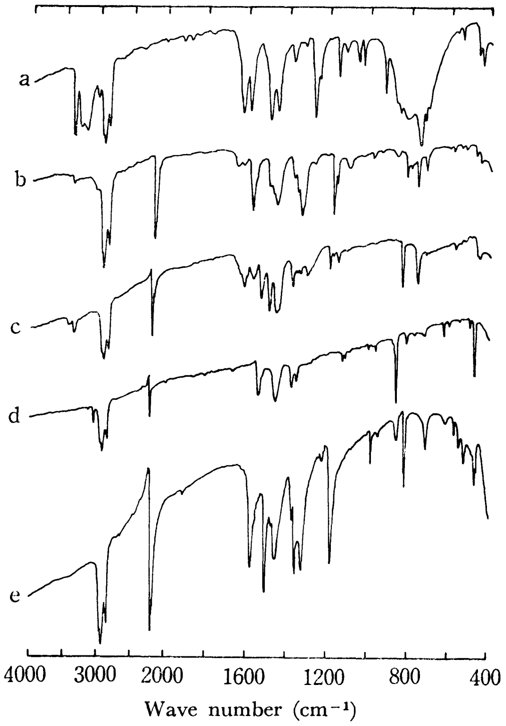

Fig. 1. Infrared absorption spectra of *o*-PD·TCNQ complex and related compounds.
(a) *o*-PD, (b) *o*-PD·TCNQ (2 : 1), (c) *o*-PD·TCNQ (1 : 1), (d) TCNQ, (e) LiTCNQ.

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

[2] M. Ohmasa, M. Kinoshita, and H. Akamatu, *ibid.*, **42**, 2402 (1969): **44**, 395 (1971).

The infrared absorption spectrum of the 2 : 1 complex indicates ionic character of the complex. As seen in Fig. 1, the C≡N stretching vibration located at 2223 cm^{-1} in neutral TCNQ is broadened and shifted to 2180 cm^{-1} in the complex. The ring C=C stretching vibration at 1540 cm^{-1} in neutral TCNQ disappears and a new band appears at 1580 cm^{-1}. Another new band is also observed at 1180 cm^{-1}. These features are identical with those of lithium salt of TCNQ, and confirm that the 2 : 1 complex is of ionic type.

Absorption bands of the donor in the 2 : 1 complex also suggest ionic character. An intense band at 1275 cm^{-1} in the spectrum of neutral *o*-PD is assigned to the ring stretching mode involving considerable C–N stretching, because its position and shape are very similar to the corresponding band of aniline.[5] This mode is shifted to 1336 cm^{-1} in the complex and the shift is in the same direction for the same vibrational mode of the *N,N*-dimethyl-*p*-phenylenediamine-TCNQ complex.[1] It is therefore concluded that the 2 : 1 complex is of ionic type. The amine part can be considered to have the form of $(o\text{-PD})_2{}^+$, because of the neutrality requirement.

In the 1 : 1 complex, the C≡N stretching vibration band is narrow and is located at 2210 cm^{-1}, and the ring stretching mode of TCNQ was observed at 1535 cm^{-1}. The location and the shape of these bands are similar to those of the corresponding bands of neutral TCNQ. The peaks at 1620, 1570, and 1492 cm^{-1} of the complex are identified with those at 1628, 1592, and 1492 cm^{-1} of neutral *o*-PD, respectively. This indicates that the 1 : 1 complex is characterized primarily as of non-bonding type.

The band at 1275 cm^{-1} of neutral *o*-PD, however, was shifted to 1305 cm^{-1} upon complex formation of the 1 : 1 composition. This suggests that the dative structure contributes considerably to the ground electronic state of the complex. In fact, the magnetic and electrical properties of the 1 : 1 complex also seem to reflect this contribution.

The difference in the electronic character can evidently be ascribed to the difference in composition, namely to the difference in the manner of molecular stacking in the crystals. The formation of an ionic complex is governed by the energy needed to charge the component molecules and by the electrostatic energy of the charged lattice. The former is determined by the ionization energy of the donor and the electron affinity of the acceptor, while the latter by Madelung's energy and polarization effects, both of which depend upon the crystal structure of the complex. In our complexes, since the ionization potential of the donor and the electron affinity of the acceptor are the same for both complexes, the electrostatic energy for salt formation seems to favour the crystal structure of the 2 : 1 complex rather than that of the 1 : 1 complex.

It is also of interest to discuss the difference in character of the 1 : 1 complex of *o*-PD·TCNQ and that of the 1 : 1 complex of *p*-phenylenediamine-TCNQ (*p*-PD·TCNQ), since the latter was found to be ionic in contrast to the former.[1] Matsunaga studied the electronic character of a number of complexes and arranged them in a diagram to correlate the character with the relative ionization potentials of donors and the relative electron affinities of acceptors.[6] The complex of *p*-PD·TCNQ is situated in the region of the complexes of non-bonding type, but very near the border line dividing the complexes having non-bonding ground states and those having dative or ionic ground states. The tendency of *p*-PD to form the complexes of dative ground states is suggested to be an exception to his diagram which reflects the effect of the size and shape of the component molecules on the electronic character. Since the ionization potentials of *o*- and *p*-PD are nearly the same,[7] the 1 : 1 complex of *o*-PD·TCNQ is also expected to situate around the border line, but in the region of the non-bonding group. The fact that the *o*-PD·TCNQ complex is found to be actually of non-bonding type verifies, therefore, the validity of the suggestion on the size and shape effects for *p*-PD complexes.

Magnetic and Electrical Properties. The magnetic and electrical properties of the complexes are summarized in Table 2, and the plots of the ESR absorption intensity against temperature are shown in Fig. 2. For both complexes, the intensity increased exponentially with temperature in a higher temperature region. The absorption intensity (I) was analysed in a similar manner to that described for the case of the *p*-PD·TCNQ complex.[1,8,9] The values of the activation energy δ, obtained from the plots of $\ln(IT)$ *vs.* $1/T$

TABLE 2. MAGNETIC AND ELECTRICAL PROPERTIES OF THE *o*-PD·TCNQ COMPLEXES

Complex	Spin concentration[a]	δ (eV)	*g*-Value	$\rho_{15^\circ\mathrm{C}}$ (ohm·cm)	*E* (eV)
1 : 1	1×10^{22}	0.11	2.0026	1.0×10^{5}	0.28
2 : 1	7×10^{21}	0.07	2.0028	1.4×10^{7}	0.45

a) Number of electrons contributing to the paramagnetism per one mole of the complex at room temperature, 296°K.

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[3] T. Takenaka, Preprints of the Symposium on Molecular and Electronic Structure, October, 1969, Fukuoka, Japan.

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

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

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

[7] The ionization potential of *o*-PD is considered to be larger by about 0.1 eV than that of *p*-PD, because the complexes of *o*-PD with *p*-bromanil and *p*-PD with *p*-bromanil show the charge-transfer band maxima at 646 and 672 mμ, respectively, in carbon tetrachloride.[1]

[8] The notation of δ is used here instead of *J* in Ref. 1.

[9] A correction was made for the intensities in the higher temperature region of the 1 : 1 complex by subtracting the intensities obtained by an extrapolation from the lower temperature side to the higher temperature side.

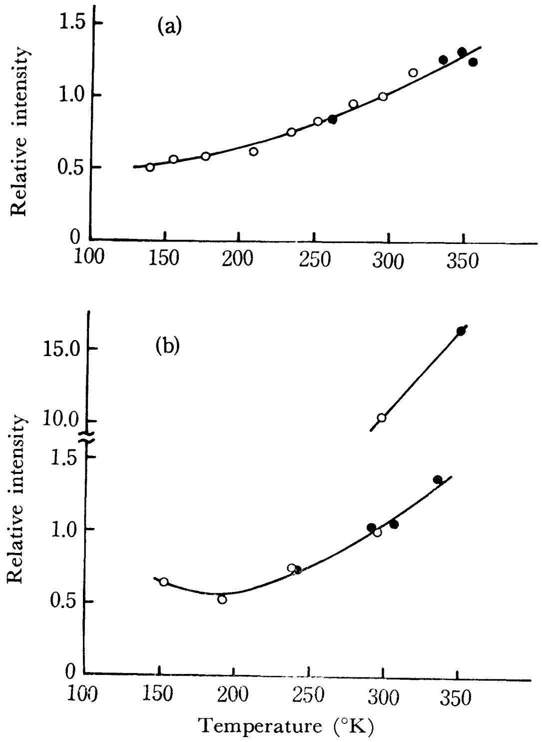

Fig. 2. Variations of ESR absorption intensities with temperature for *o*-PD·TCNQ complexes. Open circles are the points measured when the temperature was lowered, while shaded circles are the points measured when the temperature was raised.
(a) The 2 : 1 complex. The intensity changed reversibly.
(b) The 1 : 1 complex. When the temperature was raised up to 70°C, the intensity increased abruptly. However, when the temperature was lowered from 70°C, the intensity changed with the δ value coincident with that of the lower temperature region.

are given in Table 2.

When the 1 : 1 complex was warmed to 70°C in a vacuum for about 15 minutes, the ESR absorption intensity increased by a factor of 12. This phenomenon was found to be irreversible. However, the value of δ of the sample after heat treatment seems to coincide with that before the heat treatment. The nature of the paramagnetic sites does not seem to change with heat treatment.

The ESR absorption intensity of the 1 : 1 complex increased also by grinding. When the polycrystalline sample was ground in an agatemortar, the line width became slightly broadened and the intensity increased by a factor of about 5. The unpaired electrons observed in the 1 : 1 complex are, therefore, considered to be produced by an electron-transfer from the donor to the acceptor at lattice-defects and/or at the surfaces. The electron-transfer is likely enhanced by such treatments as grinding and heating.

As is seen in Table 2, the value of δ and the spin concentration of the 2 : 1 complex were found to be of the same order as those of the 1 : 1 complex. However, the spin concentration of the former was not affected when the sample was heated up to 82°C. The ESR absorption intensity changed reversibly with temperature as shown in Fig. 2.

The electrical resistivities of these complexes changed with temperature according to the equation $\rho=\rho_0 \times \exp(E/\boldsymbol{k}T)$. The values of the activation energy (E) and the specific resitivity (ρ) at 15°C are given in Table 2. Both $\rho_{15^\circ\mathrm{C}}$ and E are higher for the 2 : 1 complex than for the 1 : 1 complex.

The electrical conductivity of the 1 : 1 complex is rather high among the complexes of non-bonding type.[10,11] The complex of 1,6-diaminopyrene with *p*-chloranil[10,12] and the complex of benzidine with TCNQ containing solvent molecules[2,13] also exhibit relatively high conductivity, although they are not ionic in character. These three complexes, have the following common properties. (i) Although they are formed between strong donors and strong acceptors, their ground electronic character is not ionic but non-bonding. (ii) The ESR absorption intensity increases greatly when the crystals are ground into fine powder.[2] (iii) They exhibit relatively high electrical conductivity. These features differ greatly from typical ionic or non-ionic complexes, and seem to indicate that the ground electronic structures of these complexes are in a similar situation to each other. In fact, Matsunaga[6] has pointed out that the complex of 1,6-diaminopyrene with chloranil is located near the border line on his diagram, and such a complex exhibits relatively high conductivity. Our 1 : 1 complex is also located near the border line, and is considered to fall into such a class of complexes.

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

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

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

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