The Electrical Conductivities of Aromatic Diamine-Chloranil and -Tetracyanoethylene Charge-Transfer Complexes*

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We have reported in previous papers1,2) on the electrical conductivities of the iodine complexes of several kinds of aromatic diamines. Since then we have obtained aromatic diamine, *p*-, *m*-, and *o*-phenylenediamine (*p*-, *m*-, *o*-PDA), 1,5-naphthylenediamine (NDA), benzidine (BEN), *o*-tolidine (TOL) and *p*, *p*′-diaminodiphenylmethane (APM) complexes, in which chloral (CHL) or tetracyanoethylene (TCNE) was used as the electron acceptor. In this report we will present the results obtained from a comparison of the electrical conductivities of CHL and TCNE complexes with those of iodine complexes.

These CHL and TCNE specimens were prepared by mixing the equivalent donor and acceptor solutions. The complex crystals precipitated rapidly by cooling or from a highly concentrated solution were not suited to the observation of their electrical properties.

The chemical analysis for these CHL and TCNE complexes indicated that TCNE specimens scarcely include the solvent at all, but that CHL specimens contain a respectable amount of the solvent; the ratio between the donor and the acceptor in these complexes was 1 : 1. These CHL and TCNE complexes showed the absorption bands arising from the NH stretching vibration in the wave number region between 3455 cm^{-1} and 3140 cm^{-1}, and the signals of the electron-spin resonance at room temperature.

The magnitude and the temperature dependence of the resistivities and energies of the charge-transfer transitions obtained by previous methods1,3) are summarized in Table I for CHL complexes and in Table II for TCNE complexes. Some of these crystals were given needle-shaped forms (about $3\times0.05\times0.01$ mm.). Therefore, the lattice constants along the crystal growth axis could be found for such crystals by applying an oscillation method. These results are listed in the last column in both tables.

The following results are obtained from the data shown in Tables I and II:

1) The energy of the charge-transfer transition is more than twice the activation energy of the resistivity for the aromatic-diamine-complex specimens.

2) In the case of CHL complexes, the order of resistivity, *p*-PDA:CHL, TOL:CHL and NDA:CHL, agrees with that of the lattice constant along the crystal growth axis. On the other hand, the resistivity of BEN:TCNE, the lattice constant of which is smaller than that of NDA:TCNE, is not as low as the resistivity of NDA:TCNE.

3) The donor character of an aromatic diamine is dependent on what the acceptor molecule is; e. g., BEN is the strongest donor for an iodine acceptor, *p*-PDA is for CHL, and NDA is for TCNE.

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1) S. Nishizaki and H. Kusakawa, This Bulletin, **36**, 1681 (1963).

2) H. Kusakawa and S. Nishizaki, ibid., **38**, 313 (1965).

3) H. Kusakawa and S. Nishizaki, ibid., **38**, 783 (1965).

TABLE I. PHYSICAL PROPERTIES OF AROMATIC DIAMINE-CHLORANIL COMPLEXES

Donor	Resistivity at 20°C Ω cm.	Activation energy eV.	Energy of c. t. transition eV.	Lattice constant along crystal growth axis *A*
p-PDA	1.5×10^7	0.46	1.42	6.36
m-PDA	Complex in solution only			
o-PDA	Complex in solution only			
NDA	1.2×10^{11}	0.58	1.46	7.63
BEN	Nonstoichiometrical composition			
TOL	3.8×10^9	0.53	1.23	7.35
APM	Complex in solution only			

TABLE II. THE PHISICAL PROPERTIES OF AROMATIC DIAMINE-TETRACYANOETHYLENE COMPLEXES

Donor	Resistivity at 20°C Ω cm.	Activation energy eV.	Energy of c. t. transition eV.	Lattice constant along crystal growth axis *A*
p-PDA	2×10^{15}	0.78	2.26	8.73
m-PDA	6×10^{14}	0.93	2.11	
o-PDA	10^{16}		2.22	
NDA	1.0×10^7	0.40	1.14	6.75
BEN	1×10^{14}	0.71		6.11
TOL	10^{16}			
APM	$>10^{16}$			

4) Among the three isomers of phenylenediamine (PDA), the para substituent is the best donor; for instance, *m*-PDA and *o*-PDA do not form complex crystals with CHL, and the resistivity of the *p*-PDA-iodine system is 10^5 Ωcm., while those of *m*-PDA-isodine and *o*-PDA-iodine are 10^7 Ωcm. and 10^9 Ωcm.[4] respectively.

5) It cannot be expected that the charge-transfer complex the donor of which is nonconjugated aromatic amine, APM, will have a conductivity as good as that of conjugated amine complexes.

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[4] H. Kusakawa, unpublished.