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Electronic Properties of Some Complexes of Tetracyanoquinodimethan with Aromatic Diamines

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Complexes of tetracyanoquinodimethan have been prepared with a number of aromatic diamines which are varied in their molecular shape and ionization potential. Infrared absorption spectra have revealed most of the complexes to be ionic in character. They showed a strong ESR absorption; in regard to its temperature dependence, however, three modes of variation were observed for these solid complexes. The complexes with *N,N'*-diphenyl-*p*-phenylenediamine and *N,N'*-di-β-naphthyl-*p*-phenylenediamine were considered to be of non-bonding type and showed no ESR absorption. However, no appreciable difference in semiconductive properties has been found between the ionic type and the non-bonding type complexes, except the complex of diaminodurene-TCNQ (1 : 2). The latter showed a high electrical conductivity and a paramagnetic behavior which was nearly independent of temperature.

In recent years, Weiss' idea[1] that some organic molecular complexes are ionic in their ground state has been proved by studies of their visible[2] and infrared[3,4] absorption spectra. Usually, as expected, such ionic complexes are formed by an electron transfer from a good electron-donor to a good electron-acceptor, provided that the resulting ion radicals are sufficiently stable.

Although these ion radicals are themselves paramagnetic, it is of interest to see how their paramagnetism is modified upon aggregation. This was studied by Kainer *et al.*[5–8] in 1950's for the complexes formed between aromatic diamines and halogenated benzoquinones. They discussed three possible modes of variation of the paramagnetism with temperature. One is a normal magnetic behavior of Curie type, and others are paramagnetism controlled by thermal equilibration between magnetic and non-magnetic states.

Most complexes studied by Kainer *et al.*[5–8] showed the paramagnetism of Curie type in their temperature range. In these years, however, the complexes of *p*-chloranil with diaminodurene[9] and *p*-phenylenediamine,[10,11] and the complexes of iodine with perylene,[12] pyrene[12] and benzidine[11] have been shown to be of the other type having a magnetic state at thermally accessible position. We have also found a similar magnetic property with the complex obtained from *N,N,N',N'*-tetrametyl-*p*-phenylenediamine and 7,7,8,8-tetracyano-*p*-quinodimethan (TCNQ).[13]

Our study has been extended to a number of complexes based on TCNQ as an acceptor, using various aromatic diamines as a donor. Tetracyanoquinodimethan is known to possess a marked acceptor ability, and furthermore, it shows remarkable stability in its anion radical form, which is an important property suited to our systematic study. The complexes studied are tabulated in Table 1, in which the corresponding abbreviations are also given.

Experimental

Chemicals. 7,7,8,8-Tetracyano-*p*-quinodimethan was synthesized from 1,4-cyclohexanedione by the method described by Acker and Hertler,[14] and purified by recrystallization from acetonitrile. Diaminodurene was synthesized from durene by nitration followed by reduction, and purified by sublimation in a vacuum. Other aromatic amines were obtained from commercial sources,

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Table 1. The complexes studied and solvents used in preparation

Donor	Complex	Solvent used in preparation
p-Phenylenediamine	*p*-PD·TCNQ	Chloroform
N,N-Dimethyl-*p*-phenylenediamine	DMPD·TCNQ	Dichloromethane
N,N-Diethyl-*p*-phenylenediamine	DEPD·TCNQ (2 : 3)	Chloroform
N,N,N',N'-Tetramethyl-*p*-phenylenediamine	TMPD·TCNQ	Methanol
Diaminodurene	DAD·TCNQ (1 : 1)	Tetrahydrofuran
	DAD·TCNQ (1 : 2)	Ethanol and chloroform
o-Phenylenediamine	*o*-PD·TCNQ (2 : 1)	Dichloromethane
Benzidine	BD·TCNQ	Dichloromethane
N,N'-Diphenyl-*p*-phenylenediamine	DφPD·TCNQ	Chloroform
N,N'-Di-β-naphthyl-*p*-phenylenediamine	DNPD·TCNQ	Dichloromethane

Table 2. Determination of the chemical composition of the complexes

Complex	Wavelength used mμ	Extinction coefficient *l*/mol·cm		Composition (Donor : Acceptor)	
		Amine	TCNQ[a]	Spectral analysis	Stoichiometry
p-PD·TCNQ	249	7800	2460	1 : 0.95	1 : 1
DMPD·TCNQ	260	11400	1570	1 : 0.96	1 : 1
DEPD·TCNQ (2 : 3)	265	9730	1000	1 : 1.35	2 : 3
DAD·TCNQ (1 : 1)	243 (400)	7850 (100)[b]	2870	1 : 0.85	1 : 1
o-PD·TCNQ (2 : 1)	245	6020	2940	1 : 0.47	2 : 1
BD·TCNQ	287	25800	450	1 : 1.03	1 : 1
DφPD·TCNQ	304 (400)	28000 (200)[b]	1400	1 : 1.09	1 : 1
DNPD·TCNQ	319	26000	3300	1 : 0.82	1 : 1

a) The concentration of TCNQ was first determined from the absorbance at 400 mμ; its extinction coefficient at 400 mμ was taken to be 67600 *l*/mol·cm.

b) The contribution at 400 mμ was neglected in determining the TCNQ concentration.

and used after purification by recrystallization, sublimation or distillation under a reduced pressure. All solvents used for complex formation were commercial ones, and were used without further purification.

Complex Preparation *p*-PD·TCNQ. Deep purple polycrystals were obtained by mixing a solution of 25 mg of TCNQ in 60 m*l* of chloroform with a solution of 14 mg of *p*-phenylenediamine in 20 m*l* of chloroform at room temperature.

TMPD·TCNQ. To a saturated solution of Würster's blue perchlorate in methanol was added a saturated solution of lithium salt of TCNQ in methanol at room temperature, and dark green crystals thus formed were collected.

DAD·TCNQ (1:2). To a solution of 95 mg of diaminodurene in 70 m*l* of ethanol was introduced hydrogen iodide and then added 150 m*l* of diethyl ether. White precipitate was obtained. To a solution of 101 mg of the precipitate in 25 m*l* of ethanol was added a solution of 102 mg of TCNQ in 150 m*l* of chloroform, and the mixture was allowed to stand overnight at room temperature. Black rod crystals were obtained.

Other complexes were prepared from neutral components in a similar manner to that adopted in the preparation of *p*-PD·TCNQ. Solvents used are given in Table 1. In some cases, a complex was prepared under a nitrogen atmosphere and sealed into a sample tube without being exposed to air. Its ESR absorption was found to be identical, in every way, with that of the corresponding complex prepared in air.

Visible Absorption Measurement. To determine composition of a complex, visible absorption spectrum was examined for a dilute solution of the complex in dichloromethane, in which the complex dissociated into components of their neutral form. Their extinction coefficients at the relevant wavelengths were determined separately, as shown in Table 2. Using these values, the composition of a complex was estimated from the observed absorption spectra. In some cases, an elementary analysis was also adopted for comparison.

Infrared Absorption Measurement. Absorption spectra in the infrared region were measured using the method of Nujol mulls to determine whether the complexes were ionic or not. Lithium salt of TCNQ and bromide of the amines, as well as neutral TCNQ and amines, were used as references.

ESR Absorption Measurement. Electron spin resonance (ESR) measurements were made with a Hitachi X-band spectrometer. To control temperature, nitrogen gas at various temperatures was introduced into a cavity through a quartz dewar and blown toward a sample tube. The temperature was measured by means of a thermocouple attached to a sample. The relative spin concentrations at various temperatures were obtained by integration of derivative curves recorded. The absolute number of spins was determined at room temperature by comparing the integrated absorption intensity of a sample with that of a standard specimen of 1,1-diphenyl-2-picrylhydrazyl, which was calibrated by a static susceptibility measurement.

Electrical Resistivity. Electrical resistivity of a complex was measured in a form of compressed pellet by a DC-method.

Results and Discussion

Composition of the Complexes. Chemical composition (donor to acceptor ratio) obtained from an analysis of visible absorption spectra is given in Table 2. To a molecular complex, however, it is quite reasonable to assume the stoichiometric ratio as is given in the last column of Table 2. The composition of the complex of DEPD·TCNQ was found to be 2 : 3. The ratio was different from the one determined by Melby *et al.*[15] They have given the ratio of 1 : 2 to the complex obtained in the same manner on the basis of an elementary analysis. An elementary analysis, however, was not sensitive enough to distinguish the ratios in question. We thus tentatively adopted the ratio of 2 : 3.

Characterization of the Complexes. Recently, Matsunaga[4] has shown that infrared absorption spectra can be used successfully in characterization of charge transfer complexes of halogenated *p*-benzoquinones. This method is also applicable to TCNQ complexes. The key band in the latter case is that of the C≡N stretching vibration located around 2200 cm^{-1}. For neutral TCNQ, the band is located at 2223 cm^{-1}, and it shifts to 2203 cm^{-1} and becomes somewhat broadened for a typical ion radical salt of TCNQ with lithium.*1

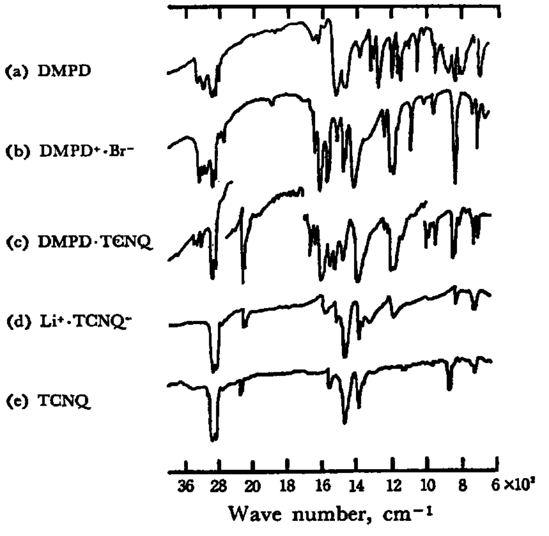

Fig. 1. Infrared absorption spectrum of the complex of DMPD·TCNQ is compared with that of related compounds; (a) DMPD, (b) its bromide, (c) the complex, (d) Li$^+$TCNQ$^-$ and (e) TCNQ.

In Fig. 1 are shown,*2 as an example, the infrared absorption spectra of DMPD, its bromide, DMPD·TCNQ, lithium salt of TCNQ, and TCNQ. The C≡N stretching band is broadened and shifted to 2200 cm^{-1} for the complex. These features are identical to those of lithium salt of TCNQ, and suggest the complex is primarily ionic in its ground state. Further supports are obtained from a comparison of the spectra in Fig. 1. For instance, the C–N stretching vibration band at 1275 cm^{-1} in DMPD disappears and, instead, a new band appears at 1385 cm^{-1} by the formation of the complex. The latter band is considered to correspond to that of the bromide at 1410 cm^{-1}. It is thus concluded that the complex of DMPD·TCNQ is of ionic type.

In a similar way, the complexes of *p*-PD·TCNQ, and DAD·TCNQ (1 : 1) were characterized as essentially of ionic type. The complex of TMPD·TCNQ was also shown to be ionic.[18] In these complexes, therefore, both donor and acceptor are considered to exist as paramagnetic ion radicals. The complex of *o*-PD·TCNQ (2 : 1) belongs almost certainly to this group because of an observed shift and broadening in the C≡N stretching vibration band, but we are not certain about the structure of the amine part.

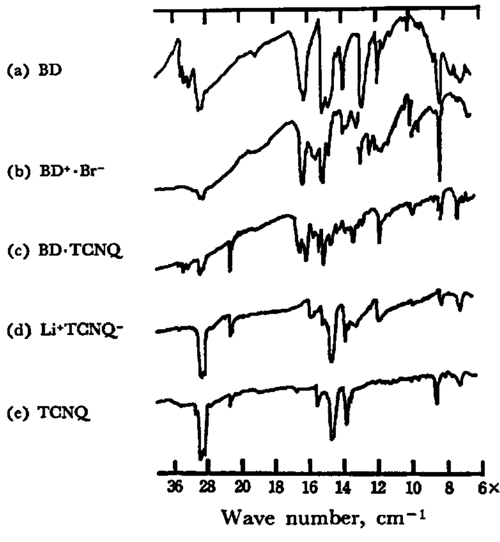

Fig. 2. Infrared absorption spectra of (a) BD, (b) its bromide, (c) the complex of BD·TCNQ, (d) Li$^+$TCNQ$^-$ and (e) TCNQ.

On the other hand, the infrared absorption spectra of DNPD·TCNQ and DφPD·TCNQ were found to be quite in accord with a superposition of spectra of neutral components. These complexes are thus

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*1 Actually, the band consists of three lines at 2171, 2189 and 2203 cm^{-1} for the anion radical salt. The absorption at 2203 cm^{-1} is the most intense one.

*2 Note that the absorption bands due to Nujol are not deleted from the spectra in Figs. 1, 2 and 3.

considered to be of non-bonding type. The complex of BD·TCNQ may also fall into this group, for which the C≡N stretching vibration band was found to be sharp and located closely to that of neutral TCNQ. As is compared in Fig. 2, however, the entire spectrum of this complex is not explained either by a superposition of ionic components or by a superposition of neutral components. At this moment, therefore, we are not conclusive, but we are of opinion that the complex may also be of non-bonding type.

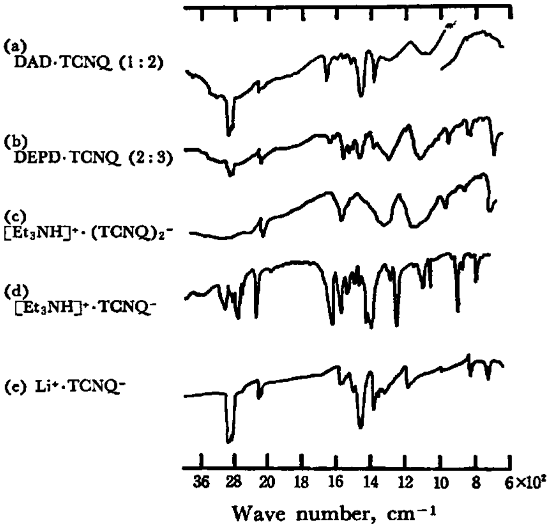

Fig. 3. Infrared absorption spectra of (a) DAD·TCNQ (1 : 2), (b) DEPD·TCNQ (2 : 3), (c) $[\mathrm{Et_3NH}]^+(\mathrm{TCNQ})_2^-$, (d) $[\mathrm{Et_3NH}]^+(\mathrm{TCNQ})^-$ and (e) $\mathrm{Li^+TCNQ^-}$.

The infrared absorption spectra of DAD·TCNQ (1 : 2) and DEPD·TCNQ (2 : 3) are shown in Fig. 3, together with those of $[\mathrm{Et_3NH}]^+(\mathrm{TCNQ})_2^-$, $[\mathrm{Et_3NH}]^+(\mathrm{TCNQ})^-$ and lithium salt of TCNQ. In these complexes, it was found that the key band around 2200 cm^{-1} was broadened, and that two new broad absorptions appeared at 1100 and 1300 cm^{-1}. These features are quite in accordance with the spectrum of $[\mathrm{Et_3NH}]^+(\mathrm{TCNQ})_2^-$.[15] Therefore, the TCNQ part of the complexes was considered to possess a similar character to that of the latter salt. The amine part of DAD·TCNQ (1 : 2) and the 1 : 2 complex of DEPD·TCNQ, on the other hand, has been assigned to an onium type cation by Melby *et al.*[15] This is very likely for the complex of DAD·TCNQ (1 : 2) because of its preparation procedure. From an infrared absorption, we could not determine whether the amine part in our 2 : 3 complex of DEPD·TCNQ takes an onium form or a positive ion radical form. When it was dissolved in acetonitrile, the complex showed a visible absorption spectrum characteristic of a positive ion radical of Würster's blue type. We thus concluded that DEPD exists as an ion radical form in the complex.

Magnetic and Electrical Properties. The magnetic and electrical properties observed for the complexes are summarized in Table 3, in which the complexes are divided into four groups, A, B, C and D for convenience, according to differences observed in the temperature dependence of ESR absorption intensities. The complexes in group A show a rapid intensity drop with the decrease in temperature, while the complex in group B shows a very slow descent. Group C includes the complexes for which the paramagnetism is of Curie type, and group D stands for the complexes of no ESR absorption.

The complexes of *p*-PD·TCNQ, DMPD·TCNQ, DAD·TCNQ (1 : 1) and *o*-PD·TCNQ (2 : 1), as well as TMPD·TCNQ,[18] fall into group A. The intensity-temperature curves are shown in Figs. 4 and 5. A common feature of this group is that the ESR absorption loses its intensity rather sharply in the higher temperature region when the temperature is lowered. In the lower temperature region, however, these complexes behave differently. For *p*-PD·TCNQ and TMPD·TCNQ, the intensity reaches to its minimum and then increases as the

Table 3. Magnetic and electrical properties of the complexes

Complex	Spin concentration[a)]	J (eV)	$\rho_{15^\circ\mathrm{C}}$, Ω·cm	E (eV)	Type
p-PD·TCNQ	3×10^{22}	0.15	4.2×10^{3}	0.17	A
DMPD·TCNQ	3×10^{22}	0.21	4.0×10^{7}	0.48	A
TMPD·TCNQ	2×10^{23}	0.08	6.8×10^{5}	0.36	A
o-PD·TCNQ (2 : 1)	7×10^{21}	0.07	1.4×10^{7}	0.45	A
DAD·TCNQ (1 : 1)	1×10^{22}	0.13	1.5×10^{6}	0.27	A
DAD·TCNQ (1 : 2)	3×10^{23}	—[b)]	1.5×10^{1}	0.04	B
DEPD·TCNQ (2 : 3)	8×10^{23}	0	3.3×10^{3}	0.08	C
BD·TCNQ	5×10^{21}	0	5.1×10^{3}	0.08	C
DϕPD·TCNQ	No signal	—	4.9×10^{5}	0.33	D
DNPD·TCNQ	No signal	—	6.7×10^{7}	0.67	D

a) Number of spins per one mole of a complex at room temperature, 296°K.
b) Slight change in intensity; about 20% decrease from 300 to 120°K.

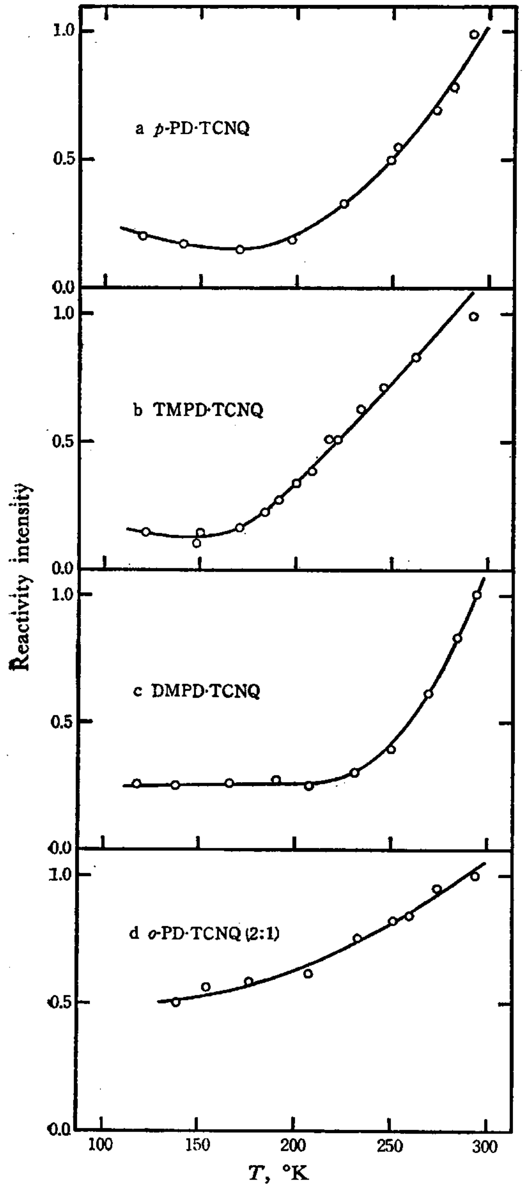

Fig. 4. Relative ESR absorption intensities of the complexes of (a) *p*-PD·TCNQ, (b) TMPD·TCNQ, (c) DMPD·TCNQ and (d) *o*-PD·TCNQ (2 : 1) are plotted against temperature. The intensities are arbitrarily normalized to unity at room temperature.

temperature decreases, while the other complexes show no minimum and their intensity traces a plateau. For these complexes, the ESR absorption intensity I in the higher temperature region was analysed by an equation

$$I = C\exp(-J/kT)/T$$

where C is a constant and J is an activation energy for generation of a magnetic state. A plot of $\ln(IT)$ *vs.* $1/T$ yielded a straight line, whence the J-values in Table 3 were obtained.[*3]

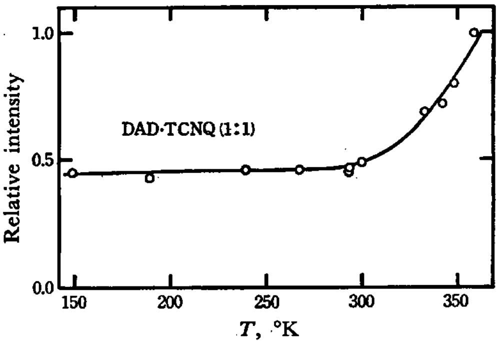

Fig. 5. Plot of relative ESR absorption intensities as a function of temperature for complex of DAD·TCNQ (1 : 1).

For the complex of DAD·TCNQ (1 : 1), there was only a slight decrease in its ESR absorption intensity below room temperature. As shown in Fig. 5, however, we observed a sharp increase in intensity when the temperature was raised above room temperature. This change was found to be completely reversible, and the J-value listed was determined from this part of temperature dependence.

Other ESR behaviors of the complexes in group A are more or less identical with each other. The line width was found to change with temperature with a single exception of *p*-PD·TCNQ. The line width was, in general, very sharp at room temperature, but it was broadened by factors of 2—5 by lowering the temperature. The complex of *p*-PD·TCNQ showed virtually no broadening effect over the whole temperature range. The absorption for the complexes of DAD·TCNQ (1 : 1), *o*-PD·TCNQ (2 : 1) and DMPD·TCNQ consisted of a single line, while the other complexes showed a structure characteristic of g-factor anisotropy. The line shape was not affected by an introduction of air for all complexes in group A.

It should be noted that the spin concentrations at room temperature are not consistent with the order of the J-values. Higher concentration may be expected for a complex with smaller J-value. The complex of *o*-PD·TCNQ (2 : 1) is of the smallest J-value, but it has the lowest concentration.

Electrical resistivity of these complexes was found to be rather high at room temperature compared to that of groups B and C. The activation energy E for electrical conduction in the equation of $\sigma = \sigma_0 \exp(-E/kT)$ was also relatively large, and always larger than that for spin excitation (J). For the complex of *p*-PD·TCNQ, however, both activation energies were found to be virtually coincident within

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[*3] A correction was made for the intensities in the higher temperature region of the complexes, *p*-PD·TCNQ and TMPD·TCNQ, by subtracting the intensities obtained by an extrapolation from the lower temperature side to the high temperature side.

a range of experimental accuracy, which would have some significance in a sense that a similar observation[12] was reported for the complexes of iodine with perylene and pyrene. In the latter complexes, the parallelism in both activation energies has strongly supported a prediction that conduction electrons (or holes) are responsible for the observed paramagnetism. However, it seems rather hasty to draw the same conclusion for the complex of *p*-PD·TCNQ by reason of the general tendency of $E > J$ in this group of complexes.

Group B consists of only one member, DAD·TCNQ (1 : 2). It should be, however, noted that this salt is different structurally from other complexes studied here. It has, as shown in Fig. 6, a unique paramagnetism similar to that found with the salts of (quinolinium)$^+$(TCNQ)$_2$$^-$ type.[16,17] The intensity-temperature curve was very similar to that of the lower temperature portion of DAD·TCNQ (1 : 1). To check the behavior at higher temperatures, we raised the temperature above room temperature, but we could not observe any steep rise of its ESR absorption intensity. Furthermore, in contrast to the complexes in group A, the absorption width was found to be very sensitive to air. In a vacuum, it gave a sharp absorption with a structure due to *g*-factor anisotropy. An introduction of air caused a remarkable broadening in the width and the structure was smeared out. The effect of air on line width is given in Table 4.

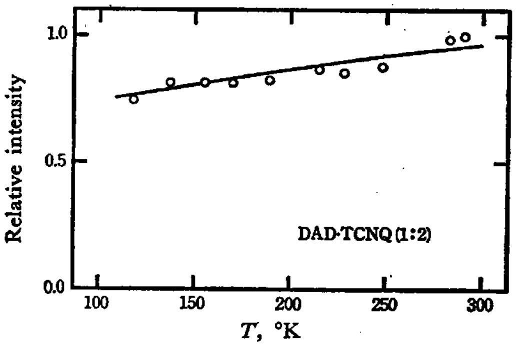

Fig. 6. Temperature dependence of relative ESR absorption intensities for DAD·TCNQ (1 : 2).

TABLE 4. EFFECT OF AIR ON THE ESR ABSORPTION LINE WIDTH

Complex	Line width* (in gauss)	
	in a vacuum	in air
DAD·TCNQ (1 : 2)	1.4_4	2.2_7
BD·TCNQ	1.1_4	3.1_2

* The line width was measured at the half height of an integrated absorption curve.

The electrical resistivity of DAD·TCNQ (1 : 2) was found to be very low and the activation energy was also small. These are again a similar feature of the salt of quinolinium-TCNQ type.[16,18] The ESR line shape of DAD·TCNQ (1 : 2) was sometimes distorted by skin-effect because of its low resistivity. Therefore, a possibility that the observed ESR absorption is due to conduction electrons may be considered. In the case of the salt of (quinolinium)$^+$(TCNQ)$_2$$^-$, the magnetic susceptibility-temperature curve has been interpreted in terms of conduction electrons.[19]

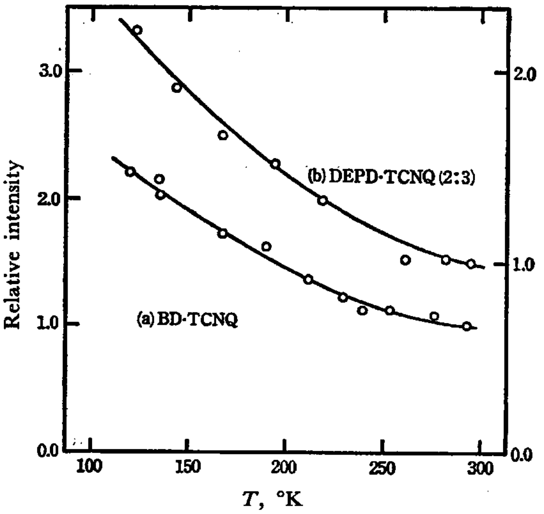

Fig. 7. The variations of ESR absorption intensities with temperature are illustrated in relative units for the complexes of (a) BD·TCNQ and (b) DEPD·TCNQ (2 : 3). The scale for (a) is shown on left, while for (b) on right. The actural intensity for (a) is smaller by a factor of about 10^2 than that for (b) at room temperature (see Table 3).

There are two complexes, DEPD·TCNQ (2 : 3) and BD·TCNQ, in group C. These complexes exhibited Curie type paramagnetism, as shown in Fig. 7, and they showed relatively low electrical resistivity and small activation energy. However, other properties of these complexes were found to differ remarkably from one another. The spin concentration of DEPD·TCNQ (2 : 3) was very high. The absorption line shape was not varied either by temperature or by air. On the other hand, the spin concentration of BD·TCNQ was found to be very low; indeed, there was only one unpaired electron over about 100 donor-acceptor pairs. The ESR absorption line shape and width of BD·TCNQ were found to be sensitive to air, whereas there was no temperature effect on them.

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A change of line width by air is indicated in Table 4.

A low spin concentration in the complex of BD·TCNQ suggests its non-bonding character, because, in complexes of non-bonding type, the spin concentration is usually very low and the ESR absorption intensity varies, in most cases, following Curie law. However, a relatively high conductivity and a small activation energy of BD·TCNQ suggest some difference in property from those of usual weak complexes. These features seem to be correlated to a difficulty found in characterizing the complex by the infrared absorption spectrum.

The complexes DϕPD·TCNQ and DNPD·TCNQ were found to be diamagnetic and classified under group D. The diamagnetism is consistent with the results in their infrared absorption spectra.

Conclusion

The complexes studied are found to show a variety of properties, magnetically, electrically and optically, even though they are formed between chemically resembling donors and the same acceptor. An ionization potential of a donor, for example, is not a determining factor of a complex character by itself. To gauge the ionization potential of these donors, we used wavelengths of absorption maxima of charge-transfer bands for the complexes of *p*-bromanil with the amines in carbon tetrachloride.[*4] The results are given in Table 5. The donors fall into two groups; most donors have the maxima in the range of 900—970 mμ, and only three donors have the maxima in 620—670 mμ. However, in the former group, for which the ionization potential is lower than that for the latter, the donors which give rise to a complex of non-bonding type are included, as well as those giving rise to an ionic complex. The donors in the latter group give also an ionic complex, although their ionization potentials are higher than those of DϕPD and DNPD. Within our experimental range, therefore, it is concluded that a character, dative or non-bonding, of a complex with a particular acceptor is determined by a conflict between ionization potential of a donor and its steric factors. This can be easily seen in a comparison between a character of TMPD·TCNQ or *p*-PD·TCNQ and that of DϕPD·TCNQ or DNPD·TCNQ.

Table 5. Charge transfer absorption maxima of the complexes of *p*-bromanil with the amines in carbon tetrachloride, as an indication of the ionization potentials

Donor	Absorption maximum
p-PD	672 mμ
DMPD	908
DEPD	950
TMPD	918
DAD	973
o-PD	646
BD	624
DϕPD	942 (453)[a]
DNPD	931 (485)[a]

a) There are two charge transfer absorption bands for the complex.

Once an ionic character is obtained for a complex, its magnetic behavior is dominated by an electronic interaction between the unpaired electrons on donor and acceptor ion radicals. If there is no interaction, the complex will show the paramagnetism of the Curie type. However, an appreciable amount of interaction may result, as discussed by Kainer *et al.*,[8] in the paramagnetism of the other type. For such an interaction, charge-transfer stabilization of the non-magnetic ground state has been suggested to explain a somewhat large activation energy for spin excitation.[20,21]

All the ionic charge-transfer complexes studied except DEPD·TCNQ (2 : 3) exhibit the latter type of paramagnetism.[*5] Therefore, the paramagnetic behavior of type in group A seems very common to the ionic complexes. In the case of DEPD·TCNQ (2 : 3), the interaction is, in our opinion, hindered by the large substituents and possibly by its anomalous composition.

Finally, it could be mentioned that the ESR behaviors of the complexes in group A are consistent, at least qualitatively, with a prediction for the ESR absorption of Wannier spin excitons.[22] The crystal structure of the 1 : 1 complexes in group A is very well considered to be similar to that of the complex of TMPD·TCNQ. In the latter complex, the donor and acceptor ions are stacked alternately and equidistantly in a face-to-face manner forming a linear chain.[23] For such a structure, it has been predicted that spin excitation produces Wannier type spin excitons, which are observable in ESR. The line width of the ESR absorption for Wannier type excitons is suggested to be approximately independent of temperature.[22]

The line width for *p*-PD·TCNQ did not change with temperature, and our attempts to observe any fine-structure and $\Delta m=\pm 2$ transition have failed for the complexes in group A. These observations may suggest the possibility of Wannier spin excitons in these solid complexes.

[*4] Since the complexes of TCNQ with some of the amines are scarcely soluble in a less polar solvent and since they dissociate into ions in a polar solvent, it is very difficult to observe a charge-transfer band of the TCNQ complexes itself.

20) P. L. Nordio, Z. G. Soos and H. M. McConnell, *Ann. Rev. Phys. Chem.*, **17**, 237 (1966).

21) H. M. McConnell, B. M. Hoffman and R. M. Metzger, *Proc. Natl. Acad. Sci. U. S.*, **53**, 46 (1965).

[*5] DAD·TCNQ (1 : 2) is eliminated in this discussion, because of its exceptional structure.

22) Z. G. Soos, *J. Chem. Phys.*, **46**, 4284 (1967).

23) A. W. Hanson, *Acta Cryst.*, **19**, 610 (1965).