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Magnetic and Optical Properties of Ionic Electron-Donor-Acceptor Complexes

Yoichiro SATO,[*1] Minoru KINOSHITA, Mizuka SANO[*2] and Hideo AKAMATU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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The magnetic susceptibilities and optical absorption spectra of a number of ionic electron-donor-acceptor complexes have been studied in a solid state. The complexes of *N,N,N'N'*-tetramethyl-*p*-phenylenediamine with *o*-chloranil and *o*-bromanil were found to have a composition of 2 : 3 and their paramagnetic susceptibilities followed the Curie-Weiss law with the Weiss constant of 0 ± 5°K in the temperature range between 77°K and room temperature. It was noted that in these complexes paramagnetism is dominated by the monopositive ion radical of the amine and not by the quinone part. In contrast to this, the complexes formed by combinations of *p*-phenylenediamine and tetramethyl-*p*-phenylenediamine with *p*-chloranil and *p*-bromanil had a composition of 1 : 1 and showed paramagnetic susceptibilities which varied with temperature according to the thermal equilibrium between magnetic and non-magnetic states. The thermal equilibrium is characterized by the activation energy determined by the interaction between the monopositive and the mononegative ion radicals of the components. The absorption spectra of 1 : 1 complexes showed a charge-transfer band in the near-infrared region, while those of 2 : 3 complexes did not. The activation energy obtained magnetically is discussed in relation to the appearance of the charge-transfer absorption band. The temperature dependence of the activation energy is also discussed.

In the previous papers,[1,2] we suggested the importance of the charge-transfer interaction between ion radicals for understanding the observed magnetic susceptibilities of the crystals made of radicals. There is a correlation between the magnetic susceptibility and the appearance of a charge-transfer band in the absorption spectrum of a radical crystal. A radical crystal which shows an intense charge-transfer band is apparently diamagnetic or at most weakly paramagnetic at room temperature. The exchange coupling constant (J) for the crystal was found to be as large as 0.05 eV or more. A crystalline radical with the exchange coupling constant $J\leq0.02$ eV exhibits a fairly weak charge-transfer band. A charge-transfer band is usually undetectable for a solid with $J<10^{-3}$ eV. We have studied a similar relationship between the magnetic and optical properties for the ionic electron-donor-acceptor complexes, which may be designated as D^+A^--type complexes. In this case, the interactions between unlike molecules are of primary importance, in contrast to the systems, previously studied, of ion radical salts where interactions between like molecules are important.

We have prepared the stable solid complexes by the combination of *p*-phenylenediamines which are strong electron donors (D) with halogenated benzoquinones which are strong electron acceptors (A). In these solid complexes, an electron transfers completely from a donor molecule to an acceptor molecule, resulting in the $|D^+A^-\rangle$ ground state and $|DA\rangle$ charge-transfer excited state, when expressed in terms of a DA pair. The situation is thus reversed when compared to usual charge-transfer complexes.

Experimental

Preparation. Ionic complexes were formed between electron donors; *p*-phenylenediamine (PD), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and electron acceptors; chloranil (*p*-CA), *o*-chloranil (*o*-CA), bromanil (*p*-BA) and *o*-bromanil (*o*-BA), according to the method described by Kainer *et al.*[3-6] The complexes were precipitated by mixing the benzene solutions of amine

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[*1] Present address: National Institute for Researches in Inorganic Materials, Bunkyo-ku, Tokyo.

[*2] Present address: Department of Materials Science, The University of Electro-communications, Chofu, Tokyo.

1) Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, **42**, 548 (1969).

2) Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, *ibid.*, **42**, 3051 (1969).

3) H. Kainer, D. Bijl and A. C. Rose-Innes, *Naturwiss.*, **41**, 303 (1954).

4) H. Kainer and A. Uberle, *Chem. Ber.*, **88**, 1147 (1955).

5) H. Kainer and W. Otting, *ibid.*, **88**, 1921 (1955).

6) D. Bijl, H. Kainer and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 765 (1959).

and quinone. The composition was found to be 1 : 1 for *p*-quinone complexes. The complex formed from TMPD and *o*-BA was found to have the composition $TMPD_2 \cdot o\text{-}BA_3$. The composition of the complex formed from TMPD and *o*-CA was not determined. It was tentatively assigned, however, to be $TMPD_2 \cdot o\text{-}CA_3$, because of the close resemblance of the magnetic and optical behavior to that of $TMPD_2 \cdot o\text{-}BA_3$.

$TMPD_2 \cdot o\text{-}BA_3$ (Found: C, 28.59; H, 2.17; N, 3.19%. Calcd: C, 28.53; H, 2.07; N, 3.50%).

Measurements. The static susceptibilities of the complexes were measured as a function of temperature with a Faraday-type magnetic balance[7] in the range from 77°K to room temperature or a somewhat higher temperature according to the stability of a compound. The absorption spectra were measured in the range from 340 to 2400 mμ for a powder sample suspended in liquid paraffin.

Results

Magnetic Susceptibilities. The susceptibilities of $TMPD_2 \cdot o\text{-}CA_3$ and $TMPD_2 \cdot o\text{-}BA_3$ were found to be strongly paramagnetic at room temperature and increased with decreasing temperature, while the susceptibilities of the other complexes were diamagnetic and their temperature variations were relatively small.

For the purpose of evaluating diamagnetic contribution, the susceptibilities of the neutral component molecules were measured. The results are given in Table 1. The susceptibilities of the *o*-quinones are seen to be somewhat less diamagnetic than those of the corresponding *p*-quinones.

Table 1. Magnetic susceptibilities of the amines and the quinones

Compound	Molar susceptibility $\chi_M \times 10^6$(emu/mol)
p-Phenylenediamine	−73
N,N,N',N'-Tetramethyl-*p*-phenylenediamine	−125
Chloranil	−113
o-Chloranil	−105
Bromanil	−148
o-Bromanil	−139

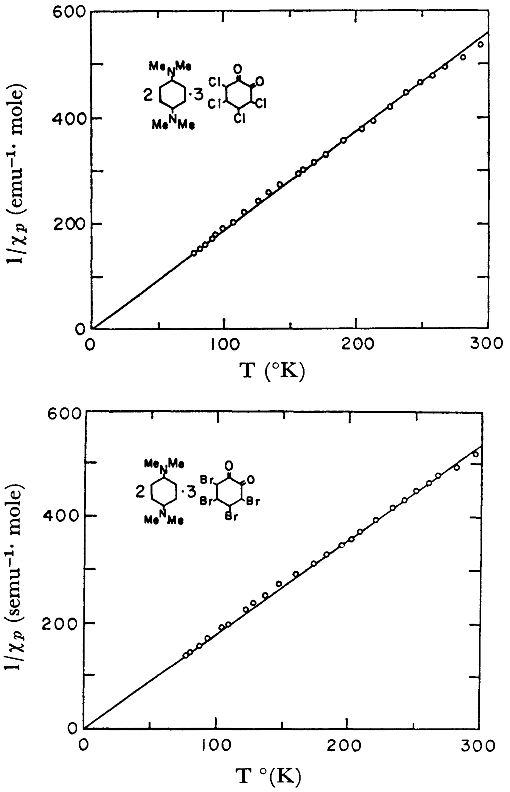

Fig. 1. Inverse paramagnetic susceptibilities of $TMPD_2 \cdot o\text{-}CA_3$ and $TMPD_2 \cdot o\text{-}BA_3$ versus temperature.

For $TMPD_2 \cdot o\text{-}CA_3$ and $TMPD_2 \cdot o\text{-}BA_3$, the sum of the susceptibilities of the neutral components was taken to be their diamagnetic susceptibility. When the inverse paramagnetic susceptibility $1/\chi_p$ was plotted against temperature, straight lines were obtained as shown in Fig. 1. The values of the Curie constant C and the Weiss constant θ were obtained from the slope of the line and its intersection on the temperature axis, respectively. The results are given in Table 2.

Table 2. Magnetic susceptibilities of the compleexes

Compound	Observed susceptibility at 296°K $\chi_M \times 10^6$ (emu/mol)	Diamagnetic susceptibility $\chi_d \times 10^6$ (emu/mol)	Paramagnetic susceptibility at 296°K $\chi_p \times 10^6$ (emu/mol)	Weiss constant θ (°K)	Curie constant C (emu °K/mol)
$TMPD_2 \cdot o\text{-}CA_3$	1297	−565	1862	0±5	0.551
$TMPD_2 \cdot o\text{-}BA_3$	1226	−694	1920	0±5	0.568
TMPD·*p*-CA	−226	−245	(19)	—	—
TMPD·*p*-BA	−230	−285	(55)	—	—
PD·*p*-CA	−180	−212	(32)	—	—
PD·*p*-BA	−231	(−259)	(28)	—	—

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[7] Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, **40**, 2539 (1967).

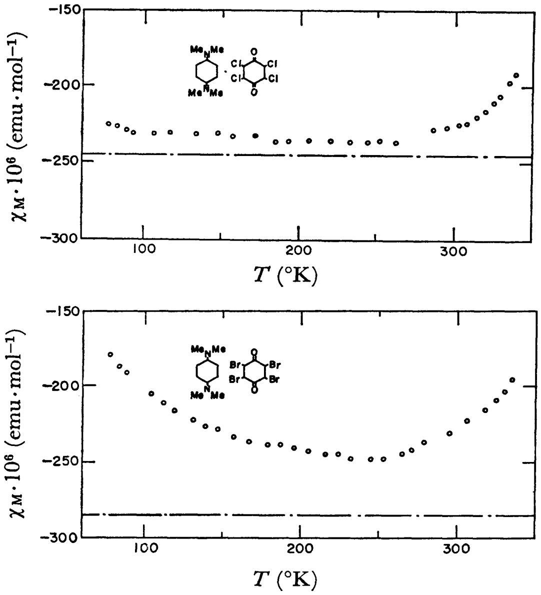

Fig. 2. Magnetic susceptibilities of TMPD·*p*-CA and TMPD·*p*-BA versus temperature.

—·—·— χ_{dia}.

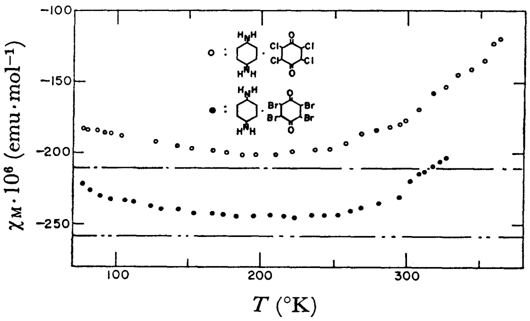

Fig. 3. Magnetic susceptibilities of PD·*p*-CA and PD·*p*-BA versus temperature.

—·—·—·— χ_{dia}.
—··—··—··—

TABLE 3. DIAGNETIC PARTS OF THE COMPLEXES

Compound	χ_d(obs) $\times 10^6$ (emu/mol)	χ_d(calc) $\times 10^6$* (emu/mol)
TMPD·*p*-CA	−245	−238
TMPD·*p*-BA	−285	−274
PD·*p*-CA	−212	−185
PD·*p*-BA	(−259)	−221

* The sum of the values found for the neutral components given in Table 1.

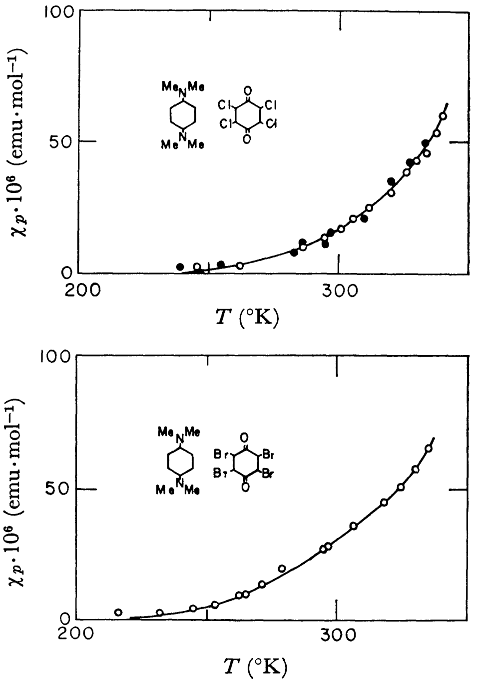

Fig. 4. Intrinsic paramagnetic susceptibilities of TMPD complexes.

The susceptibilities of TMPD·*p*-CA, TMPD·*p*-BA, PD·*p*-CA and PD·*p*-BA are plotted as a function of temperature in Figs. 2 and 3. The general feature of temperature dependence resembles each other. In a higher temperature region the susceptibility decreased with decreasing temperature, but it increased through a minimum in a lower temperature region. The diamagnetic contribution was evaluated by assuming that the susceptibility change in the lower temperature region was dominated by the paramagnetic susceptibility of an impurity which followed the Curie law.*3 The diamagnetic susceptibilities thus obtained are given in Table 3, which are in reasonable agreement with the sum of the values for neutral components. The intrinsic paramagnetic susceptibilities, after corrections for the diamagnetic and impurity parts were made, are plotted as a function of temperature in Figs. 4 and 5.

The observed susceptibilities of a given complex exhibited slightly different values among the samples which had been prepared independently. The difference, however, was considered to be caused by a variation in the impurity content, since the difference in susceptibility was found to be proportional to $1/T$ within experimental errors. The intrinsic susceptibility determined after the above-mentioned corrections gave the same value for the different samples.

Electrton Spin Resonance. In order to obtain information on the origin of unpaired electrons, *g*-values were determined for powder samples by

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*3 The assumption seems to be plausible for the reasons mentioned in the following paragraph. It has, in fact, been supported for TMPD·*p*-CA by ESR experiments (Ref. 6).

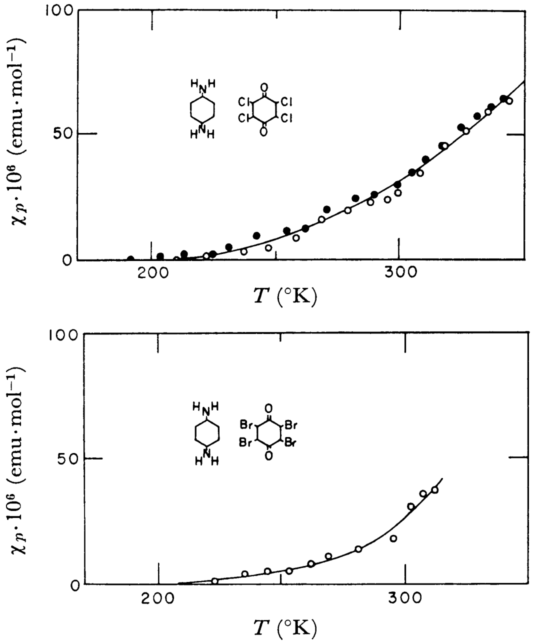

Fig. 5. Intrinsic paramagnetic susceptibilities of PD complexes.

Table 4. g-Factors

$TMPD_2 \cdot o$-CA_3	2.0032	$TMPD^+$	2.0032*
$TMPD_2 \cdot o$-BA_3	2.0036	PD^+	2.0030
TMPD·p-CA	2.0050	p-CA^-	2.0057**
TMPD·p-BA	2.0065	p-BA^-	2.0088**
PD·p-CA	2.0045 (g_{av})		
PD·p-BA	2.0065 (g_{av})		

* Kinoshita and Akamatu, Ref. 18.

** M.S. Blois, Jr., H.W. Brown and J.E. Maling, "Free Radicals in Biological Systems," ed. by M.S. Blois, Jr., *et al.*, Academic Press, New York and London (1961), p. 117.

ESR measurements at room temperature. The values are given in Table 4. A single exchange-narrowed absorption line was observed for the complexes; TMPD·p-CA, TMPD·p-BA, $TMPD_2 \cdot o$-CA_3 and $TMPD_2 \cdot o$-BA_3. An axially symmetric g-factor was observed with the p-phenylenediamine complexes, which is in agreement with the result obtained by Ottenberg, *et al.*[8] and Hughes and Soos.[9] The principal g-values were determined to be: $g_{\parallel}=2.0023$, $g_{\perp}=2.0056$ for PD·p-CA and $g_{\parallel}=2.0020$, $g_{\perp}=2.0087$ for PD·p-BA. The average value, $g_{av}=(g_{\parallel}+2g_{\perp})/3$, is given in Table 4[*4]

The g-values of the p-quinone complexes were found to be intermediate between the values of the components, while those of $TMPD_2 \cdot o$-CA_3 and $TMPD_2 \cdot o$-BA_3 were close to the g-value of Würster's blue ion ($TMPD^+$).

Absorption Spectra. The solid p-quinone complexes showed broad absorption bands as shown in Figs. 6 and 7. It was noted that the spectra of TMPD·p-CA and TMPD·p-BA resembled each other and also those of PD·p-CA and PD·p-BA.

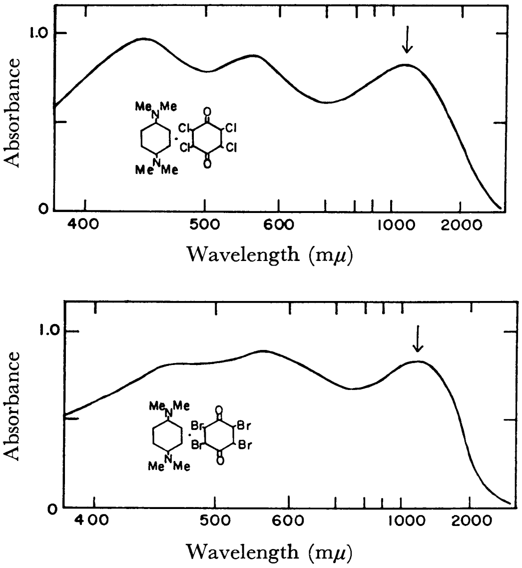

Fig. 6. Absorption spectra of solid TMPD·p-CA and TMPD·p-BA. Arrows indicate the charge-transfer bands.

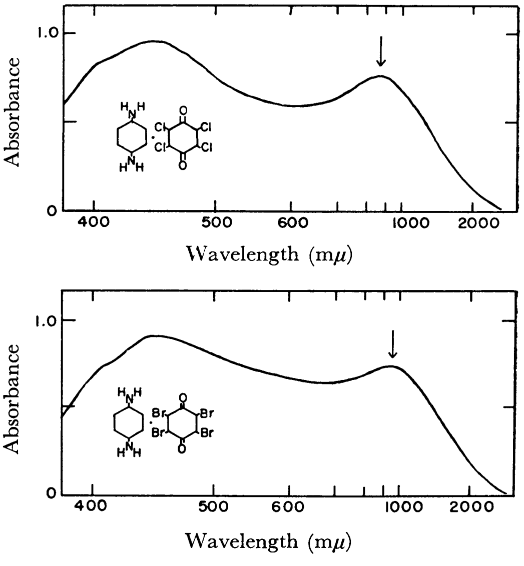

Fig. 7. Absorption spectra of solid PD·p-CA and PD·p-BA, where the charge-transfer bands are indicated by arrows.

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8) A. Ottenberg, C. J. Hoffman and J. Osiecki, *J. Chem. Phys.*, **38**, 1898 (1963); M. E. Browne, A. Ottenberg and R. L. Brandon, *ibid.*, **41**, 3265 (1964).

9) R. C. Hughes and Z. G. Soos, *J. Chem. Phys.*, **48**, 1066 (1968).

[*4] Static susceptibility data showed that the impurity paramagnetism contributed appreciably to the observed paramagnetic susceptibilities of TMPD·p-CA, TMPD·p-BA, PD·p-CA and PD·p-BA, but no separate ESR signal was observed at room temperature.

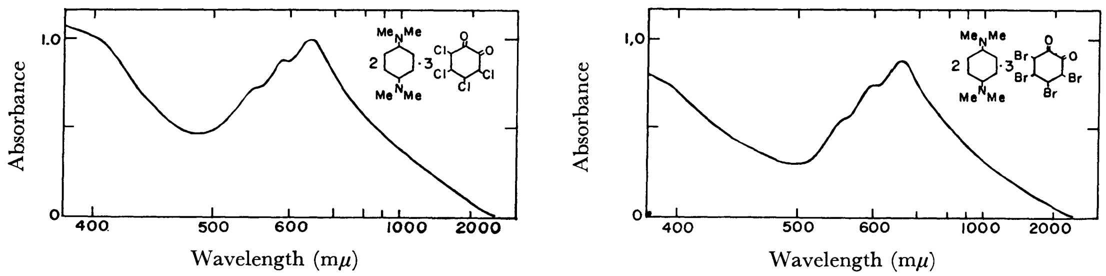

Fig. 8. Absorption spectra of solid $TMPD_2 \cdot$o-CA_3 and $TMPD_2 \cdot$o-BA_3.

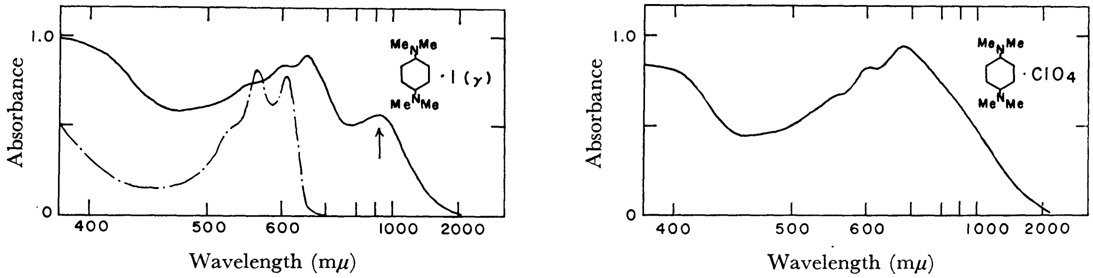

Fig. 9. Absorption spectra of TMPD·I (γ-form) and $TMPD \cdot ClO_4$.
——— Solid spectra, —·—·— $TMPD^+$ in CH_2Cl_2 solution

In contrast to the broad structureless bands of these complexes, $TMPD_2 \cdot$o-CA_3 and $TMPD_2 \cdot$o-BA_3 showed spectra in which the band around 600 mμ had a well-defined structure as seen in Fig. 8. In the observed region, the two spectra were identical as far as position and general features were concerned. For the purpose of comparison, the solid spectra of Würster's blue perchlorate ($TMPD \cdot ClO_4$) and Würster's blue iodide (TMPD·I, γ-form) are shown in Fig. 9. The spectrum of $TMPD \cdot ClO_4$ is in agreement with those observed by other investigators.[10-12] The positions of the absorption peaks are given in Table 5.

Discussion

$TMPD_2 \cdot$o-$TMPD_2 \cdot$o-CA_3. As evidenced by the strong paramagnetism, these complexes are considered to be fundamentally ionic, though they are expected to include a neutral quinone per formula unit. The observed value of the Curie constant indicates that there are only two free spins in a formula unit instead of four spins expected from the simple consideration that there are two monopositive $(TMPD)^+$ and two mononegative (o-CA^- or o-BA^-) ion radicals and a neutral quinone molecule per formula unit.

Table 5. Approximate positions of the absorption peaks of the solid spectra

	(mμ)
TMPD·p-CA	440, 550, 1200
TMPD·p-BA	460, 550, 1200
PD·p-CA	400, 445, 900
PD·p-BA	415, 445, 950
$TMPD_2 \cdot$o-CA_3	540, 595, 650
$TMPD_2 \cdot$o-BA_3	540, 595, 650
$TMPD \cdot ClO_4$	550, 600, 670
TMPD·I (γ-form)	550, 595, 650, 940

It is noted that the g-value of $TMPD_2 \cdot$o-CA_3 coincides with that of the monopositive ion of TMPD in $TMPD \cdot ClO_4$, and that of $TMPD_2 \cdot$o-BA_3 is close to this value. Moreover, the band structure around 600 mμ shows close resemblance with those found for $TMPD \cdot ClO_4$ and TMPD·I as compared in Figs. 8 and 9 and also in Table 5. It seems certain that the peaks are due to Würster's blue ion. Thus, it is concluded that the strong paramagnetism of these complexes is almost entirely due to $TMPD^+$ ion radicals. Since the neutrality condition requires the existence of negative ions, the question remains why the paramagnetic contribution from the quinone anion radicals is undetectable. Although no further attempts have been made to elucidate the question,[*5] the following explanation is possible: 1) The cations and anions form separate column in the crystal. The cations are nearly free, while the anions are strongly coupled with each other due to the different manner of stacking in the columns. As a result, the cations contribute to paramagnetism strongly, while the

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10) G. R. Anderson, *J. Chem. Phys.*, **47**, 3853 (1967).
11) Y. Iida, This Bulletin, **41**, 2615 (1968).
12) T. Sakata and S. Nagakura, *ibid.*, **42**, 1497 (1969).

[*5] No detailed information on the quinone part was obtained from the absorption spectra of Fig. 8.

anions only slightly. 2) The anions exist in certain diamagnetic form, *e. g.*, as dinegative ions or as diamagnetic anions produced by chemical reaction. It is noted that the interaction between Würster's blue ions in these complexes is quite small, in fact the smallest among those observed for other Würster's blue ion radical salts.

Kainer and Überle[4] reported that the complexes formed from TMPD and *o*-quinones were 1:1 complexes. Although the absorption spectra were not explicitly shown, they described the same observations mentioned above, *i. e.*, the appearance of a band with structure in the visible region and the absence of absorption in the near-infrared region in contrast to the case of *p*-quinone complexes. Moreover, they observed strong paramagnetism which corresponded to only one spin per formula unit contrary to their expectation of two spins.[4,6] The highest radical concentration of 0.80 spins per unit of TMPD·*o*-BA in their report corresponds to 2.0 spins per unit of $TMPD_2 \cdot o\text{-}BA_3$. Therefore, their complexes also seem to have the composition 2 : 3 rather than 1 : 1.

TMPD·*p*-CA; TMPD·*p*-BA. Magnetic and optical data are in agreement with those reported by Kainer and Überle[4] and Pott and Kommandeur.[13] The absorption bands in the visible region are reasonably assigned to the intramolecular transitions of the ionized component molecules but not those of neutral components. For TMPD·*p*-CA, the bands at 550 and 440 mμ may be ascribed to $TMPD^+$ and $p\text{-}CA^-$, respectively, and for TMPD·*p*-BA, the bands at 550 and 460 mμ may be due to $TMPD^+$ and $p\text{-}BA^-$, respectively.[*6] These complexes are therefore considered to consist of the amine monopositive and the quinone mononegative ions. The band at approximately 1200 mμ in each spectrum is assigned to the charge-transfer band as pointed out previously on the basis of the polarization spectrum.[14] de Boer and Vos[15] have revealed the alternant face-to-face stacking of $TMPD^+$ and $p\text{-}CA^-$ molecules in the crystal. The interaction between D^+ and A^- is therefore thought to be important and the charge-transfer absorption should be ascribed to the transition of the type $|\cdots D^+A^-D^+A^-D^+A^-\cdots\rangle \rightarrow |\cdots D^+A^-D^0A^0D^+A^-\cdots\rangle$. The molecular stacking in TMPD·*p*-BA seems to be similar in view of the close resemblance of the magnetic and optical behavior.

The interpretation of the absorption spectra is consistent with the result from ESR measurements. The fact that the *g*-values of these complexes are close to the average *g*-values of the component ions indicates an equal contribution of the cation and anion radicals to the paramagnetism.[16] As will be discussed below, the static susceptibility data show that the spins in these complexes are coupled by rather strong antiferrromagnetic interaction of about 0.08 eV.

PD·*p*-CA; PD·*p*-BA. The absorption bands of these complexes in the visible region are also assigned to the intramolecular transitions of the amine monopositive and the quinone mononegative ions. The band in the near-infrared region in each spectrum may also be due to the charge-transfer interaction between D^+ and A^- ions.[14] The *g*-values of these complexes also indicate that the cations and anions contribute equally to paramagnetism.

Thus, the magnetic and optical properties of the complexes studied here are explained on the basis of the completely ionized component molecules in the ground state and strong antiferromagnetic interaction between D^+ and A^- ions. Moreover, it is noted that the charge-transfer bands of these complexes are strong. As a result, it is concluded that the correlation between the exchange coupling constant and the intensity of the charge-transfer band is also present in ionic donor-accepter complexes, in which the interaction between unlike molecules, D^+ and A^-, is important. This implies that the nature of the exchange interaction in D^+A^--type complexes is essentially the same as that in the previously studied D^+D^+-type or A^-A^--type complexes. It also suggests the importance of the charge-transfer stabilization of the singlet ground state in the determination of the observed values of exchange coupling constant. The same argument may also hold for the molecular complexes of diaminodurene-chloranil[17] and TMPD-tetracyano-*p*-quinodimethane.[18]

Temperature Variation of Exchange Coupling Constant

The values of exchange coupling constant (J) can be evaluated by comparison of the intrinsic paramagnetic susceptibilities with a theoretical model; the singlet-triplet model or the linear Ising model. For $TMPD_2 \cdot o\text{-}BA_3$ and $TMPD_2 \cdot o\text{-}CA_3$, the exchange coupling constants were fairly small, being estimated to be $J \lesssim 4 \times 10^{-4}$ eV from the observed Weiss constant of 0 ± 5°K. For the complexes containing *p*-quinones, the values of J were evaluated by two methods. The apparent activation energy E, expressed in the formula

$$\chi_p = (C/T) \exp(-E/kT) \qquad (1)$$

was obtained by plotting $\log(\chi_p T)$ against $1/T$. In

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[13] G. T. Pott and J. Kommandeur, *Mol. Phys.*, **13**, 373 (1967).

[*6] The assignment of the band at 440 mμ to $p\text{-}CA^-$ ion radical is in agreement with the argument given by Andre and Weill, *Mol. Phys.*, **15**, 97 (1968).

[14] T. Amano, H. Kuroda and H. Akamatu, This Bulletin, **41**, 83 (1968).

[15] J. L. de Boer and A. Vos, *Acta Cryst.*, **B24**, 720 (1968).

[16] M. Kinoshita, This Bulletin, **36**, 307 (1963).

[17] D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

[18] M. Kinoshita and H. Akamatu, *Nature*, **207**, 291 (1965).

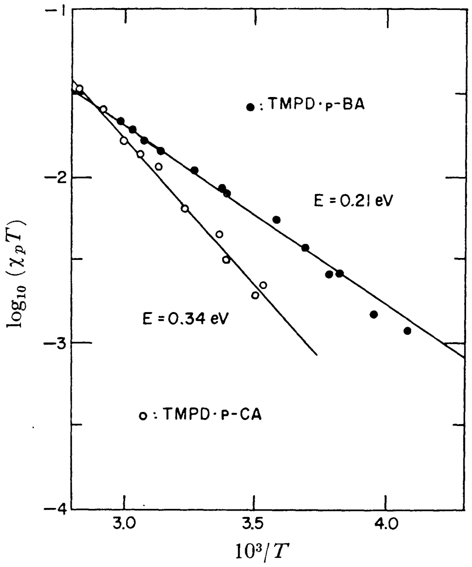

Fig. 10. Plots of log $\chi_p T$ against $1/T$ for TMPD·*p*-CA and TMPD·*p*-BA.

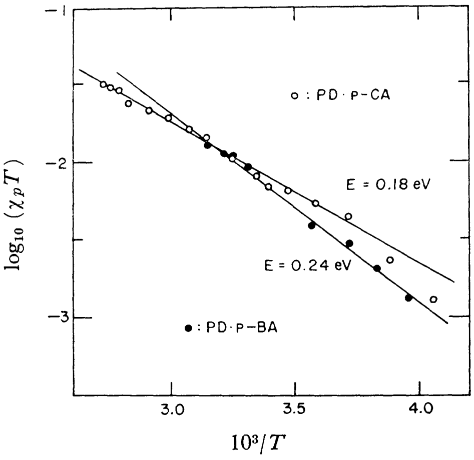

Fig. 11. Plots of log $\chi_p T$ against $1/T$ for PD·*p*-CA and PD·*p*-BA.

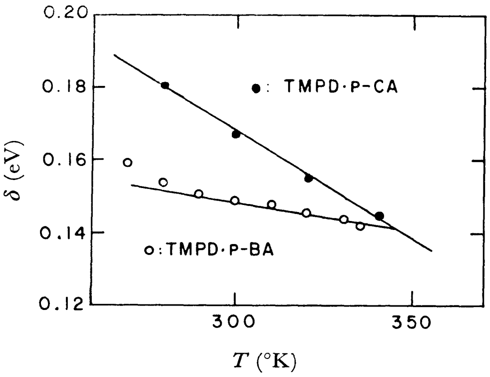

Fig. 12. Temperature variations of the singlet-triplet separation δ ($=2J$) for TMPD·*p*-CA and TMPD·*p*-BA.

TABLE 6. TEMPERATURE VARIATIONS OF EXCHANGE COUPLING CONSTANTS

	δ_0 ($=E$) (ev)	δ(eV) at 300°K	α(ev/°K)	$\delta_0+\alpha T$ at 300°K	J(eV) at 300°K
TMPD·*p*-CA	0.34	0.17	-6.0×10^{-4}	0.16	0.09
TMPD·*p*-BA	0.21	0.15	-1.8×10^{-4}	0.16	0.08
PD·*p*-CA	0.18	0.15	-0.8×10^{-4}	0.16	0.08
PD·*p*-BA	0.24	0.15	-4.4×10^{-4}	0.11	0.08

the case of the singlet-triplet model, E corresponds to the energy separation $\delta(=2J)$ between the singlet ground state and the thermally accessible triplet state ($E=\delta$), and in the case of the linear Ising model it corresponds to J ($E=J$). The plots of $\log(\chi_p T)$ against $1/T$ are shown in Figs. 10 and 11. Direct comparison of experimental data with theoretical curves, by finding the best fit, also gives the value of J. The singlet-triplet model with $\delta=0.15$ eV accounted for the experimental plots for TMPD·*p*-BA and PD·*p*-CA fairly well. The susceptibility rise for TMPD·*p*-CA and PD·*p*-BA, however, was so steep that neither of the models could explain the result. For a closer study, we calculated the values of J at several points of temperature by comparing the experimental susceptibilities with the theoretical ones. The results obtained with the singlet-triplet model are shown in Figs. 12 and 13. It appears that δ is a linear function of temperature and that the temperature variation is small for TMPD·*p*-BA and PD·*p*-CA, and quite large for TMPD·*p*-CA and PD·*p*-BA. The values of δ obtained by the above procedures are given in Table 6. The largest difference between E and δ is noted for TMPD·*p*-CA, *i. e.*, $E=0.34$ eV and $\delta=0.17$ eV at 300°K.

If δ is a linear function of temperature, we may write

$$\delta=\delta_0+\alpha T \tag{2}$$

where δ_0 and α are constants. The slope of the

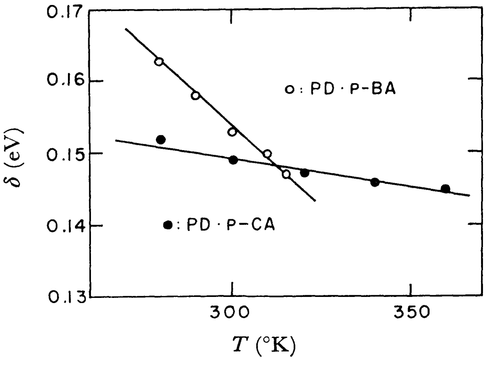

Fig. 13. Temperature variations of the singlet-triplet separation δ ($=2J$) for PD·*p*-CA and PD·*p*-BA

plot of $\log(\chi_p T)$ against $1/T$ gives δ_0 rather than δ itself. Therefore, we put $E=\delta_0$ and see if the large discrepancy between E and δ may be explained by relation (2). The values of α are obtained from the slopes of the straight lines shown in Figs. 12 and 13. The agreement between δ and $\delta_0+\alpha T$ is good as seen from Table 6, which indicates that δ decreases linearly with temperature. It would be appropriate therefore to employ the values of $J(=\delta/2)$ given in the last column of Table 6, *i. e.*, approximately 0.08 eV for all these complexes. If the linear Ising model is employed, a larger value of about 0.11 eV is obtained. It seems that the large effective change in the exchange coupling constant found for TMPD·*p*-CA and PD·*p* BA suggests the temperature variation of intermolecular interactions associated with variation in intermolecular distance. For TMPD·*p*-CA it may be related to the gradual phase transition suggested by Pott and Kommanduer.13)