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The Reflection Spectra of Complex Salts of the Tetracyanoquinodimethane Anion Radical

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Reflection measurements of the pressed pellets of two 2 : 3 complex salts and six 1 : 2 complex salts of the tetracyanoquinodimethane (TCNQ) anion radical were carried out over the 5000—43000 cm^{-1} range by the use of Avery's method. The polarized normal-incidence reflection was measured for the $Ph_3PCH_3(TCNQ)_2$ single crystal. The observed results were examined on the basis of the composite-system method. For 2 : 3 salts, the transition energy and the oscillator strength are interpreted by the use of the N-A-A model (N: $TCNQ^0$ and A-A: TCNQ anion dimer); it is concluded that the interaction between the two components, N and A-A, is weak. In the solid-state spectra of 1 : 2 salts, the assignments were made by the use of the polarization results of the normal-incidence reflection of the $Ph_3PCH_3(TCNQ)_2$ crystal. Besides the four transitions corresponding to those of 2 : 3 salts, two new CT bands with weak intensities were observed and assigned. Except for quinolinium$(TCNQ)_2$, a spectral change correlative to the electrical conductivity was found in the 1 : 2 salts and discussed in relation to the extent of the delocalization of the negative charge of $(TCNQ)_2^-$. The spectrum of quinolinium$(TCNQ)_2$ exhibits a remarkable intensity decrease compared with those of the other 1 : 2 salts.

It is known that anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) exhibit interesting physical properties. The 1 : 2 complex salts, $M^+(TCNQ)_2^-$, and the 2 : 3 complex salts, $(M^+)_2(TCNQ)_3^{2-}$, have been especially extensively investigated with respect to their structure[1-5] and their magnetic,[6-12] electrical,[13-16] and optical[17-22] properties. Previously, we measured the reflection intensity of the simple salts of the TCNQ anion radical, and discussed three typical types of crystalline electronic states and the correlation between the intensity of the interradical charge-transfer (CT) band and the singlet-triplet splitting of the ground state.[22] On the basis of this knowledge of the electronic structures of the simple salts, we aimed to investigate the electronic states of the complex salts containing formally-neutral TCNQ ($TCNQ^0$) besides the anion radical ($TCNQ^-$). In the present study, we measured the polarized normal-incidence reflection for a single crystal of methyltriphenylphosphonium$(TCNQ)_2$, $Ph_3PCH_3(TCNQ)_2$ and discussed the character of each electronic transition on the basis of these polarization results. Furthermore, we measured the reflection of the pressed pellets of eight complex salts of the TCNQ anion radical and obtained the oscillator strength (f) for each transition. On the basis of these experimental results (peak positions and oscillator strengths) and the knowledge of the electronic structures of the simple salts, we discuss the electronic structure of complex salts, together with its relation to the electrical and the magnetic data.

Experimental

Materials. The samples used in this experiment were prepared by the method described in the literature.[13] The eight complex salts investigated were morpholinium$_2(TCNQ)_3$ ($Mor_2(TCNQ)_3$), $Cs_2(TCNQ)_3$, $(CH_3)_3NH(TCNQ)_2$, $Ph_3PCH_3(TCNQ)_2$, $(C_2H_5)_3NH(TCNQ)_2$, *N*-ethylquinolinium$(TCNQ)_2$($EtQ(TCNQ)_2$), bipyridinium$(TCNQ)_2$ ($Bip(TCNQ)_2$), and quinolinium$(TCNQ)_2$ ($Q(TCNQ)_2$). Large single crystals suitable for the measurement of the polarized normal-incidence reflection were obtained for $Ph_3PCH_3(TCNQ)_2$.[13]

Measurements and Analysis. The reflection intensities were usually measured with pressed pellets of the samples over the range from 5000 to 43000 cm^{-1}. The experimental details are the same as those described in a previous paper.[23] The polarized normal-incidence reflection of the single crystal was measured for $Ph_3PCH_3(TCNQ)_2$ over the range from 5000 to 37000 cm^{-1}. The analysis of these reflection data was carried out by Avery's method for the pressed pellets, and by Kramers-Kronig transformation for the single crystal. The treatment of the inaccessible spectral regions in the Kramers-Kronig analysis follows the method of Roessler.[24] The A and B values of the approximate equation of:

$$\theta(\omega_0) = A\ln\left|\frac{a+\omega_0}{a-\omega_0}\right| - \frac{1}{\pi}\int_a^b \ln\sqrt{R(\omega)}\,\frac{d}{d\omega}\times\left(\ln\left|\frac{\omega+\omega_0}{\omega-\omega_0}\right|\right)d\omega + B\ln\left|\frac{b+\omega_0}{b-\omega_0}\right|$$

were determined from the observed reflectivities in the zero-absorbing region, the observation being carried out in the spectral region from a to b. The refractive index (n) and the extinction coefficient (k) were thus determined, and the oscillator strength (f) for each transition was calculated by means of this equation: $f=\frac{m}{e^2 n_0}\int 4n(\nu)k(\nu)\nu d\nu$, where n_0 is the number of the molecules in a unit volume and where ν is the frequency of the incident light. In the figures of the present paper, the $4\pi n(\nu)k(\nu)/2.303\,\lambda C$ value (ε') will be plotted to show the wave-number dependence of the absorption intensity of the solid-state spectrum (C: molar concentration; λ: wavelength of the incident light).

Results and Discussion

In the crystal of $Ph_3PCH_3(TCNQ)_2$ at room temperature, tetrads of TCNQ molecules with the interplanar spacings of 3.22 Å, 3.24 Å and 3.22 Å compose a one-dimensional column.[5] The interplanar spacing between tetrads is 3.57 Å. In a tetrad, molecules are overlapped with a shift along the long axis of the TCNQ molecule (Y axis), and there are two crystallographycally independent molecules (II-I-I′-II′). The small difference observed between the

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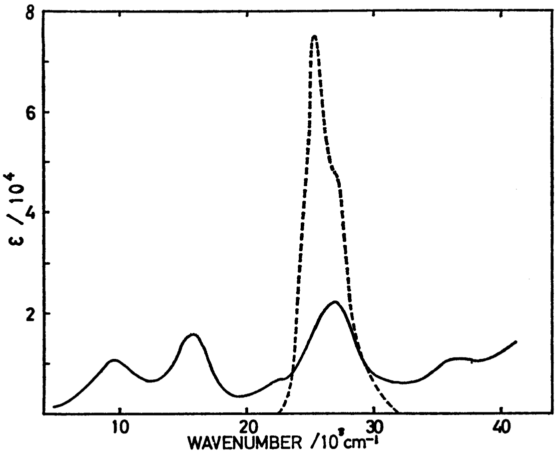

Fig. 1. The absorption spectrum of TCNQ in acetonitrile and the solid-state spectrum of NH_4TCNQ.

molecular structures of I and II suggests that the negative charge is slightly localized on the I molecule. Therefore, we will at first investigate the electronic structure of $Ph_3PCH_3(TCNQ)_2$ by the use of the simple model of N-A-A-N (A and N designate $TCNQ^-$ and $TCNQ^0$ respectively).

Figure 1 shows the absorption spectra of $TCNQ^0$ in an acetonitrile solution and of NH_4TCNQ in the solid state.[22] From the SCF-LCAO-MO-CI calculation of $TCNQ^0$ by the use of the molecular structure[25] in the TCNQ crystal, the lowest electronic transition observed at 25.3×10^3 cm^{-1} (f=1.01) is assigned to the 8→9 locally-excited (LE) electronic transition polarized parallel to the Y axis. The 8 and 9 molecular orbitals are the highest occupied and the lowest vacant ones respectively. In the previous paper, the peaks at 9.5×10^3, 16.0×10^3, and 26.9×10^3 cm^{-1} of NH_4TCNQ solid were assigned to the 9→9′ CT transition between $TCNQ^-$ and $TCNQ^-$, the 8→9 LE transition, and the 9→10 LE transition of $TCNQ^-$ respectively.[22] These LE transitions are polarized parallel to the Y axis. The analysis of the solid-state spectrum revealed that the NH_4TCNQ solid contains the dimer (A-A) of $TCNQ^-$. Therefore, the superposition of the two spectra in Fig. 1 gives the tentative absorption spectrum of the above-mentioned N-A-A-N model without any interaction between N and A.

Polarized Normal-Incidence Reflection of the Ph_3PCH_3 ($TCNQ)_2$ Single Crystal. Figure 2 shows the normal-incidence reflections of the (100) face with the polarized lights along four directions ($b_{//}$, $b_\perp$, $c_{//}$, $c_\perp$) over the range from 5×10^3 cm^{-1} to 37.0×10^3 cm^{-1}. Table 1 shows the square of the direction cosine of the component of the molecular axis projected on (100) to the polarization direction. I and II designate the two crystallographycally independent TCNQ's. Iida suggested the assignment of the transition observed in the infrared region as a CT transition between $TCNQ^-$ and $TCNQ^0$, or as a direct transition to the electrical conduction state.[19] Since Ph_3PCH_3 $(TCNQ)_2$ exhibits an intermediate conductivity, we adopted the former assignment. The transition moment of the CT transition is parallel to the I-II direction in Table 1; therefore, the former assignment sug-

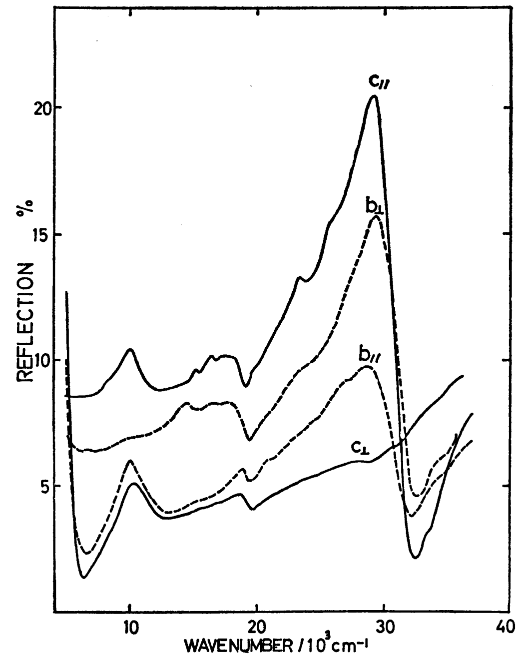

Fig. 2. The normal incidence reflection on (100) face of $Ph_3PCH_3(TCNQ)_2$ single crystal. The four spectra were obtained with the incident light polarized parallel and perpendicular to the b and c crystallographic axes.

TABLE 1. SQUARE OF DIRECTION COSINE OF THE COMPONENT OF MOLECULAR AXIS PROJECTED ON (100) TO THE POLARIZATION DIRECTION

		$b_{//}$	$b_\perp$	$c_{//}$	$c_\perp$
Long axis of TCNQ(Y)	I	0.36	0.64	0.98	0.01
	II	0.48	0.52	0.94	0.06
Short axis of TCNQ(X)	I	0.01	0.98	0.85	0.15
	II	0.03	0.96	0.88	0.12
I-II(I-I′)[a]		1.00	0.00	0.26	0.74
II-II′ [a]		1.00	0.00	0.22	0.77

a) The direction connecting the molecular centers.

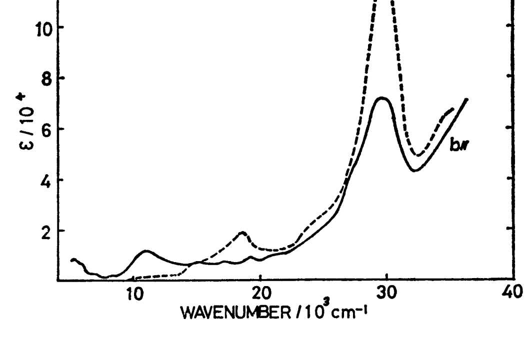

Fig. 3. The absorption spectra obtained from Kramers-Kronig analysis on (100) face of $Ph_3PCH_3(TCNQ)_2$ single crystal. The solid and the dashed curves were obtained with the incident light polarized parallel and perpendicular to the b axis.

gests that the infrared band is not found in the polarized spectrum perpendicular to the b axis ($b_{\perp}$). Therefore, the $b_{\perp}$ polarized reflection spectrum can be analysed by the equation of Roessler ($A=0.012$ and $B=-0.18$). The obtained spectrum is shown in Fig. 3. As may be seen from Table 1, for the other three polarization directions the infrared band has intensity and the zero-absorbing region is not found. Since the A and B values depend on the respective electronic transitions below $5\times10^3\,\mathrm{cm}^{-1}$ and above $37.0\times10^3\,\mathrm{cm}^{-1}$, and since the former transition is ascribed to a CT transition between TCNQ$^-$ and TCNQ^0, and the latter, mainly to the LE transitions, the following relations can be estimated from Table 1:

$$B(c_{/\!/})<B(b_{\perp})<B(b_{/\!/})<B(c_{\perp})$$
$$A(b_{/\!/})<A(c_{\perp})<A(c_{/\!/})<A(b_{\perp})$$

Under these conditions, the A and B values were parametrized so as not to give the negative extinction coefficient. The obtained spectra are shown in Figs. 3 and 4. Since the absolute intensity is sensitive to the values of the parameters, no detailed discussion of the absorption intensity is carried out for the single crystal.

From the above polarization results, the I and II bands can clearly be assigned to the CT transitions, and the IV and VIII bands, to the LE transitions polarized parallel to the Y axis (LE(Y)). Although the other, weak peaks are not discussed in detail, it is noticeable that the V and VII bands were assigned with the CT polarization. In comparison with the tentative spectrum of the N-A-A-N model, the I and II bands are assigned to the 9→9′ CT transition from TCNQ$^-$ to TCNQ^0 and 9→9′ CT transition between TCNQ$^-$ and TCNQ$^-$. The IV and VIII bands are assigned to the 8→9 LE transition of TCNQ$^-$ and the superimposed transition of the 9→10 LE transition of TCNQ$^-$ and the 8→9 LE transition of TCNQ^0. Since the peak of the lowest transition (I) was reported at $2.9-3.3\times10^3\,\mathrm{cm}^{-1}$ by Iida,[19] the energy separations between the I and V bands and between the II and VII bands are about $16\times10^3\,\mathrm{cm}^{-1}$; this value nearly coincides with the transition energy of the 8→9 LE transition of TCNQ$^-$. Therefore, the CT bands, V and VII, can possibly be assigned to 8→9′ CT transitions from TCNQ$^-$ to TCNQ^0 and to the 8→9′ CT transition between TCNQ$^-$ and TCNQ$^-$ (Table 2). Sakai *et al.* reported that the reversible pressure-induced absorption band was found at around $20\times10^3\,\mathrm{cm}^{-1}$ at high pressures with respect to $(C_2H_5)_3$-NH(TCNQ)$_2$ and Q(TCNQ)$_2$.[20] This experimental result is explained by the intensity increase of these new CT bands. The present assignments are consistent with those by Iida[19] for the I, IV, and VIII bands; also, the ambiguity of the assignment of the II band is excluded by this polarization measurement.

Table 2. Polarized absorption spectrum of $Ph_3PCH_3(TCNQ)_2$ single crystal by normal reflection analysis (in $10^3\,\mathrm{cm}^{-1}$)

	$b_{/\!/}$	$b_{\perp}$	$c_{/\!/}$	$c_{\perp}$	Assignment
I	<5	—	<5	<5	CT(A9→N9)
II	11.0	—	10.5	11.0	CT(A9→A9′)
III	15.2	15.0	15.3	—	
IV	—	18.5	18.5	—	LE(Y)(A8→9)
V	19.2	—	—	19.2	CT(A8→N9)
VI	—	24.0	24.0	—	
VII	27.0	—	—	—	CT(A8→A9′)
VIII	29.8	29.8	29.4	—	LE(Y)(A9→10, N8→9)

The Solid-state Spectra of the Pressed Pellets. The solid-state spectra and the refractive index, n, of the pressed pellets of the eight complex salts are shown in Figs. 5—8. Since four predominant transitions are observed in this spectral region, they are designated by CTI, CTII, YI, and YII in the increasing order of the transition energy; they correspond to the I,

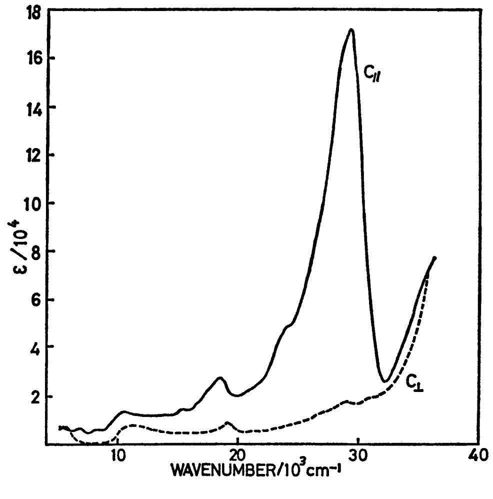

Fig. 4. The absorption spectra obtained from Kramers-Kronig analysis on (100) face of $Ph_3PCH_3(TCNQ)_2$ single crystal. The solid and the dashed curves were obtained with the incident light polarized parallel and perpendicular to the c axis.

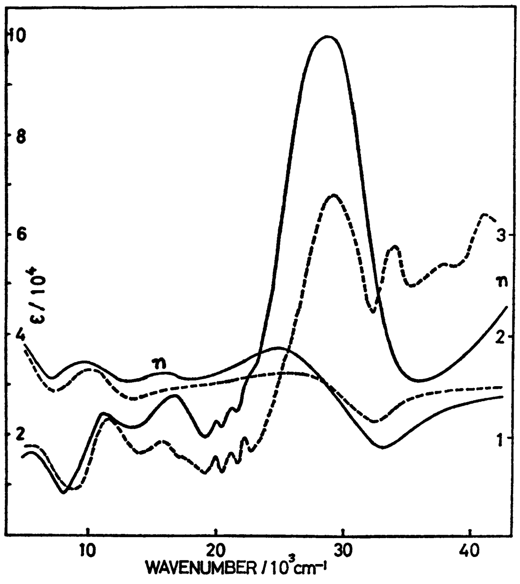

Fig. 5. The solid-state spectra and the refractive index n of $Mor_2(TCNQ)_3$ (----) and $Cs_2(TCNQ)_3$ (——).

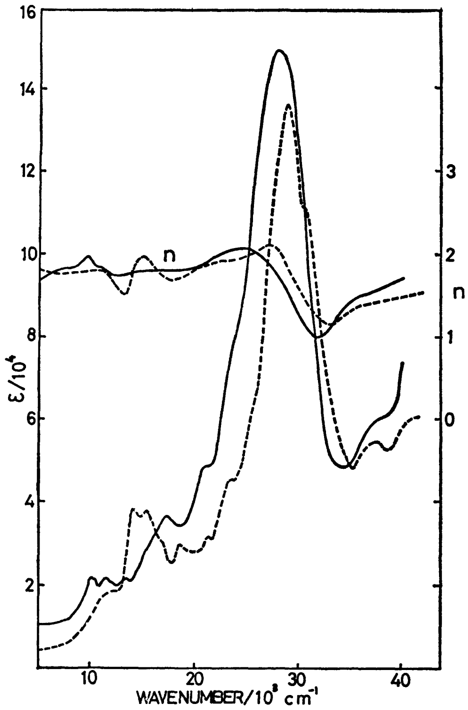

Fig. 6. The solid-state spectra and the refractive index n of $(CH_3)_3NH(TCNQ)_2$ (----) and $Ph_3PCH_3(TCNQ)_2$ (——).

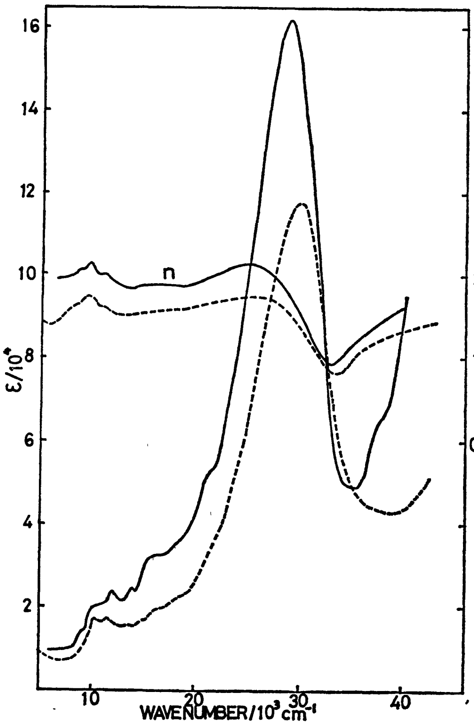

Fig. 7. The solid-state spectra and the refractive index n of $(C_2H_5)_3NH(TCNQ)_2$ (----) and $EtQ(TCNQ)_2$ (——).

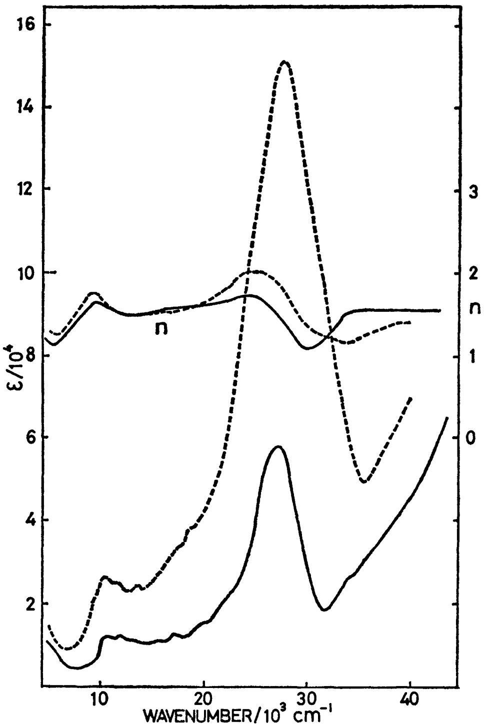

Fig. 8. The solid-state spectra and the refractive index n of $Bip(TCNQ)_2$ (----) and $Q(TCNQ)_2$ (——).

II, IV, and VIII bands of the $Ph_3PCH_3(TCNQ)_2$ crystal respectively. The origin of the two or three weak peaks observed at 20—$23\times10^3\,cm^{-1}$ of the 2 : 3 complex salts and some 1 : 2 complex salts is not clear, but these peaks are reproducible. For all the 1 : 2 complex salts except for $Q(TCNQ)_2$, a weak peak was observed at about $14\times10^3\,cm^{-1}$; it corresponds to the III band in the polarized crystalline spectrum of $Ph_3PCH_3(TCNQ)_2$. The III band exhibits polarization behavior a little different from that of the YI band (Figs. 3 and 4) and can be observed clearly when the YI band becomes obscure ($EtQ(TCNQ)_2$ and $Bip(TCNQ)_2$). Therefore, this peak is considered to have a different electronic origin from the YI band. The peak positions and the oscillator strengths are tabulated in Table 3, together with the solid-state results of NH_4TCNQ (Group A) and RbTCNQ-II (Group B) of the simple salt[22] and the electronic transition of $TCNQ^0$ in acetonitrile.

The crystal structures have been reported for the five complex salts investigated in this study.[1–5] In all cases, the TCNQ molecules compose a one-dimensional column. In the case of the 2 : 3 complex salts ($Mor_2(TCNQ)_3$[4]) and $Cs_2(TCNQ)_3$[1]), TCNQ molecules in a column form a triad which consists of two $TCNQ^-$ and one $TCNQ^0$. Among the 1 : 2 complex salts, $Ph_3PCH_3(TCNQ)_2$[5] and $(C_2H_5)_3NH(TCNQ)_2$[2] contain a tetrad unit which consists of two $TCNQ^-$ and two $TCNQ^0$. However, in the $Q(TCNQ)_2$ crystal,[3] the TCNQ column is composed of equally spaced TCNQ molecules and one electron per two TCNQ molecules is completely delocalized.

The 2 : 3 Complex Salts. As have been mentioned above, the TCNQ column of the 2 : 3 complex salts is represented as a repeat of N(1/2)-A-A-N(1/2). N(1/2) means that the N's on both sides half belong to this repeating unit. Therefore, we will discuss the electronic states of this repeating unit by the

TABLE 3. TRANSITION ENERGY AND OSCILLATOR STRENGTH OF SOLIDS OF TCNQ COMPLEX SALTS (σ: in $10^3\ \mathrm{cm}^{-1}$)

	CTI		CTII		YI		YII			R	J
	σ	f	σ	f	σ	f	σ	f	$\Delta\sigma_{1/2}$	Ω cm	eV
$\mathrm{Mor_2(TCQ)_3}$	~5.0	0.5	11.7	0.6	16.0 17.8	0.5	29.2	2.5	7.8	10^5 [13]	0.31[11]
$\mathrm{Cs_2(TCNQ)_3}$	5.5	0.3	11.1	0.5	16.8	0.7	28.5	3.7	8.0	9×10^4 [13]	0.14[9]
$\mathrm{(CH_3)_3NH(TCNQ)_2}$			12.0	0.27	14.1 15.4	0.7	29.0 30.7	4.4	7.0	5×10^6 [14]	>0.2[9]
$\mathrm{Ph_3PCH_3(TCNQ)_2}$	<5.0		10.2 11.7	0.4	17.6		28.2	5.5	7.5	50[14]	0.062[6]
$\mathrm{(C_2H_5)_3NH(TCNQ)_2}$	<5.0		10.2 11.7	0.3	16.3		29.9	4.8	9.5	20[13]	0.034[6]
$\mathrm{EtQ(TCNQ)_2}$			10.2 11.8	0.4	16.0		29.0	6.0	8.5	8[13]	
$\mathrm{Bip(TCNQ)_2}$	<5.0		10.3 11.6	0.5	~17.0		27.8	6.2	10.0	0.5[13]	
$\mathrm{Q(TCNQ)_2}$	<5.0		~11.0	~0.2	17.1		27.0	1.5	6.4	0.15[13]	
$\mathrm{NH_4TCNQ}$			9.5	0.24	16.0	0.25	26.8	0.54	5.0	6×10^4 [13]	
RbTCNQ-II			7.4	0.39	16.7	0.33	28.1	1.5	7.0	10^2	
TCNQ in $\mathrm{CH_3CN}$							25.3 27.0	1.0			

$\Delta\sigma_{1/2}$: half width of the YII band

method of the composite molecule, the components of which are A-A and N. In this unit, the TCNQ radicals (A-A) overlap each other with a shift along the short axis of the TCNQ radical. This packing is the same as that for the anion dimer of Group A of the simple salts. Therefore, the electronic states of the anion dimer of $\mathrm{NH_4TCNQ}$ (Group A)[22] and $\mathrm{TCNQ^0}$ in acetonitrile are used as component states.

To discuss the electronic states in the energy region treated in this study, it is sufficient to take into account the following excited states of the components: the 8→9 (LEI) and the 9→10 (LEII) excited states of $\mathrm{TCNQ^-}$, the 8→9 LE state of $\mathrm{TCNQ^0}$ (LEN), and the CT excited state between $\mathrm{TCNQ^-}$ (9) and $\mathrm{TCNQ^-}$ (9′) (CTA). Furthermore, the CT configuration between two components (CTN) is considered. Therefore, the electronic configurations are as follows:

$$\mathrm{G} = \mathrm{G_{AA}}\cdot\mathrm{G_N}$$
$$\mathrm{AYI^{\pm}} = \mathrm{LEI^{\pm}}\cdot\mathrm{G_N}$$
$$\mathrm{AYII^{\pm}} = \mathrm{LEII^{\pm}}\cdot\mathrm{G_N}$$
$$\mathrm{NY^{\pm}} = \mathrm{G_{AA}}\cdot\mathrm{LEN^{\pm}}$$
$$\mathrm{CTA^{\pm}} = \mathrm{CT^{\pm}}\cdot\mathrm{G_N}$$
$$\mathrm{CTN^{\pm}} = 1/2[\{|8_A\bar{8}_A9_A8'_A\bar{8}'_A9'_N| - |8_A\bar{8}_A\bar{9}_A8'_A\bar{8}'_A9'_N|\} \pm \{|8_A\bar{8}_A9_N8'_A\bar{8}'_A\bar{9}'_A| - |8_A\bar{8}_A\bar{9}_N8'_A\bar{8}'_A9'_A|\}]\cdot\mathrm{G_N}$$

and

$$\mathrm{G_{AA}} = 1/\sqrt{2}\{|8_A\bar{8}_A9_A8'_A\bar{8}'_A\bar{9}'_A| - |8_A\bar{8}_A\bar{9}_A8'_A\bar{8}'_A9'_A|\}$$
$$\mathrm{G_N} = |8_N\bar{8}_N|$$
$$\mathrm{LEI^{\pm}} = 1/2[\{|8_A\bar{9}_A9_A8'_A\bar{8}'_A\bar{9}'_A| - |9_A\bar{8}_A\bar{9}_A8'_A\bar{8}'_A9'_A|\} \pm \{|8_A\bar{8}_A9_A9'_A\bar{8}'_A\bar{9}'_A| - |8_A\bar{8}_A\bar{9}_A8'_A\bar{9}'_A9'_A|\}]$$
$$\mathrm{LEII^{\pm}} = 1/2[\{|8_A\bar{8}_A10_A8'_A\bar{8}'_A\bar{9}'_A| - |8_A\bar{8}_A\overline{10}_A8'_A\bar{8}'_A9'_A|\} \pm \{|8_A\bar{8}_A9_A8'_A\bar{8}'_A\overline{10}'_A| - |8_A\bar{8}_A\bar{9}_A8'_A\bar{8}'_A10'_A|\}]$$
$$\mathrm{LEN^{\pm}} = 1/2[\{|8_N\bar{9}_N| - |\bar{8}_N9_N|\} \pm \{|8'_N\bar{9}'_N| - |\bar{8}'_N9'_N|\}]$$
$$\mathrm{CT^{\pm}} = 1/\sqrt{2}\{|8_A\bar{8}_A9'_A8'_A\bar{8}'_A\bar{9}'_A| \pm |8_A\bar{8}_A9_A8'_A\bar{8}'_A\bar{9}_A|\}$$

where $\mathrm{i_N}$, $\mathrm{i_A}$, $\mathrm{i'_A}$, and $\mathrm{i'_N}$ designate the molecular orbitals of N, A, A′, and N′ respectively of the N(1/2)-A-A-N(1/2) model. The ± signs denote the symmetric and the antisymmetric properties with respect to the symmetric center. The doubly occupied molecular orbitals 1—7 are neglected. The configuration interactions are:

$$\begin{array}{ll|llllll}
\text{Symmetric} & \mathrm{C} & 0 & & & & & \\
 & \mathrm{CTN^+} & \sqrt{2}\beta(9_A9_N) & E^+_{\mathrm{CTN}} & & & & \\
 & \mathrm{CTA^+} & 2\beta(9_A9'_A) & 0 & E^+_{\mathrm{CTA}} & & & \\
 & \mathrm{AYI^+} & 0 & 0 & -\sqrt{2}\beta(8_A9'_A) & E^+_{\mathrm{AYI}} & & \\
 & \mathrm{AYII^+} & 0 & \beta(10_A9_N) & \sqrt{2}\beta(9_A10'_A) & 0 & E^+_{\mathrm{AYII}} & \\
 & \mathrm{NY^+} & 0 & -\beta(9_A8_N) & 0 & 0 & 0 & E^+_{\mathrm{NY}}
\end{array}$$

$$\begin{array}{ll|lllll}
\text{Asymmetric} & \mathrm{CTN^-} & E^-_{\mathrm{CTN}} & & & & \\
 & \mathrm{NY^-} & \beta(9_A8_N) & E^-_{\mathrm{NY}} & & & \\
 & \mathrm{CTA^-} & 0 & 0 & E^-_{\mathrm{CTA}} & & \\
 & \mathrm{AYI^-} & 0 & 0 & \sqrt{2}\beta(8_A9'_A) & E^-_{\mathrm{AYI}} & \\
 & \mathrm{AYII^-} & -\beta(10_A9_N) & 0 & \sqrt{2}\beta(9_A10'_A) & 0 & E^-_{\mathrm{AYII}}
\end{array}$$

where $\beta(i_A j_N)=\int i_A(1)\ H(1)\ j_N(1)\ d\tau_1$ and where H(1) is the one-electron Hamiltonian of the crystal. The asymmetric configuration matrix almost splits into two parts, and the 3×3 part is the same as the configuration matrix of the anion dimer.[22)]

Really, except for a new band, CTI, based on the CT transition between two components, the observed spectra of the 2 : 3 salts are similar to the superposed spectrum of the two components, with a small blue shift caused by the stabilization of the ground state due to the interaction with CTN$^+$. The observed oscillator strengths of YI(0.5) and YII(2.5) of Mor$_2$-(TCNQ)$_3$ agree with the calculated values (YI: 0.5 and YII: 2.1) for the N(1/2)-A-A-N(1/2) model without any interaction between A and N, using the solid-state spectrum of NH$_4$TCNQ for A-A and the acetonitrile spectrum of TCNQ^0 for N. These results reveal for the 2 : 3 salts that the interaction between the two components is weak in the excited states. For Cs$_2$(TCNQ)$_3$, a weak hyperchromism was observed.

The singlet-triplet (S-T) splittings of the ground state reported by the magnetic measurements are 0.31 eV for Mor$_2$(TCNQ)$_3$[11)], 0.14 eV or 0.16 eV for Cs$_2$(TCNQ)$_3$,[6,9)] and 0.16—0.29 eV for Group A of the simple salts.[6,7,12)] In the present treatment of the composite system, the stabilization of the singlet ground state becomes larger by the interaction with the low-energy ^{S}CTN configuration for the 2 : 3 salts than for the anion dimer. However, since the triplet ground state is also stabilized by the interaction with ^{T}CTN for the 2 : 3 salts, it is reasonable that the S-T splitting of the 2 : 3 salts is not very different from that of the anion dimer (Group A of the simple salts).

The 1 : 2 Complex Salts. To discuss the electronic structure of the 1 : 2 salts, we can at first adopt the simple model of N-A-A-N.[26)] The electronic configurations are analogous to those of the 2 : 3 complex salts. The difference in the configuration energies between the 2 : 3 and the 1 : 2 complex salts is considered to be not very large with respect to the LE and CTA configurations, because the changes in the interplanar spacings and the molecular structure are small. However, the configuration energy of CTN is lower for the 1 : 2 salts than for the 2 : 3 salts because of a difference in the electrostatic repulsion between anion radicals. This is consistent with the observed red shift of the CTI band and the small changes of three other band positions of the 1 : 2 salts compared to those of the 2 : 3 salts.

The CTII bands of the 1 : 2 salts show the vibrational structure. Since the vibrational frequency (1300—1500 cm^{-1}) agree well with that (1600 cm^{-1}) observed for the 11.8×10^3 cm^{-1} band of the TCNQ$^-$ monomer, the assignment of the CTII band to LE transition has been proposed.[19)] However, as the CT character of the CTII band was determined by our polarization experiment, the vibrational structure is attributed to a small quantity of the TCNQ$^-$ monomer. The magnetic susceptibility measurement also reported the TCNQ$^-$ monomer as an intrinsic impurity.[9)]

Our previous work on the simple salts[22)] showed that the separations between the CTII and YI bands are larger for the salts of Group B than for the salts of Group A, as may be seen from Table 3 (6500 cm^{-1} for NH$_4$TCNQ and 9300 cm^{-1} for RbTCNQ-II). This was explained by the difference in the configuration interaction between the CTA and AYI configurations. A symmetry consideration of the molecular orbitals reveals that the CTA and AYI configurations interact for the A-A overlapping form of Group B (an overlap with a shift along the Y axis) and not for that of Group A (an overlap with a shift along the X axis). The overlapping form between anions of the 1 : 2 salts is the same as that of Group B, and that between anions of the 2 : 3 salts, the same as that of Group A. However, the corresponding CTII-YI separations in the spectra of the 1 : 2 salts range from 4.3 to 6.6×10^3 cm^{-1} and are not so large as those of the 2 : 3 salts (4.3 and 5.7×10^3 cm^{-1}). From the polarized reflection analysis, the CTN configuration from the 8 orbital of A to the 9 orbital of N is located just above the AYI configuration. The interaction between these two configurations based on $\beta(9_A 9_N)$ removes the YI band to the lower-energy side, so it is reasonable that the separation between the YI and CTII bands becomes not so large.

The observed transition energies and the oscillator strengths are shown in Table 3 in the decreasing order of electrical resistivity. As may be seen from Table 3 and Figs. 6—8, the solid-state spectra of the 1 : 2 salts are divided into three main groups. The first salt, (CH$_3$)$_3$NH(TCNQ)$_2$, exhibits no CTI band and a weak CTII band; this reveals the small CTN and CTA contributions in the ground state. The YI band appears at a position intermediate between those of the first LE transitions of the TCNQ$^-$ monomer and the TCNQ$^-$ dimer in the aqueous solution, and the YII band shows the same 1700 cm^{-1} shoulder as the LE band of TCNQ^0 in acetonitrile. These two features show weak TCNQ$^-$–TCNQ$^-$ and TCNQ$^-$–TCNQ^0 interactions in the excited states. The second group contains Ph$_3$PCH$_3$(TCNQ)$_2$, (C$_2$H$_5$)$_3$NH(TCNQ)$_2$, EtQ(TCNQ)$_2$, and Bip(TCNQ)$_2$. These salts exhibit a gradual spectral change as the electrical resistivity decreases; the dispersion of the refractive index near 5000 cm^{-1} becomes larger, which reflects the intensity increase in the CTI band: the intensity of the CTII band increases, the YI band becomes more obscure, and the oscillator strength and the half-width of the YII band increase. The increase in the absorption intensity of the two CT bands reveals the increase in the electron delocalization in the ground state; this is consistent with the tendency of the electrical property. The absolute absorption intensities of the YI and YII bands becomes nearly double the intensities calculated from the solid-state data of the simple salts and the solution data of TCNQ^0. In the range corresponding to these LE transitions of TCNQ$^-$ and TCNQ^0, several CT bands were estimated. However, the intensities of these bands are not enough large for us to interpret the remarkable hyperchromism of the YII band. Therefore, it is considered that the electron delocalization also makes an important contribution. It is noticeable that the effect of the electron delocalization is found not only in CT transitions, but also in LE transitions for the 1 : 2 salts.

The S-T splittings of the ground state have been reported for $(CH_3)_3NH(TCNQ)_2$ (>0.2 eV),⁹⁾ $Ph_3PCH_3(TCNQ)_2$ (0.062 eV),⁶⁾ and $(C_2H_5)_3NH(TCNQ)_2$ (0.034 eV)⁶⁾ on the basis of magnetic measurements. This remarkable difference between the salts belonging to the first and second groups can be explained by the difference in the extent of delocalization of the negative charge of $(TCNQ)_2^-$. The previous discussion showed that the contribution of the CTN^+ configurations to the ground state is smallest for $(CH_3)_3NH(TCNQ)_2$ in the 1 : 2 salts investigated here, therefore, the negative charge is located almost entirely on one TCNQ. However, for the two salts of the second group, the delocalization of the negative charge occurs to some extent. This delocalization makes the CT transition between A and A less important than the CT transition between A and N; therefore, the part of the S-T splitting due to the stabilization of the singlet ground state by the interaction with the ^{S}CTA configuration becomes less important.

The third group contains only $Q(TCNQ)_2$. The solid-state spectrum of $Q(TCNQ)_2$ is very different from those of the other 1 : 2 salts (Fig. 8). Its characteristics are as follows; the absorption tail near 5×10^3 cm^{-1} becomes clear, the intensity of the YII band becomes remarkably small, and the intensity as a whole becomes smaller than those of the other 1 : 2 salts. The relatively strong intensity of the absorption near 20×10^3 cm^{-1} makes the YI band obscure. The fact that $Q(TCNQ)_2$, with the highest electrical conductivity among the eight complex salts investigated here, exhibits the clearest tendency for the intensity to increase near 5×10^3 cm^{-1} is consistent with the results of the other optical study. An infrared study of $Q(TCNQ)_2$ at 1.5 K reported that the broad absorption beginning from 500 cm^{-1} with the absorption maximum near 3000 cm^{-1}, was the transition to the electrical conduction band,²¹⁾ and that the increase in the intensity of this band is accompanied by an increase in the electrical conductivity.¹⁸⁾ On the other hand, a study of the crystal structure reported the complete delocalization of the negative charge of $(TCNQ)_2^-$ in the ground state.³⁾ The delocalization of the negative charge makes the chance of the A-A pair occurrence less than that of the A-N pair occurrence. Since the CTA transition and CTN transition are based on the above pair structure, the oscillator strength ratio of CTI to CTII is expected to become larger than in the other 1 : 2 complex salts. As is seen in Fig. 8, this tendency is consistent with the experimental results. Furthermore, the charge delocalization transforms the molecular structure³⁾ and, as a result, changes the oscillator strengths of the LE transitions. This is considered one of the reasons for the intensity decrease in the LE transitions of $Q(TCNQ)_2$. The relatively strong intensity near 20×10^3 cm^{-1} also supports the large extent of the delocalization.

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26) For the case of $(C_2H_5)_3NH(TCNQ)_2$, the interplanar spacing in a tetrad are 3.24, 3.32 and 3.24 Å, and that between the neighbouring tetrads in 3.30 Å.²⁾ However, the model of N-A-A-N is also applicable to this case, because the interaction between N's is weak in comparison with that between A's.