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The Reflection Spectra of Simple Salts of the Tetracyanoquinodimethane Anion Radical

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The reflection measurements were carried out for fourteen simple salts of the tetracyanoquinodimethane (TCNQ) anion radical over the range from 5000 to 42000 cm^{-1} by Avery's method. The solid-state spectra show three bands (CT, YI, and YII) and exhibit distinct differences depending on the cation species. According to the differences in the transition energy (σ_i) and the oscillator strength (f_i), the fourteen salts were classified into three groups (A, B, and C). The solid-state spectra of Group A resemble that of the dimer in an aqueous solution. Group B is characterized by the red shift of the CT band and the intensity increase in the YII band. The spectra of Group C exhibit a vibrational structure in the YI band which is similar to the monomer spectrum in an aqueous solution. Moreover, the large dispersion of the refractive index and the intensity increase in the bands of local excitation were observed for Group C. The electronic structures of these groups were studied by the use of the composite-system method. By taking account of the crystal structure of RbTCNQ-I, belonging to Group A, the stabilization energy (J^*) of the ground state was calculated from σ_{CT} and f_{CT}. The J^* values for ten salts in Group A correspond well to the singlet-triplet separation in the ground state observed by ESR measurements.

The electrical,[1-4] magnetic,[5-9] and optical properties,[10,11] and the crystal structures[12-20] have been extensively investigated with the anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ). These results indicate that, in the crystalline state, the mode of the packing of TCNQ radicals exerts an important effect on the physical paoperties. X-ray crystal analysis studies clarified that TCNQ radicals form a one-dimensional column in a crystal and that the interplanar spacing is 3.16—3.6 Å.[12-20] The rather short interplanar spacing causes the strong charge-transfer (CT) interaction between TCNQ radicals in a column which is essential to an understanding of the electronic

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properties. The absolute absorption intensity of the solid state gives quantitative knowledge about that interaction. The crystals of these radical salts, however, exhibit strong absorptions over the visible and ultraviolet regions, so that the transmission measurement is very difficult. On the other hand, the reflection measurement is useful for the determination of a strong absorption intensity, as has been described in the previous paper.[21]

In the present study, we measured the reflection intensities of the pressed pellets of fourteen simple salts of TCNQ anion radical and obtained the oscillator strength (f) for each transition. On the basis of these results and the reported crystal structures, we classify the fourteen simple salts into three groups and discuss the characteristics of each group.

Experimental

Materials. The samples used in this experiment were prepared by the method described in the literature[1] except for the Rb salts. RbTCNQ-I was prepared by the diffusion method described by Hoekstra,[18] and RbTCNQ-II was obtained by the rapid mixing of two hot acetonitrile solutions of RbI and TCNQ. The fourteen simple salts of TCNQ used are LiTCNQ, NaTCNQ, KTCNQ, RbTCNQ-I, RbTCNQ-II, CsTCNQ, NH_4TCNQ, (Ph_3PCH_3)TCNQ, MorpholiniumTCNQ (MorTCNQ), $BaTCNQ_2$, $FeTCNQ_2 \cdot 3H_2O$, $CoTCNQ_2 \cdot 3H_2O$, $NiTCNQ_2 \cdot 3H_2O$, and $MnTCNQ_2 \cdot 3H_2O$.

Measurements. The samples were ground with an agate mortar and were pressed by a KBr disc presser at about 10 kbar. The reflection intensity of the pressed pellet was measured by means of an apparatus constructed by our laboratory. The experimental details are the same as those described in the previous paper.[21] By the analysis of these reflection data, the refractive index (n) and the extinction coefficient (k) were determined, and the oscillator strength (f) for each transition was calculated by means of the equation:

$$f = \frac{m}{e^2 n_0} \int 4n(\nu)k(\nu)\nu d\nu.$$

Here, n_0 is the number of molecules in a unit volume and ν is the frequency of light. The f values were calculated in this study per TCNQ radical. 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 of TCNQ radical, λ: wavelength).

Results and Discussion

Figure 1 shows the absorption spectra of LiTCNQ in an aqueous solution and a solid-state spectrum obtained from the reflection measurements. The TCNQ anion radical exhibits a reversible dimerization in the aqueous solution when the temperature is varied.[22] The monomer and the dimer spectra in the aqueous solution are shown in Fig. 1. From an open-shell SCF–LCAO–MO–CI calculation, t e electronic transitions at 11800 and 24800 cm^{-1} of the monomer spectrum were assigned to the locally-excited (LE) transitions in a TCNQ radical, polarized parallel to the long axis (y) of the anion radical. The present calculatoin shows that, in the region up to 50000 cm^{-1}, another band with a strong intensity (f=0.8) appears at 43000 cm^{-1}, polarized parallel to the short axis (x) of the anion radical. In the dimer state, the low-energy CT configuration exists and interacts with the LE configurations. The bands at 15800 and 36200 cm^{-1} of the dimer are shifted from the monomer positions by the interaction with the CT configuration, and the band at 11000 cm^{-1} has the CT character.

The observed solid-state spectra exhibit distinct differences depending on the species of the cation. On the basis of the transition energies (σ_i) and the oscillator strengths (f_i) of the solid-state spectra, the fourteen

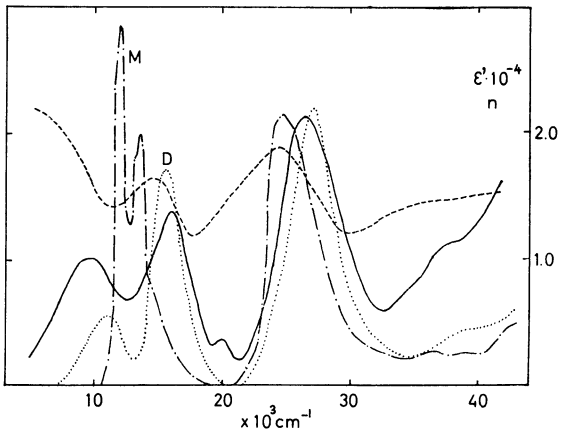

Fig. 1. The absorption spectra of LiTCNQ in the aqueous solution; monomer (M) and dimer (D). The solid-state spectra (——) and the refractive index (------) of LiTCNQ.

Table 1. Transition energy and oscillator strength of three groups of TCNQ simple salts (in cm^{-1})

	A1	A2	A3	B	Dimer in H_2O	C	Monomer in H_2O
σ_{CT}	9.7×10^3	8.8×10^3	11.0×10^3	7.4×10^3	11.0×10^3	10.2×10^3	
$\sigma_{YI}-\sigma_{CT}$	6.7	6.5	5.5	9.3	4.8	13.7[a]	11.8×10^3[a]
$\sigma_{YII}-\sigma_{YI}$	11.1	11.0	11.2	11.4	10.5	26.6[b]	23.8[b]
f_{CT}	0.24—0.41	0.26—0.28	0.25	0.39	0.09	0.1	
f_{YI}	0.25	0.36	0.41	0.33	0.22	0.51	0.27
f_{YII}	0.56	0.75	1.0	1.5	0.46	1.1	0.47
Cation	Li, K, Rb-I, NH_4, Ni	Fe, Co, Mn	Na, Ph_3PCH_3	Cs, Rb-II		Ba, Mor	

a) Transition energy of the YI band.
b) Transition energy of the YII band.

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simple salts of the TCNQ radical were summarized into three groups (A, B, and C), as may be seen in Table 1. Here, the absorption peaks are denoted as CT, YI, and YII. The common feature of Group A is that the f_{YI}/f_{YII} ratio (0.5) and the $\sigma_{YI}-\sigma_{CT}$ (5000—6000 cm^{-1}) and $\sigma_{YII}-\sigma_{YI}$ splittings (11000 cm^{-1}) are all almost equal to those of the dimer in the solution. However, the oscillator strengths of the YI band of Group A, with respect to that of the dimer in the solution, are equal for the TCNQ salts of the Li, K, Rb-I, NH_4, and Ni cations, 1.5 times for the salts of the Mn, Co, and Fe cations, and 2.0 times for those of the Na and (Ph_3PCH_3) cations. Therefore, Group A is further divided into three subgroups, A1, A2, and A3 (Fig. 2).

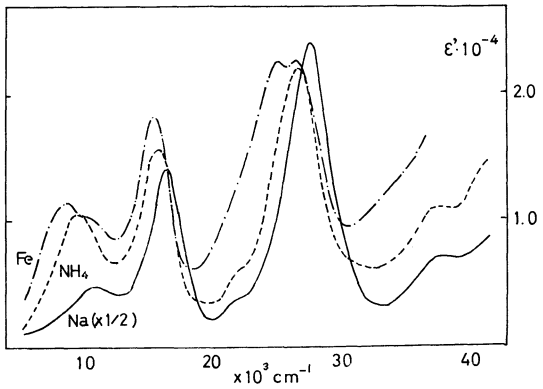

Fig. 2. The solid-state spectra of Al(NH_4TCNQ), A2(Fe-TCNQ$_2$·3H_2O) and A3(NaTCNQ). ε' in this work is the value per one TCNQ radical.

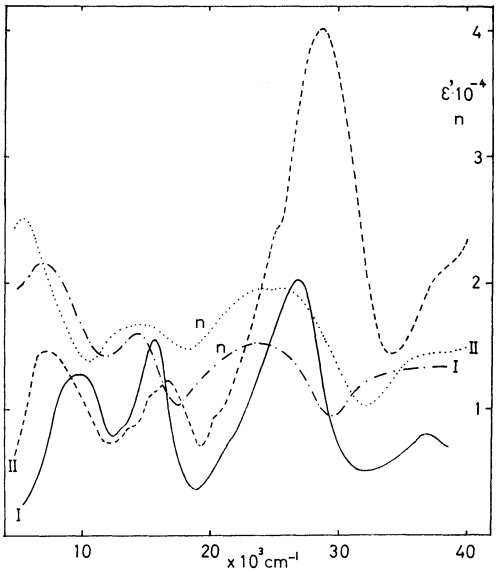

Fig. 3. The solid-state spectra and the refractive indexes of RbTCNQ-I(I) and RbTCNQ-II(II).

Figure 3 shows the solid-state spectra of RbTCNQ-I and RbTCNQ-II, together with the wave number dependence of the refractive indexes (n). The CT bands of RbTCNQ-II and CsTCNQ have an asymmetric shape and appear at 7400 and 7200 cm^{-1} respectively. These show a distinct red shift compared with the CT bands of Group A, and as a result, the

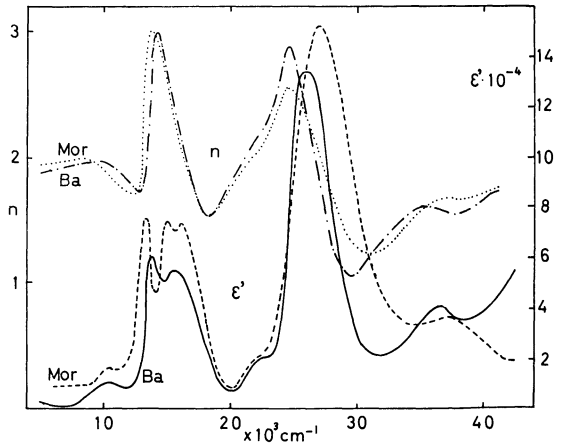

Fig. 4. The solid-state spectra and the refractive indexes of MorpholiniumTCNQ(Mor) and BaTCNQ$_2$(Ba).

$\sigma_{YI}-\sigma_{CT}$ splitting (9000 cm^{-1}) becomes large. The YII band increases remarkably in intensity. These two salts belong to Group B.

As may be seen in Fig. 4, the YI bands of the solid-state spectra of BaTCNQ$_2$ and MorTCNQ exhibit some structure, and the oscillator strengths of the YI and YII bands are larger than those of Groups A and B, especially for MorTCNQ, while the f_{YI}/f_{YII} ratios are about 0.5. The intensity of the CT band is very weak and is almost equal to that of the dimer in the solution. From the above-mentioned features, these two salts are denoted as Group C. The observed transition energies and oscillator strengths of the fourteen simple salts are tabulated in Table 2.

Group A. The solid-state spectra of Group A are shown in Figs. 1—3 and Figs. 5 and 6. Among these ten simple salts, the crystal structure has been

Table 2. Observed transition energy and oscillator strength of fourteen simple salts (σ_i: in cm^{-1})

	σ_{CT}	f_{CT}	σ_{YI}	f_{YI}	σ_{YII}	f_{YII}
Li	9.8×10^3	0.26	16.2×10^3	0.25	26.6×10^3	0.56
NH_4	9.5	0.24	16.0	0.25	26.9	0.54
Rb-I	9.8	0.31	15.7	0.23	27.1	0.56
Na	11.0	0.25	16.5	0.41	27.7	1.0
Ph_3PCH_3	10.5	0.24	15.3	0.39	26.4	0.88
K	9.5	0.36	16.0	0.27	27.7	0.62
Ni	9.0	0.44	15.7	0.49	25.3^s 26.7	1.0
Fe	8.6 10.5^s	0.58	15.4	0.63	25.5 26.9	1.3
Co	8.8 10.5^s	0.52	15.4	0.78	25.0^s 26.6	1.5
Mn	9.0^b	0.52	15.3	0.69	25.0^s 25.8	1.7
Rb-II	7.4	0.39	16.7	0.33	28.1	1.5
Cs	7.2 9.3^s	0.22	14.0^s 16.0	0.30	27.5	0.86
Ba	10.0	0.17	13.8 15.4	1.0	26.2	2.2
Mor	10.5	~0.1	13.5 15.1 16.1	0.89	27.0	2.1

s: shoulder b: broad

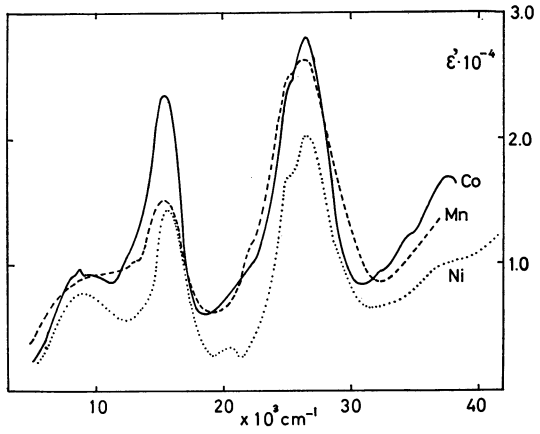

Fig. 5. The solid-state spectra of $MnTCNQ_2 \cdot 3H_2O$(Mn), $CoTCNQ_2 \cdot 3H_2O$(Co), and $NiTCNQ_2 \cdot 3H_2O$(Ni).

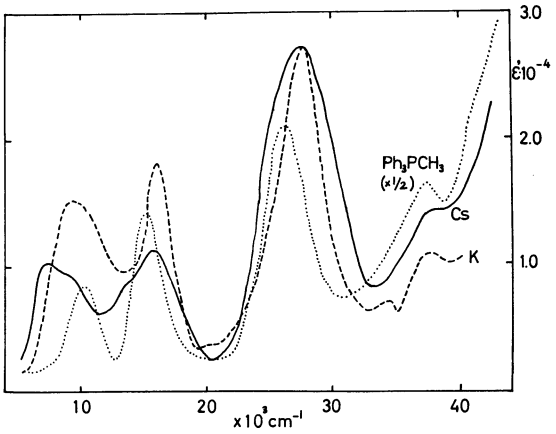

Fig. 6. The solid-state spectra of KTCNQ(K), CsTCNQ(Cs) and Ph_3PCH_3TCNQ.

reported for RbTCNQ-I,[18] and for KTCNQ[20] as the preliminary data. In the crystal of RbTCNQ-I, the dimer of TCNQ radicals (the radical spacing is 3.159 Å) form a one-dimensional column (the interval between the dimers is 3.484 Å). In the dimer unit, the radicals overlap each other, with a shift (0.84 Å) along the x axis. In the case of KTCNQ, the axis of the radical column almost coincides with the axis normal to the molecular plane.

The TCNQ radical has one odd electron in the ninth molecular orbital (φ_9). By our calculation of the open-shell SCF–CI, the lowest LE state was assigned to the $\varphi_8 \rightarrow \varphi_9$ transition, and the second lowest LE state, mainly to the $\varphi_9 \rightarrow \varphi_{10}$ transition; the higher LE state is found at 43000 cm^{-1} in the region up to 50000 cm^{-1}. Therefore, in this study of the electronic structure of the solid state, it is sufficient to take account of the interaction between the ground (G), LEI, LEII, and CT configurations. The CT configuration under consideration corresponds to the $\varphi_9 \rightarrow \varphi_{9'}$ transition (φ_9 and $\varphi_{9'}$ denote the MO's of the two radicals forming a dimer unit).

$$G = 1/\sqrt{2}\,(|8\bar{8}98'\bar{8}'\bar{9}'| - |8\bar{8}\bar{9}8'\bar{8}'9'|)$$

$$\mathrm{LEI}^{\pm} = 1/2[(|8\bar{8}98'\bar{8}'\bar{9}'| - |9\bar{8}\bar{9}8'\bar{8}'9'|) \pm (|8\bar{8}99'\bar{8}'\bar{9}'| - |8\bar{8}\bar{9}8'\bar{9}'9'|)]$$

$$\mathrm{LEII}^{\pm} = 1/2[(|8\bar{8}108'\bar{8}'\bar{9}'| - |8\bar{8}\bar{1}08'\bar{8}'9'|) \pm (|8\bar{8}98'\bar{8}'\bar{1}0'| - |8\bar{8}\bar{9}8'\bar{8}'10'|)]$$

$$\mathrm{CT}^{\pm} = 1/\sqrt{2}\,(|8\bar{8}9'8'\bar{8}'\bar{9}'| \pm |8\bar{8}98'\bar{8}'\bar{9}|)$$

The doubly occupied MO's φ_1—φ_7 are neglected. Here, the + and − signs denote the symmetric and the antisymmetric properties with respect to the symmetric center. Since the TCNQ molecule has the symmetry of D_{2h}, LEI and LEII do not interact with CT for the above-mentioned two modes of radical packing. Therefore, the configuration interaction occurs only between G and CT^+. The oscillator strength (f_{CT}) and the transition energy (σ_{CT}) of the CT band are calculated as follows:

$$f_{CT} = 1.085 \times 10^{-5} \frac{\beta^2 \sigma_{CT} R_{CT}^2}{\sigma_{CT}^2 + \beta^2}$$

and:

$$\sigma_{CT} = 1/2(E_{CT} + \sqrt{E_{CT}^2 + 4\beta^2}) \quad (\sigma_{CT}: \text{in } cm^{-1}).$$

Here, E_{CT} is the configuration energy of CT^+, and β is the interaction parameter between G and CT^+. R_{CT} is the distance between the radical centers in Å units. Then, from the observed values of σ_{CT}, f_{CT}, and R_{CT}, the β value can be calculated as follows:

$$|\beta| = \sigma_{CT}\left(1.085 \times 10^{-5} \frac{\sigma_{CT} R_{CT}^2}{f_{CT}} - 1\right)^{-1/2}$$

Moreover, the stabilization energy (J^*) of the ground state is obtained as β^2/σ_{CT}. Table 3 shows the values of $|\beta|$ and J^* calculated from the reflection data. The value of R_{CT} was known only for KTCNQ (3.5 Å) and RbTCNQ-I (3.42 Å); therefore, for the other eight salts, R_{CT} was assumed to be 3.42 Å. For the R_{CT} value of 3.8 Å, the change in the $|\beta|$ value is less than 10%.

Table 3. Parameters obtained from the reflection data of group A

	σ_{CT} $10^3 cm^{-1}$	f_{CT}	β eV	J^* eV	E_{CT} $10^3 cm^{-1}$	J_{ESR} eV
Li	9.8	0.26	0.62	0.32	7.2	0.23±0.2[4]
NH_4	9.5	0.24	0.58	0.32	7.2	
Rb-I	9.8	0.31	0.70	0.41	6.5	0.29±0.2[4]
Na	11.0	0.25	0.64	0.30	8.6	0.16±0.01[24]
PH_3PCH_3	10.5	0.24	0.62	0.33	8.2	
K	9.5	0.36	0.76	0.50	5.4	0.26±0.01[24]
Ni	9.0	0.22	0.54	0.26	6.9	
Fe	8.6	0.29	0.64	0.39	5.4	
Co	8.8	0.26	0.60	0.33	6.2	
Mn	9.0	0.26	0.60	0.32	6.4	
Dimer in H_2O	11.0	0.087	0.32	0.07	10.4	

On the basis of the crystal data for RbTCNQ-I, the overlap integral ($S_{99'}$) between φ_9 and $\varphi_{9'}$ was calculated by the use of the Slater-type AO's[23] as 0.037. On the other hand, β is related to $\beta_{99'}$ by this equation; $\beta = 2\beta_{99'}$. Here, $\beta_{99'} = \int \varphi_9(1)\, H^c(1)\, \varphi_{9'}(1)\, d\tau_1$ and $H^c(1)$ is the one-electron Hamiltonian of the crystal. $|\beta_{99'}|$ was found from the reflection data to be 0.35 (Table 3). The ratio of $|\beta_{99'}|$ to

23) F. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

$S_{99'}$ thus obtained is 9.5; this is reasonable. Table 3 shows the signlet-triplet splitting (J_{ESR}) of the ground state as determined by the ESR studies.[4,24] The ground configuration for the dimer system splits into the singlet (^{S}G) and the triplet (^{T}G) terms due to the exchange interaction (K) between the two unpaired electrons. By means of Mulliken's approximation, K and β are expressed as follows:

$$K = -A/2(S_{99'})^2$$

and:

$$\beta = -AS_{99'}$$

$$A = -\int\varphi_9(1)\varphi_9(2)\mathscr{H}\varphi_9(1)\varphi_9(2)d\tau_{12} - \int\varphi_9(1)\varphi_{9'}(2)\mathscr{H}\varphi_9(1)\varphi_{9'}(2)d\tau_{12}$$

where $\mathscr{H}$ is the Hamiltonian for the dimer system. Then, J_{ESR} is related to K and J^* by this equation:

$$J_{ESR} = -2K + J^* = AS_{99'}(1+A/\sigma_{CT}).$$

For the case of RbTCNQ-I, the A/σ_{CT} value is evaluated to be 13 from the observed values of J_{ESR} (0.29 eV), σ_{CT} (1.2 eV), and the calculated $S_{99'}$ (0.037). Therefore, the effect of the exchange interaction is almost negligible. The correspondence of J^* and J_{ESR} is good, taking account of the experimental error and the assumptions used for the calculation. The small value of J^* (0.07 eV) for the dimer in the solution is also reasonable.

If there is interaction between the CT^- and LE^- configurations, the f_{YI}/f_{YII} ratio differs from that of the dimer in the solution, as is the case with a very weak interaction. However, the f_{YI}/f_{YII} ratio and the $\sigma_{YI}-\sigma_{CT}$ and $\sigma_{YII}-\sigma_{YI}$ splittings observed for Group A show only slight change, and they are almost equal to the corresponding values of the dimer in the solution. Therefore, it seems that the salts belonging to Group A take the same packing form of the radical pair as RbTCNQ-I. The absolute intensities of the LE bands increase from A1 to A2 and A3, while the f_{YI}/f_{YII} ratio stays constant. The reason for this increase is not clear.

Table 4. Results of open-shell SCF–CI calculation

	RbTCNQ-I		RbTCNQ-II	
	cm^{-1}	f	cm^{-1}	f
LEI	9770	0.33	11300	0.28
LEII	21900	0.68	22200	0.74
LEIII	43300	0.77	43900	0.76

Group B. The crystal structure of RbTCNQ-II was reported by Shirotani *et al.*[19] TCNQ radicals form one-dimensional columns, in which the radicals are piled with equal spacing, with a shift of 1.86 Å along the y axis.

The transition energy and the oscillator strength of the radical monomer were calculated by the use of the molecular structures of RbTCNQ-I and RbTCNQ-II (Table 4). The slight difference in the bond lengths has a considerable effect on these transitions. Although the quantitative coincidence with the experimental values is not sufficient, it may be said that the f_{LEI}/f_{LEII} ratio is smaller for RbTCNQ-II than for RbTCNQ-I. First, we will consider the dimer model in discussing the electronic states of RbTCNQ-II solid. For the type of the radical packing of RbTCNQ-II, the $CT^{\pm}$ configurations interact with all the configurations under consideration. The matrices for the configuration interaction are:

Symmetric	G	0			
	LEI^+	0	E_I^+		
	$LEII^+$	0	0	E_{II}^+	
	CT^+	$2\beta_{99'}$	$-\sqrt{2}\beta_{89'}$	$\sqrt{2}\beta_{910'}$	E_{CT}^+
Asymmetric	LEI^-	E_I^-			
	$LEII^-$	0	E_{II}^-		
	CT^-	$\sqrt{2}\beta_{89'}$	$\sqrt{2}\beta_{910'}$	E_{CT}^-	

Here, $E_{CT}^+=E_{CT}^-(=E_{CT})$ was assumed. The configuration energies were estimated in the following way. The configuration energies of the locally-excited states, E^+ and E^-, show splitting by the interradical interaction, V, of the transition dipoles. The transition moments obtained from the open-shell calculation are almost equal for LEI and LEII. Therefore, the V values calculated on the basis of the crystal structures are -0.56 and -0.23 eV for RbTCNQ-I and RbTCNQ-II respectively. By the use of the reflection results and V, $E_I=1/2\ (E_I^+ + E_I^-)=1.00$ eV and $E_{II}=1/2\ (E_{II}^+ + E_{II}^-)=2.42$ eV were obtained for RbTCNQ-I. As may be seen in Table 4, the calculated E_I and E_{II} are higher for RbTCNQ-II than for RbTCNQ-I by 1500 and 300 cm^{-1} respectively. These differences were added to the E_I and E_{II} values obtained above for the RbTCNQ-I crystal. Thus, for the RbTCNQ-II crystal, E_I and E_{II} were determined to be 1.19 and 2.46 eV, and E_I^+, E_{II}^+, E_I^-, and E_{II}^- were calculated to be 0.96, 2.23, 1.42, and 2.69 eV respectively. E_{CT} was treated as a parameter (0.50—1.50 eV), and the values of β_{ij} were varied over the range of $k=-10$——-50 ($\beta_{ij}=kS_{ij}$). The S_{ij} used was calculated by the use of the Slater-type AO's.[23] The oscillator strengths were calculated on the basis of the transition moments obtained by the open-shell calculation for LEI and LEII. By comparison with the experimental results of RbTCNQ-II, a good fit was obtained by the set of $k=-20$ and $E_{CT}=0.75$ eV (Table 5). When the radicals are piled in an infinite column, f_{CT} becomes twice as large as f_{CT} for the dimer unit. Since the

Table 5. Calculated transition energies based on the dimer model for RbTCNQ-II

	Calcd		Obsd	
	σ	f	σ	f
CT	0.92 eV	0.20	0.93 eV	0.39
YI	1.72	0.40	2.09	0.33
YII	2.95	0.56	3.52	1.48

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Table 6. Transition energy and oscillator strength of group C

	$BaTCNQ_2$		MorTCNQ		Monomer in H_2O		Dimer in H_2O	
	cm^{-1}	f	cm^{-1}	f	cm^{-1}	f	cm^{-1}	f
CT	10000	0.09	10500	0.1			11000	0.09
YI	13800 15400	0.5	13500 15100 16100	0.9	11800 13400 14700	0.27	15800	0.22
YII	26200	1.1	27000	2.1	24800	0.47	26300	0.46

calculated CT band shows the 93% CT character, 0.20 corresponds to $0.39\times1/2$. Since this calculation does not take account of the effect of the infinite column and makes use of several assumptions, no quantitative discussion is available. The magnitudes of $k=-20$ and $E_{CT}=0.75$ eV are reasonable. In this treatment, the observed large intensity increase in the YII band could not be explained. This shows the importance of the long-range interaction. The calculations were carried out on the basis of Rhodes' [25] theory for intensity borrowing. The $\sum_{m}^{*n} G_{am\beta n}e_{am}e_{\beta n}$ factor for the YI and YII bands was four times as large for RbTCNQ-II as for RbTCNQ-I. Although a detailed discussion is impossible without the knowledge of the higher energy LE bands, it is clear that RbTCNQ-II is more sensitive to the intensity borrowing than is RbTCNQ-I.

Group C. Table 6 shows the transition energy and the oscillator strength of Group C, together with the data of the monomer and the dimer in the aqueous solution. The YI band of the monomer spectrum has a very sharp vibrational structure, the main vibrations of which are 1600 and 2900 cm^{-1} (Fig. 1). The vibrations of the YI bands, about 1600 cm^{-1} for $BaTCNQ_2$, and 1600 and 2700 cm^{-1} for MorTCNQ, are assigned to the above vibrations. The CT bands of both salts have an intensity almost equal to that of the dimer in the solution. On the other hand, the intensities of the LE bands show a remarkable increase, especially for MorTCNQ. The intense dispersion of the refractive index near the peaks of the LE bands is characteristic of Group C. This dispersion is one of the reasons for the large oscillator strength of the LE bands. Recently, it was reported that the MorTCNQ crystal contains the dimer unit of the TCNQ radicals, overlapping each other with a little shift along the x axis, and that its spacing is 3.28 Å.[26] For this mode of the radical packing, the interaction does not occur between the CT^- and the LEI^- configurations. The vibrational structure of the YI band may, therefore, be retained. Our observation of the weak CT band and the presence of the vibrational structure suggests a small contribution of the CT interaction in the solid state. However, the intensity increase in the LE bands and the outstanding dispersion of the refractive index cannot be discussed in detail at present.

The Relation of the Optical Spectrum to the Other Physical Properties. The magnitudes of the electrical resistivities of the salts of Group A are all in the order of 10^3—10^5 ohm cm, except for the case of the (Ph_3PCH_3) TCNQ (4×10^{10} ohm cm).[1,27] The salts of Group B have resistivities of 10^2 (RbTCNQ-II)[28] and 3×10^3 ohm cm (CsTCNQ).[27] By an analysis of the solid-state spectra, the CT components of the ground states are found to be a little larger for Group A (25%) than for Group B (20%). These results show that the resistivity is not sensitive to the CT character of the ground states. The TCNQ anion radical salts of Group A show the dimer formation in the solid state. On the other hand, in the salts of Group B, the radicals are piled up by equal spacings. Therefore, it may be suggested that the presence of the alternation of the radical spacing makes the resistivity large. The recent work on the MorTCNQ crystal structure also supports the above suggestion. This crystal exhibits a large alternation of the planar spacing between TCNQ anion radicals (3.28 and 3.61 Å) and shows a large electrical resistivity (10^9 ohm cm).[27]

The phase transitions of the TCNQ simple salts were observed by measurements of the absolute paramagnetic susceptbility and the electrical conductivity.[29,30] The transition temperatures are in the range of 338—391 K[29] or 348—395 K[30] for NaTCNQ, KTCNQ, and RbTCNQ-I. For RbTCNQ-II and CsTCNQ, they are 231 and 254 K[29] (210 K)[30] respectively. From our conclusion that the optically-classified groups take a different radical packing in the solid state, it is very reasonable that Group A and B behave differently in the phase transitions.

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