August, 1985] *Bull. Chem. Soc. Jpn.*, *58*, *2279—2284 (1985)*

Electronic Structures of 3,4:3′,4′-Bis(tetramethylene)-2,2′,5,5′-tetrathiafulvalene–TCNQ and 3,4:3′,4′-Bis(tetramethylene)-2,2′,5,5′-tetrathiafulvalene–1,4-Dihydro-1,4-bis(dicyanomethylene)-triptycene Complex Crystals

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(Received March 19, 1985)

Experimental results of the polarized reflection spectra and the calculated absorption spectra of 3,4:3′,4′-bis(tetramethylene)-2,2′,5,5′-tetrathiafulvalene (OMTTF)-TCNQ and OMTTF-1,4-dihydro-1,4-bis(dicyanomethylene)triptycene(DBTCNQ) crystals are discussed by developing approximate theoretical models, based on the CT mechanism. The electronic structures conform well that, OMTTF-TCNQ is a neutral crystal whereas, OMTTF-DBTCNQ is ionic. Furthermore, the temperature dependent spin susceptibilities imply the former as diamagnetic and the latter as a regular Heisenberg antiferromagnet.

Recently many scientists show keen interests in the field of highly conducting charge-transfer (CT) complexes. In this regard, complexes of TCNQ as the acceptor and TTF as the donor are the most widely investigated. In this class of complexes, the donor (D) and the acceptor (A) form segregated columns of their own in a mixed valence state[1] ($DD^+DD^+\cdots$ and $AA^-AA^-\cdots$). They are characterized by metallic conductivity ($\sigma \sim 10^2$—10^3 ohm^{-1}cm^{-1}) and an intense reflectance in the infrared region. Discovery of such high conductivities in the quasi-one-dimensional materials stimulated people greatly to design, synthesize and subsequently to investigate into the CT complexes of the new derivatives of TTF and TCNQ. Many attempts were successful[2] although lots of the crystals were found to belong to another category. Here, the complexes are of the simplest stoichiometry (1:1) and they form mixed stacks of alternating donors and acceptors either in the neutral ($\cdots$DADADA$\cdots$) or in the ionic ($\cdots D^+A^-D^+A^-\cdots$) forms and consequently exhibit insulating to semiconductive behavior ($\sigma \sim 10^{-9}$—10^{-3} ohm^{-1}cm^{-1}). The overlap between D and A hybridizes these states so that the solids in this class are only nominally neutral (**N**) or nominally ionic (**I**) in their ground states.[3]

In this paper we shall report on the electronic spectra and electronic structures of two such mixed stack complex crystals with OMTTF as the common donor. Figure 1 shows their molecular structures. The first crystal is the OMTTF–TCNQ[4] which has been suggested to be neutral from the structural analysis.[5] The second one is a new complex[6] between OMTTF and DBTCNQ.[7] The polarized reflection spectra and hence the calculated absorption spectra by Kramers-Kronig transformation[8] are presented and theoretical interpretations are made with a special emphasis on the CT bands. It has been found that OMTTF–DBTCNQ is an ionic complex,[6] accordingly the ESR measuerments are performed to find its spin susceptibility. The results of the optical and magnetic studies are interpreted in terms of the CT mechanism based on the calculations of the interactions between the MOs of the donor and the acceptor.

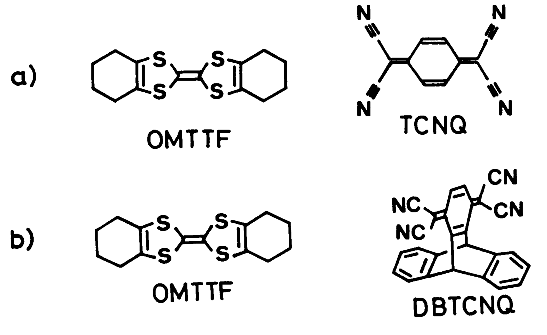


Fig. 1. Molecular structures of (a) OMTTF–TCNQ and (b) OMTTF–DBTCNQ.

Experimental

The crystals of OMTTF–TCNQ and OMTTF–DBTCNQ were of needle shape and lustering surfaces. In the structural analysis,[5] OMTTF–TCNQ crystal is reported as triclinic, $P\bar{1}$. In one of our previous papers,[1] we have reported the cell constants in a different way: $a'=b$, $b'=c$, $c'=a$, $\alpha'=\beta$, $\beta'=\gamma$, and $\gamma'=\alpha$, the dashed parameters being of our previous paper. OMTTF–DBTCNQ on the other hand, is monoclinic, $C2/c$.[6] The lattice parameters are: $a=18.535$ Å, $b=14.417$ Å, $c=14.906$ Å, $\beta=98.890°$, $Z=4$ and there exists one distorted C_6H_6 (solvent) per molecular complex. The oscillation/Weissenberg photographs were used to select suitable crytal faces for the spectral measurements.

Optical Spectra. The polarized reflection spectra on the (100) plane of OMTTF–TCNQ single crystal have been observed in the range of 3000—35000 cm^{-1} by a reflection spectrophotometer designed in our laboratory. Similar measurements on the (010) plane of OMTTF–DBTCNQ were performed in the range of 5000—25000 cm^{-1}. For both the crystals spectral measurements, one parallel to the needle axis and the other perpendicular to it, were made. Corresponding absorption spectra were then calculated by the Kramers-Kronig transformation.[8] The crystal oscillator strength along the α-axis was evaluated as:

$$f^{\alpha} = 4.32 \times 10^{-9}\int n_{\alpha}(\nu)\varepsilon_{\alpha}(\nu)\mathrm{d}\nu \qquad (1)^{9,10)}$$

where, ν is the wave number, n_α and ε_α are the α-components of the refractive index and the molar extinction coefficient, respectively.

ESR Measurements. The ESR absorptions were observed by a Varian-E 112 X-band spectrophotometer at 100 KHz field modulation. Measurements were made at the field strength of 3248 Gauss and care was taken with the microwave power so as to prevent saturation effect, if any, of the ESR signal especially at low temperatures. At least 20 single crystals of OMTTF-DBTCNQ and 3 of OMTTF-TCNQ were used due to their size factors. In the crystal setting of both the crystals, the needle axes were kept approximately perpendicular to the magnetic field direction. The absolute intensities of the ESR absorptions were obtained by integration of the derivative curves. Temperature dependent ESR were observed in the range of 1.6—293 K with an accuracy of ±1 K. The spin susceptibility was calculated by comparing the measured intensity with that observed for DPPH and then with spin susceptibility of the latter.[11]

Results and Discussion

Electronic Spectra. *a) OMTTF-TCNQ Crystal:* The polarized reflection spectra parallel and perpendicular to the crystal c-axis as observed on the (100) plane are shown in Fig. 2. In this spectra, there are two low energy bands and two other humps in the //c component. The corresponding absorptions calculated by the K-K transformation[8] are represented by Fig. 3. In the //c spectra, the lowest absorption arises near 5000 cm^{-1} and the second one which is very sharp, in the region of 17200 cm^{-1}. There are also a number of feeble absorptions but all in the high energy side. The ⊥c component, on the other hand, shows almost no absorption over a wide range of the observed spectra. Therefore, a comparative study between these two spectra reveals that, both the bands of 5000 and 17200 cm^{-1} are absolutely polarized along the c-axis of the crystal. At this stage, a close look into the crystal packings as depicted in Figs. 4 (a) and 4 (b) will provide an important clue to characterize them: The molecular components, OMTTF and TCNQ, stack alternately along the c-axis with the average molecular planes almost perpendicular to it (interplanar distance, 3.53 Å). Therefore, it would be appropriate to suggest these two as the CT bands where OMTTF donates its electrons to the TCNQ molecule: the first absorption is due to the first charge transfer, CT$_1$ and the second one is due to the second charge transfer, CT$_2$. In the photoelectron spectra, TMTTF showed closely situated two levels at 6.40 eV (b_{1u}) and 7.99 eV (a_{1u}) which are about 12800 cm^{-1} (1.59 eV) apart.[13] Therefore, in OMTTF-TCNQ, if the CT band from the HOMO is found at 5000 cm^{-1}, the CT$_2$ band appearing at 17200 cm^{-1} may be assigned to the transition from the second HOMO of OMTTF, because, energy separation (12200 cm^{-1}) between these two bands is close to the difference in energy of the first and second HOMOs in the TMTTF molecule.

In order to estimate the CT state energy, secular

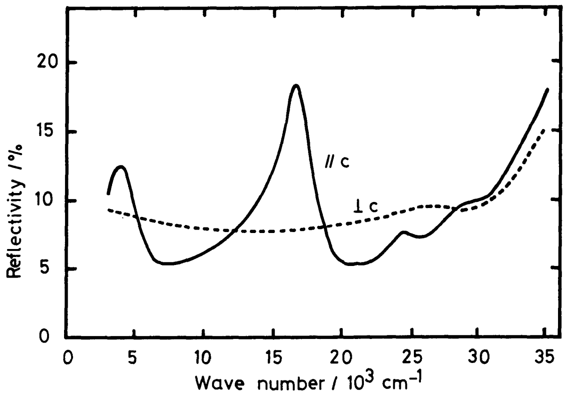


Fig. 2. Polarized reflection spectra of the OMTTF-TCNQ crystal on the (100) plane.

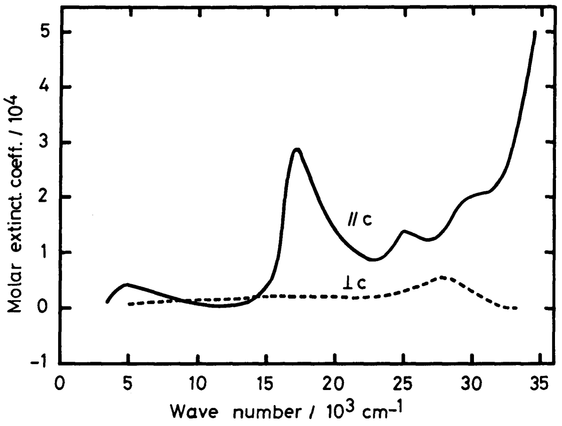
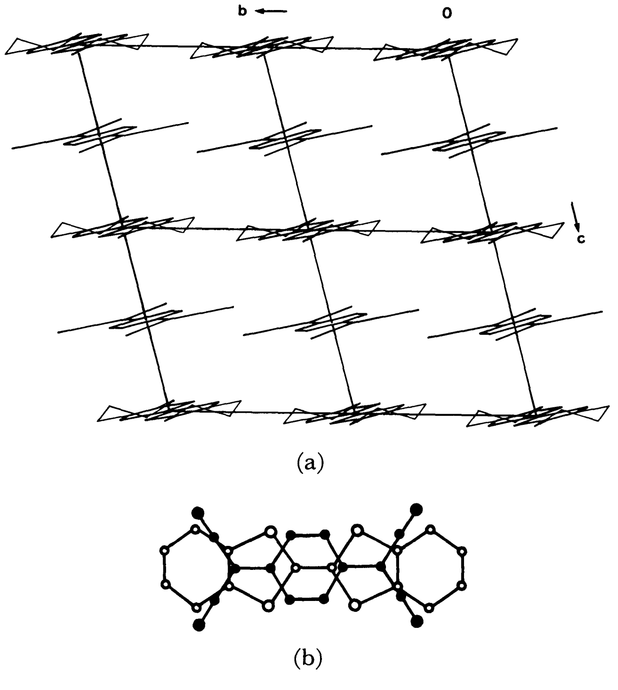


Fig. 3. Calculated absorption spectra of OMTTF-TCNQ on the (100) plane.



(a)

(b)

Fig. 4. (a) Projection figure of the OMTTF-TCNQ crystal onto (100). (b) Mode of overlap of the component molecules in the crystal.

Table 1. Values of ionization potential(I_P), electron affinity(E_A), coulomb(C)/madelung(M) energy, polarization energy(P), CT configuration energy(Δ) and the calculated mixing coefficients a and b of the crystals

Complex	Transition type	I_P (eV)	E_A (eV)	C/M (eV)	P (eV)	Δ (eV)	a	b
OMTTF-TCNQ	CT_1	6.5	2.80	2.96	0.2	0.54	0.995	0.103
	CT_2	8.0	2.80	2.95	0.2	2.05	0.981	0.196
OMTTF-DBTCNQ	back CT	6.5	2.85	3.84	0.7	0.89	0.130	0.992

equation of the following form may be solved. Considering the ground configuration at the zero level and the CT configuration energy to be denoted as Δ, the equation follows:

$$\begin{vmatrix} \Delta - E & 2t_{\mathrm{Ak,Dl}} \\ 2t_{\mathrm{Ak,Dl}} & -E \end{vmatrix} = 0 \tag{2}$$

In this equation, Δ may be defind as:

$$\Delta = I_p - E_A - C - P \tag{3}$$

where, I_P is the ionization potential, E_A the electron affinity, C the Coulomb potential in the DA pair and P is the polarization energy (positive) of the crystal. Again, $t_{\mathrm{Ak,Dl}}$ is the transfer integral and may be related to the overlap integral, $S_{\mathrm{Ak,Dl}}$, approximately as:

$$t_{\mathrm{Ak,Dl}} = KS_{\mathrm{Ak,Dl}}\left(\frac{W_{\mathrm{Ak}}+W_{\mathrm{Dl}}}{2}\right) \tag{4}$$[1,12]

where, W_{Ak} and W_{Dl} are the respective MO energies and K is a semiempirical constant lying in the range of 1.0—2.0.

For the crystal of OMTTF-TCNQ ionization energies that are yet to explore, were approximated to be 6.5 eV (I_p^1) and 8.0 eV (I_p^2) with reference to those of TMTTF.[13,14] From the MO calculations by Pariser-Parr-Pople method, the two transitions in this crystal may be considered as: CT_1:$D_7 \rightarrow A_9$ and CT_2:$D_6 \rightarrow A_9$, subscript denoting the number of MO counted from the bottom in the concerned molecule. The associated orbital overlaps ($S_{\mathrm{A9,D7}}$ and $S_{\mathrm{A9,D6}}$) are 0.00367 and 0.02315 so that, transfer integrals may be estimated as t_1=−0.0290 and t_2=−0.2125 eV provided K=1.7 in Eq. 4. Moreover, considering Ohno-Klopman's approximations Coulomb energies as calculated are 2.96 eV (CT_1) and 2.95 eV (CT_2). Now, if we assume that the polarization energy (unknown yet) be as small as 0.2 eV, Δ in Eq. 3 may be estimated as 0.54 eV (Δ_1) and 2.05 eV (Δ_2). Therefore, solving the respective secular equations our theoretical CT transition energies obtained are 0.55 and 2.22 eV which are fairly comparable to the observed values of 0.62 and 2.13 eV, respectively. To estimate approximately the contribution of these CT states to the crystal ground state, mixing coefficients a and b in the wave function,

$$\Psi_G = a\Psi_0 + b\Psi_1 \tag{5}$$[15]

were calculated and are shown in Table 1. Respective magnitudes of a and b thus suggest that, in the ground state crystal of OMTTF-TCNQ is mostly neutral and, in its CT interaction, contribution of the CT_2 is more than that of the CT_1. The observed and the calculated degrees of charge transfer, oscillator strengths and the stabilization energy as displayed in Table 3 are in reasonable agreement. The larger value of the degree of charge transfer of CT_2 than that of CT_1 indicates that the former configuration is quite significant in the CT interaction. Following the theoretical calculations, CT stabilization energy in the ground state is found to be 2.02 kcal mol^{-1}† of which ≈93% (1.88 kcal mol^{-1}) is accounted as the contribution of the CT_2 configuration. The large f_2 of the CT_2 transition may be attributed as due to the allowed character of the transition from the second HOMO(D_6) of OMTTF to the LUMO(A_9) of TCNQ. In contrary, CT_1 transition seems to be of forbidden type as can be decided by the difference in the symmetry of the HOMO and the LUMO, because, the transfer integral between the molecular orbitals of different symmetry will be negligibly small. Nevertheless, both the CT_1 and CT_2 configurations stabilize the crystal ground state only to a certain extent, so that the crystal as a whole is almost neutral in its ground state.

b) OMTTF-DBTCNQ Crystal: Presence of two benzene rings in the DBTCNQ molecule creates a novelty in the crystal of OMTTF-DBTCNQ. One would notice interestingly that, in the crystalline state OMTTF and DBTCNQ form linear stacks in an alternating fashion along the c-axis (average interplanar distance ≈3.60 Å) in a pattern such that the molecular planes of OMTTF and TCNQ moiety of DBTCNQ are almost parallel (Figs. 5 (a) and 5 (b)). As compared with the mode of overlapping in OMTTF-TCNQ crystal, there is a lateral shift of TCNQ moiety along its short axis. By comparing its powder spectra with those of $K^+DBTCNQ^-\cdot 2H_2O$ and $OMTTF^+BF_4^-$, Nakasuji *et al.*[6] suggested that OMTTF-DBTCNQ is an ionic complex. In this paper polarized electronic spectra will conform the assignments of the spectra and the ionic ground state.

The observed reflection spectra polarized parallel and perpendicular to the crystal c-axis are shown in Fig. 6 and the corresponding absorption spectra in Fig. 7. In the absorption spectra, the ⊥ c component

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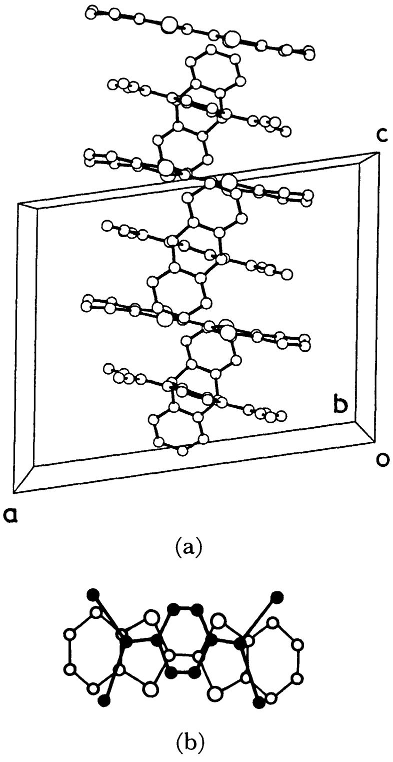
† 1 $\mathrm{cal_{th}}$=4.184 J.



(a)

(b)

Fig. 5. (a) Crystal packing of OMTTF and DBTCNQ on the (010) plane. Solvent molecules (C_6H_6) have been excluded for clarity. (b) Mode of overlapping of the OMTTF molecule and the TCNQ moiety in the crystalline state.

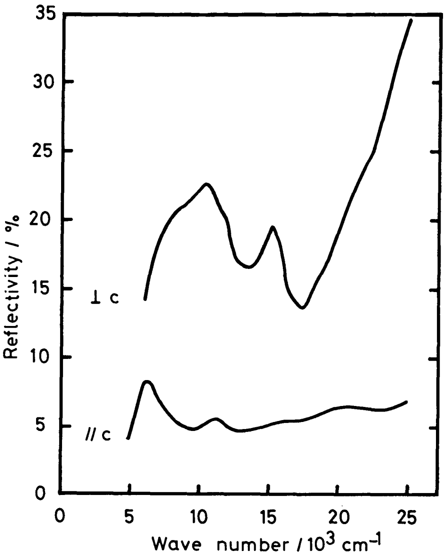


Fig. 6. Reflection spectra of OMTTF-DBTCNQ on the (010) plane.

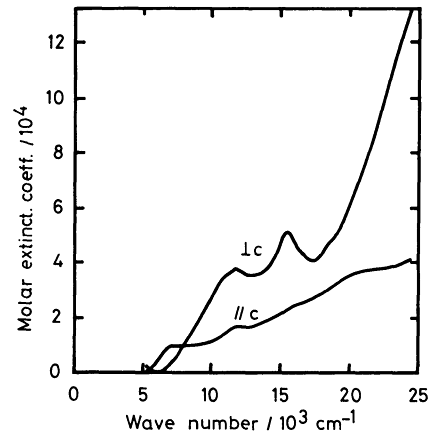


Fig. 7. Calculated absorption spectra of OMTTF-DBTCNQ crystal on the (010) plane.

shows its first absorption in the region of 11800 cm^{-1} which may be suggested as due to the first local excitation (LE_1) in the TCNQ moiety of DBTCNQ, since in solution the first excitation in TCNQ$^-$ has been observed[16] near 12000—13000 cm^{-1}. At the similar energy region ($\approx$11800 cm^{-1}) there is a small absorption also in the //c spectra which may be interpreted as the perpendicular component of the former absorption. This is justified because, the molecular planes of OMTTF and TCNQ moiety are not exactly perpendicular to the c-axis, rather inclined to it (roughly by 10—15°). The next absorption at around 15400 cm^{-1} in the ⊥ c spectra may be interpreted as due to a local excitation in OMTTF$^+$ since an absorption at 17000 cm^{-1} of this cation radical has been observed in its powder spectra[6] and also one of the local excitations in TTF$^+$ has been found near 18000 cm^{-1}.[17] Ultimately, the lowest absorption of 7200 cm^{-1} in the //c component indicates its unique polarization in a direction which is close to the stacking axis. Therefore, it is typical of the CT band and the ionicity in the complex strongly suggests it to be associated with the "back charge transfer" where, an electron transfer occurs from the HOMO of the TCNQ$^-$ moiety to the LUMO of the OMTTF$^+$ radical.

Using the P-P-P method we have performed MO calculations of OMTTF-DBTCNQ also which referred to $\phi_9 \rightarrow \theta_7$ as the CT transition. Here, ϕ and θ are the HOMO and LUMO of DBTCNQ anion and OMTTF cation respectively and the subscripts denote the numbers of MOs in the ions. In addition, considering Ohno-Klopman's approximations, overlap integral calculated was 0.00721 so that the transfer integral may be estimated as $t=-0.0573$ eV at the value of $K=1.7$.

In the case of ionic crystals, we like to prefer back CT configuration energy, Δ', to be defind as:

$$\Delta' = M + P + E_A - I_P \qquad (6)$$

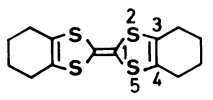
Here, M represents the negative of the crystal Madelung energy and the other parameters have the similar significances as in Eq. 3. From the very difference in the redox potentials of TCNQ and DBTCNQ of 0.18 and 0.23 V, respectively, electron affinity of the latter may be assumed to be increased by only 0.05 eV from that of TCNQ, *i,e.*, E_A(DBTCNQ)=2.85 eV. To have an estimation of the crystal Coulomb energy we have computed Madelung energy of OMTTF-DBTCNQ by the

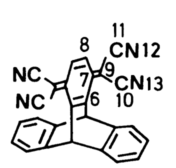
Ewald method[18] following Metzger's expressions.[19] The computation program written here was tested with NaCl, $TMPD^+$-$TCNQ^-$ and $TMPD^+$-ClO_4^- and all of them have shown good coincidence with those calculated by Metzger.[19,20] For the OMTTF-DBTCNQ crystal, detailed charge distributions at different atom positions were calculated by the P-P-P method and they are represented in Table 2. Two runs, at η=15.00 and η=20.00, were made with this charge distribution model and the results are shown in Table 2. Thus the estimated Madelung energy of magnitude of 3.846±0.002 eV may merely be as enough as to ionize a DA pair since, $I_P-E_A \simeq 3.65$ eV is our guess about this complex. Therefore, to find an approximate fit to the observed spectra we have considered $\Delta' \simeq 0.89$ eV which needed obviously a polarization energy of 0.7 eV. This amount is larger than that of the neutral crystal of OMTTF-TCNQ and also seems to be reasonable because, polarization energies of TTF and its methyl-substituted derivatives lie in the range of 0.9—1.4 eV and that of TCNQ is 2.1 eV.[14]

TABLE 2. DELOCALIZED ATOMIC CHARGE DISTRIBUTIONS (BY P-P-P METHOD), CONVERGENCE PARAMETER(η) AND THE COMPUTED MADELUNG ENERGY OF OMTTF-DBTCNQ

Atom No.[a)]	Atomic charge/|e|	η	Madelung energy (eV mol^{-1})
1	0.093		
2	0.176		
3	0.027		
4	0.031		
5	0.173	15.00	−3.84401
6	−0.067		
7	−0.072		
8	−0.055		
9	−0.195		
10	−0.010	20.00	−3.84754
11	−0.008		
12	−0.043		
13	−0.050		

a) For numbering, see below.





The large value of b (Table 1) of the OMTTF-DBTCNQ crystal suggests a highly ionic ground state. Our calculated degree of charge transfer and oscillator strength (based on an ionic complex) are comparable with the observed data (Table 3) and all of them suggest an ionic ground state of the OMTTF-DBTCNQ crystal with an additional stabilization (ΔE=0.33 kcal mol^{-1}) due to the back charge transfer.

Spin Susceptibility: In the ESR measurements, crystal of OMTTF-TCNQ showed only a feeble room temperature absorption with an approximate *g* of 2.0015. Moreover, in the range of 2.8—300 K no phase transition was found to occur. The observed spin susceptibility was of the order of 10^{-8} emu mol^{-1} most of which may be due to the contamination of crystals with certain paramagnetic impurities.

The ionic crystal, on the other hand, exhibited a single line absorption in the range of 1.6—293 K except a little distortion at 1.6 K. This is because, at low temperatues, ESR intensity shows a small Curie-like upturn which is characteristic of the extrinsic Curie-impurities commonly found in organic salts. However, *g* value of this crystal was found to be 2.066 at room temperature and increased only by 0.3% at 4.2 K.

The spin susceptibility of OMTTF-DBTCNQ was calculated from the observed intensity and it was corrected by subtracting the contribution of Curie-impurity which showed the Curie constant, C= 7.82×10^{-3} emu K mol^{-1}. The resulting temperature dependence is shown by solid circles as in Fig. 8. A finite spin value near T=0 and presence of a rounded maximum in the temperature dependent spin susceptibility lead to suggest that, OMTTF-DBTCNQ is a typical example of the regular Heisenberg antiferromagnet.[21] An approximate Hamiltonian for such a one-dimensional Heisenberg regular chain is given by:

$$H = \sum_{i=1}^{N} J \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} \qquad (7)^{22)}$$

where, J represents equal interaction with both the neighbors along the chain and $\boldsymbol{S}_i$ is the spin vector of the ith radical. For a regular Heisenberg antiferro-

TABLE 3. CALCULATED AND OBSERVED TRANSITION ENERGIES(ΔE^i_{CT}), DEGREES OF CHARGE TRANSFER(b_i^2), OSCILLATOR STRENGTHS(f_i) AND THE STABILIZATION ENERGIES(ΔE) IN THE GROUND STATES OF THE CRYSTALS

Complex		CT$_1$[a)]			CT$_2$			
		ΔE^1_{CT}	b_1^2	f_1	ΔE^2_{CT}	b_2^2	f_2	ΔE
		cm^{-1}	%		cm^{-1}	%		kcal mol^{-1}
OMTTF-TCNQ	calcd	4438	1.1	0.020	17915	3.7	0.266	2.02
	obsd	5000	3.2	0.065	17200	10.1	0.706	
OMTTF-DBTCNQ	calcd	7424	1.6	0.049				0.33
	obsd	7200	4.4	0.133				

a) For OMTTF-DBTCNQ, back CT.

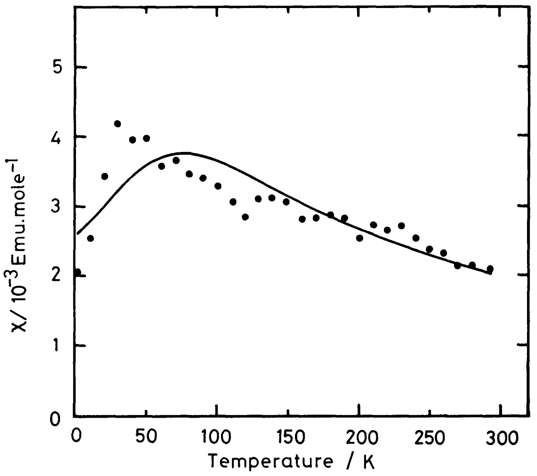


Fig. 8. Temperature dependent spin susceptibility of the OMTTF–DBTCNQ crystal. Solid circles are the experimental points and the solid line is the Bonner-Fisher susceptibility at J=0.005 eV.

magnet Soos[23] has expressed the exchange energy as:

$$J = 2|t|^2/\Delta E_{\mathrm{CT}} \tag{8}$$

provided, $\Delta E_{\mathrm{CT}} \gg t$. Here, t is Mulliken's CT integral and ΔE_{CT} the energy of CT transition. Our observed spin susceptibility fits moderately well to the Bonner-Fisher model[24] which is calculated for J=0.005 eV by using the formulation of Torrance *et al.*;[25] solid line in Fig. 8 represents the calculated values. This value of J is comparable, at least in order, to the expected value of 0.007 eV which may be obtained from equation (8) using our estimated values of t and CT transition energy.

Thus, from so far we have investigated, we find a quite good correlation between the magnetic behaviors and the electronic structures of the two crystals. The OMTTF–TCNQ with two CT transitions and a nearly diamagnetic behavior identifies itself as an almost neutral crystal and probably it has a high energy triplet above its singlet ground state. On the other hand, OMTTF–DBTCNQ is characterized by a single CT transition due to the back charge transfer and magnetically behaves as a simple regular Heisenberg antiferromagnet with a small exchange interaction between the ion radicals along its infinite chain. These facts suggest that OMTTF–DBTCNQ is a highly ionic crystal and the ionicity in the ground state approaches almost to unity. In particular, this OMTTF–DBTCNQ is the third CT crystal as reported yet,[26] with a nearly fully ionic ground state and it follows regular Heisenberg antiferromagnetism strictly over a wide range of temperature.

The authors thank the Instrument Center, Institute for Molecular Science, Okazaki, for the use of a Varian spectrophotometer. This research was supported by the grant in aids of special research project on properties of molecular assemblies (No. 59112003) from the Ministry of Education, Science and Culture.

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