Synthesis, Crystal Structure, and Physical Properties of the Charge-Transfer Complex Bis[benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene]-tetrafluorotetracyanoquinodimethan, $(BTT)_2(TCNQF_4)$

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The semiconductive 2:1 charge-transfer complex between benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene and 2,2′-(2,3,5,6-tetrafluoro-2,5-cyclohexadiene-1,4-diylidene)bis[propanedinitrile], $(BTT)_2(TCNQF_4)$, crystallizes in the monoclinic system, space group $P2_1/c$, with the following cell constants: $a=8.893(2)$ Å, $b=10.589(2)$ Å, $c=18.528(4)$ Å, $\beta=114.52(1)^\circ$, $V=1587.5(10)$ Å^3, $D_x=1.61$ g cm^{-3}, and $Z=2$. The crystal structure of $(BTT)_2(TCNQF_4)$ consists of stacking columns of alternating donor dyads and acceptor monads (DAD units) along the crystallographic b axis. Side-by-side sulfur-sulfur contacts shorter than the sum of the van der Waals radii were found along the axis between BTT molecules on the neighboring columns. Polarized reflectance spectra were measured with the single crystal of $(BTT)_2(TCNQF_4)$ at room temperature, showing a charge-transfer band polarized parallel to the stacking direction. The degree of charge transfer was estimated to be 0.21 from the oscillator strength and the transition energy of the charge-transfer band. From this, as well as the electric and magnetic properties of the complexes and the atomic distances for $TCNQF_4$, it was concluded that $(BTT)_2(TCNQF_4)$ is a weakly ionized charge-transfer complex.

Benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (BTT) is one of aromatic molecules with heteroatoms at the periphery, which may act to increase transverse interchain interactions in the solid consisting of molecular stacking columns. BTT was first synthesized by Hart and Sasaoka[1)] as a model chalcogen-bridged hexaradiarene, a molecule of considerable theoretical interest. However it was also shown by them that BTT forms air- and moisture-stable crystalline 1:1 charge-transfer (CT) complexes with the electron acceptors TCNE, TCNQ, DDQ, and chloranil.[1,2)]

Recently, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), which is an electron-donating aromatic molecule with heteroatoms at the periphery, was found to form side-by-side contacts shorter than the sum of the van der Waals radii between the heteroatoms.[3)] This fact prompts us to investigate CT complexes based on BTT in order to find another electron donor which could form side-by-side contacts between molecules, since BTT gives CT complexes with some electron acceptors. 2,2′-(2,3,5,6-tetrafluoro-2,5-cyclohexadiene-1,4-diylidene)bis[propanedinitrile] (commonly abbreviated to tetrafluorotetracyanoquinodimethan $TCNQF_4$) is an electron acceptor having a redox potential higher than that of chloranil, TCNE, TNCQ, and DDQ. $TCNQF_4$ was therefore chosen as an electron acceptor to find ionic CT complexes, which might exhibit interesting electric and magnetic properties.

The present paper describes the synthesis and crystal structure of 2:1 CT complex of BTT with $TCNQF_4$, $(BTT)_2(TCNQF_4)$.[4)] The polarized reflectance spectra observed for $(BTT)_2(TCNQF_4)$ are discussed on the basis of the crystal structure. The degree of charge transfer in $(BTT)_2(TCNQF_4)$ is estimated from the molecular geometry of $TCNQF_4$ and also from the oscillator strength and the transition energy of the CT band observed in the reflectance spectra. The electric and magnetic properties are discussed in relation to the degree of charge transfer.

Experimental

BTT was prepared according to the procedures described by Hart and Sasaoka.[1)] $TCNQF_4$ was kindly provided by Professor Gunzi Saito of the Institute for Solid State Physics. $(BTT)_2(TCNQF_4)$ was obtained by the following way: 41.8 mg (0.170 mmol) of BTT and 46.0 mg (0.166 mmol) of $TCNQF_4$ were dissolved into a hot acetonitrile solution under an argon atmosphere and then the solution was allowed to stand until it cooled to room temperature. The precipitate was filtered off and washed with small amount of acetonitrile to give 47.4 mg (73%) of dark-green long-needle crystals of $(BTT)_2(TCNQF_4)$. Found: C, 56.22; H, 1.51; N, 7.08%; Calcd for $(C_{12}H_6S_3)_2C_{12}N_4F_4$: C, 56.24; H, 1.57; N, 7.29%. A 1:2 mixture of chlorobenzene and acetonitrile was also used as the solvent.[5)] The crystals of the same composition with larger width were obtained from the mixture.

X-Ray diffraction intensities were measured at room temperature with the θ–2θ scan technique on a Rigaku automated four-circle diffractometer employing Mo $K\alpha$ radiation ($2\theta \leqq 60^\circ$) and were corrected for Lorentz and polarization effects, but not for the absorption. The dimensions of the crystal used were 0.10×0.25×0.40 mm.

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The structure was solved by the direct method and refined by the block-diagonal least-squares procedure to an R value of 0.063 with unit weight, using 2581 independent reflections ($|F_o|>3\sigma(|F_o|)$). Anisotropic thermal parameters were adopted for all non-hydrogen atoms, and the hydrogen atoms were refined isotropically. Atomic scattering factors and anomalous scattering corrections were taken from International Tables for X-ray Crystallography.[6] Observed and calculated structure factors, anisotropic thermal factors, and positional parameters for H atoms are deposited as Document No. 8809 at the Office of the Chemical Society of Japan. Calculations were carried out on a FACOM-U1300 computer at Toho University and a HITAC M680H computer at the Computer Centre of the University of Tokyo with a local version of UNICS.[7]

The polarized reflectance spectra at normal incidence on the ab and ac planes were measured at room temperature over the spectral range from 8000 to 28000 cm^{-1} using a microspectrophotometer described briefly in a previous paper.[8]

The dc conductivity along the needle (crystallographic b) axis of the single crystal was measured in the temperature range between 240 and 300 K by means of the two probe method.

The static magnetic susceptibility for 37 mg of the tiny crystals oriented randomly was measured with a Faraday-type susceptometer over the temperature range from 2 to 300 K at 3 T. The details of the apparatus were described previously.[9]

Crystal Structure

$(BTT)_2(TCNQF_4)$ crystallizes in the monoclinic system, space group $P2_1/c$, with the following cell constants: a=8.893(2) Å, b=10.589(2) Å, c=18.528(4) Å, β=114.52(1)°, V=1587.5(10) Å^3, Z=2, D_x=1.61 g cm^{-3}, and μ(Mo $K\alpha$)=47.1 mm^{-1}. The positional parameters for the atoms are given in Table 1. The atomic numbering schemes and the molecular geometries within the BTT donor and the $TCNQF_4$ acceptor are shown in Fig. 1. The $TCNQF_4$ molecule is located on a center of symmetry. The BTT and $TCNQF_4$ molecules are nearly planar with maximum diviations from their least-squares planes by 0.06 Å [S(1)] and 0.13 Å [F(2)], respectively. No anomalous bond distances and angles are found for both molecules.

The crystal structure of $(BTT)_2(TCNQF_4)$, as illustrated in Fig. 2, consists of stacks of alternating donor dyads and acceptor monads, extending along the crystallographic b axis. Within these stacking columns, the interplanar separations between two donors and between donor and acceptor are 3.42 Å and 3.29 Å respectively. The latter separation is an average value because of the slightly unparallel overlap with the dihedral angle of 5.5° between the planes. Crystallographic symmetry requires that the components

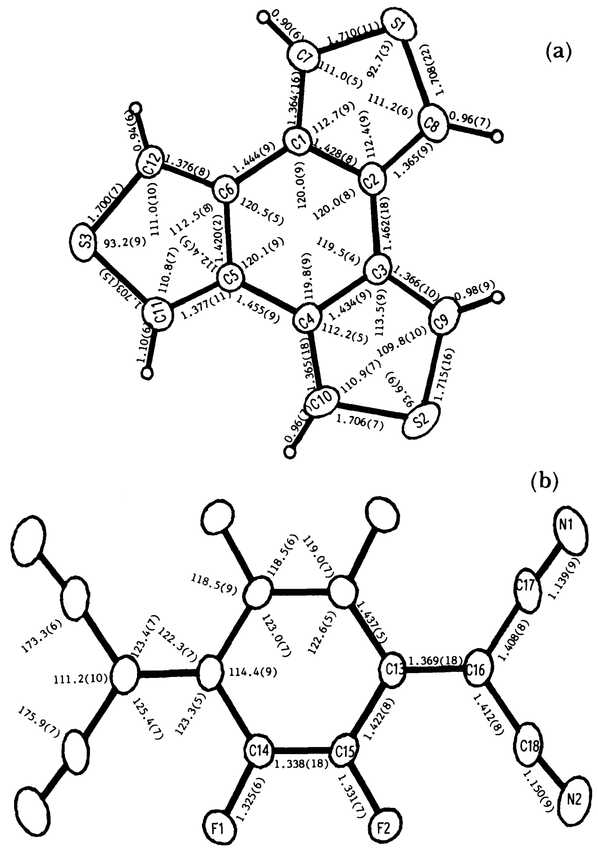


Fig. 1. Atomic numbering schemes and molecular geometries of the BTT donor (a) and the $TCNQF_4$ acceptor (b).

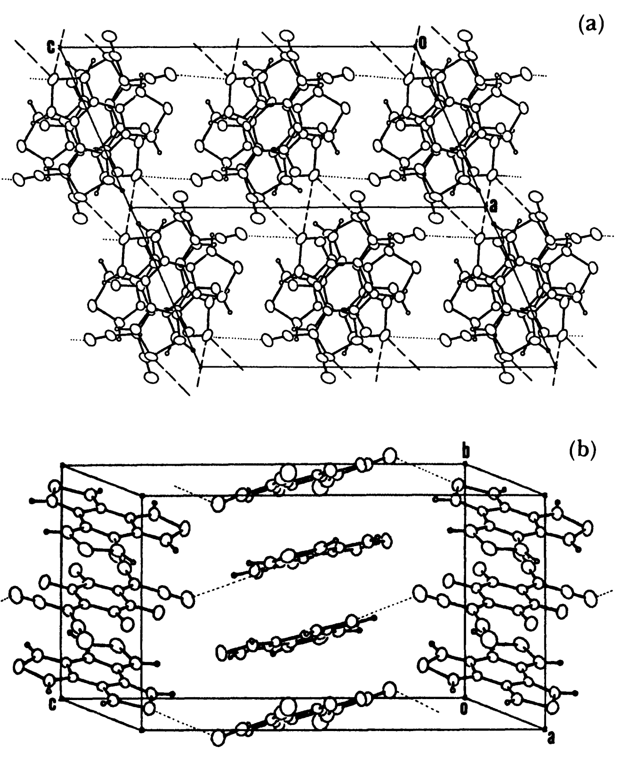


Fig. 2. Projection of the structure on the ac (a) and bc (b) planes. Broken lines represent S–S contacts shorter than the sum of vdW radii 3.70 Å between BTT molecules. Dotted lines represent S–N contacts between BTT and $TCNQF_4$ molecules.

of the donor dyads be parallel. The donor–acceptor interplanar separation is unusually short for a sulfur containing donor and rather close to that observed in the TCNQ complexes with donors containing no sulfur atoms, $(perylene)_3(TCNQ)$ (3.37 Å)[10] and (benzidine)(TCNQ) (3.24 Å)[11] which exhibit a strong CT band.[12,13]

Table 1. Positional Parameters (×10⁴) and Equivalent Isotropic Thermal Parameters (Å²) for $(BTT)_2(TCNQF_4)$ with Esd's in Parantheses. $B_{eq}=(3/4)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$

	x	y	z	$B_{eq}(\times 10^2)/Å^2$
S(1)	6191(2)	2771(2)	7283(1)	237(2)
S(2)	630(2)	2661(2)	3728(1)	236(2)
S(3)	8011(2)	4347(2)	4423(1)	217(2)
C(1)	6192(5)	3240(4)	5939(3)	133(6)
C(2)	4555(5)	2836(4)	5786(3)	139(6)
C(3)	3282(5)	2806(4)	4973(3)	143(7)
C(4)	3683(6)	3208(4)	4334(3)	143(7)
C(5)	5362(6)	3597(4)	4497(3)	144(3)
C(6)	6597(6)	3593(4)	5287(3)	133(7)
C(7)	7215(6)	3249(5)	6727(3)	187(8)
C(8)	6384(7)	2541(6)	6465(3)	205(9)
C(9)	1667(6)	2461(6)	4734(3)	202(8)
C(10)	2345(7)	3170(5)	3619(3)	203(9)
C(11)	5958(7)	4003(5)	3959(3)	199(9)
C(12)	8115(7)	3968(5)	5334(3)	184(9)
F(1)	4897(4)	−658(3)	6387(2)	213(5)
F(2)	2182(4)	−789(3)	5083(2)	218(5)
N(1)	−673(7)	−1074(7)	3469(4)	340(11)
N(2)	1693(7)	562(6)	2218(3)	301(10)
C(13)	3503(6)	−81(4)	4281(3)	143(6)
C(14)	4952(6)	−347(4)	5706(3)	148(7)
C(15)	3568(6)	−417(5)	5036(3)	151(7)
C(16)	2081(6)	−169(5)	3600(3)	174(8)
C(17)	564(6)	−649(6)	3550(3)	225(9)
C(18)	1957(7)	232(6)	2850(3)	213(9)

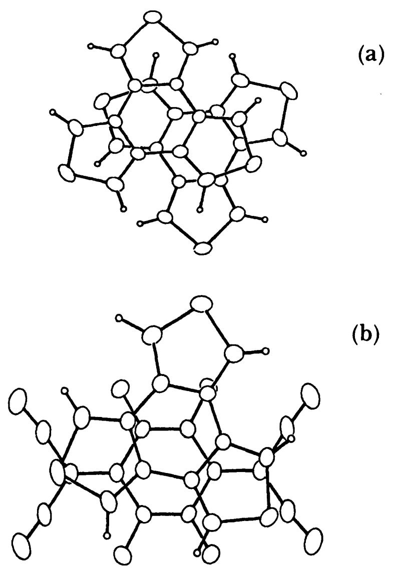


Fig. 3. Molecular overlapping modes of the donor–donor (a) and donor–acceptor (b) pairs.

The donor–donor and donor–acceptor molecular overlapping modes are shown in Fig. 3. Within the donor dyad the BTT molecule is rotated by approximately 60° with respect to the neighboring molecule so that the sulfur atoms at the periphery of the neighboring molecules keep away from each other. The central benzene rings of BTT are stacked in a ring-over-bond motif found commonly in planar aromatic hydrocarbons. One of the in-plane twofold rotation axes of BTT is rotated by 18° with respect to the molecular long-axis of $TCNQF_4$.

A significant feature of the crystal structure of $(BTT)_2(TCNQF_4)$ is that the interchain side-by-side sulfur-sulfur contacts shorter than the sum of the van der Waals radii (vdW) are found along the a axis. Short contacts between S(2)–S(3^{i}) at 3.572(4) Å and S(3)–S(3^{i}) at 3.567(2) Å (2×vdW(S)=3.70 Å), where i represents the key to symmetry code $1+x$, y, z, are indicated by the broken lines in Fig. 2(a). No sulfur-sulfur contacts shorter than the sum of vdW is found along the c axis. However close contact between S(3) and N(2^{ii}) at 3.41(6) Å (vdW(S)+vdW(N)=3.35 Å; ii represents the key to symmetry code $1-x$, $1/2+y$, $1/2-z$) is found along the c axis as shown in Fig. 2(b). The S–N contacts along the c axis are restricted within a DAD unit, whereas the S–S contacts along the a axis extend over an infinite chain. These findings demonstrate that BTT is capable of forming multi-dimensional molecular networks as expected from its molecular structure.

Polarized Reflectance Spectra

Figure 4 shows the reflectance spectra of $(BTT)_2(TCNQF_4)$ for light polarizations parallel to the crystallographic a, b, and c axes. Figure 5 shows the frequency dependent conductivity $\sigma(\tilde{\nu})$ of $(BTT)_2(TCNQF_4)$ calculated from the reflectance spectra

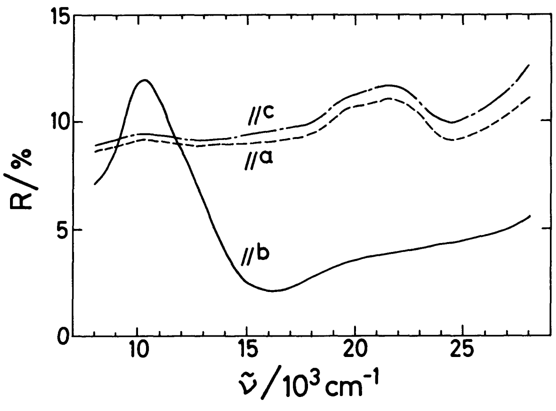


Fig. 4. Reflectance spectra of $(BTT)_2(TCNQF_4)$ with the polarization parallel to the crystallographic a, b, and c axes.

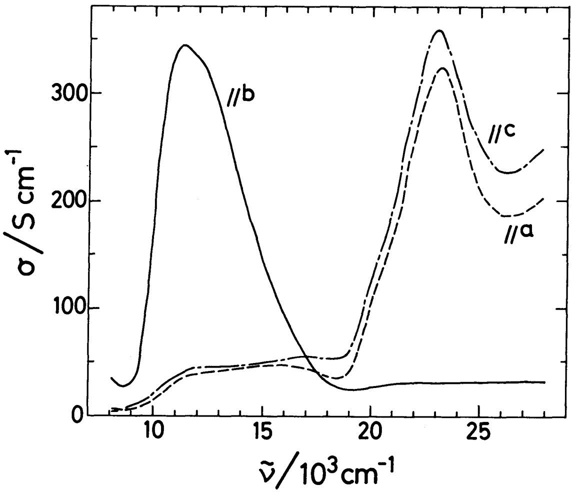


Fig. 5. Frequency dependent conductivity $\sigma(\tilde{\nu})$ of (BTT)$_2$(TCNQF$_4$) with the polarizations parallel to the a, b, and c axes obtained by a Kramers-Kronig analysis of the reflectance spectra.

using the modified Kramers-Kronig transformation technique.[14] A conductivity peak appears in the near infrared region of the //b spectrum, whereas another peak appears in the visible region of the //a and //c spectra.

The conductivity peak located at 11200 cm^{-1} is almost completely polarized in the b axis which is parallel to the stacking direction and nearly perpendicular to the molecular planes of BTT and TCNQF$_4$. Since the lowest intramolecular excitations in BTT, TCNQF$_4$, and TCNQF$_4^-$ are expected to be polarized parallel to the planes, this peak would not be attributable to such intramolecular excitations, even if the low-lying excitation in TCNQF$_4^-$ appears in the region between 11000 and 15000 cm^{-1}.[15] The polarization direction of excitation corresponding to the conductivity peak is approximately parallel to the direction passing through the molecular centers of the donor and the acceptor. Therefore the conductivity peak at 11200 cm^{-1} can safely be attributed to the CT excitation between BTT and TCNQF$_4$,. The CT excitation band is asymmetric and tails to the high frequency side. A possible interpretation of the asymmetric band shape is superimposing of the progressional vibronic bands, since a more clear superimposed shoulder is sometimes observed for the CT band of the mixed-stack CT complexes such as (perylene)$_3$(TCNQ).[12]

The conductivity peak appearing at 23100 cm^{-1} in the //a and //c spectra would be attributed to the intramolecular excitation in TCNQF$_4$. Absorption spectrum of TCNQF$_4$ exhibits an intense peak at 22900 cm^{-1} in a solid and at 26000 cm^{-1} in a solution,[16] while BTT shows absorption peaks at positions higher than 30000 cm^{-1}.[1] Thus it is unlikely to attribute the conductivity peak to the intramolecular excitation in BTT. It is clear from the //a, //b, and //c spectra that the conductivity peak is almost polarized along the ac plane in which the molecular planes of TCNQF$_4$ lie. The conductivity peak located at 23100 cm^{-1} is therefore most likely assigned to the low-lying intramolecular excitation in TCNQF$_4$.

Degree of Charge Transfer

It is of great importance to know the degree of charge transfer from the donor to the acceptor in order to discuss the physical properties of (BTT)$_2$(TCNQF$_4$). The value of the degree of CT ρ from donor D to acceptor A may be related to the oscillator strength f by[17]

$$f = \frac{4\pi mc}{\hbar}\tilde{\nu}_{\mathrm{CT}}|R_{\mathrm{DA}}|^2\rho = 3.254\times10^{-5}\tilde{\nu}_{\mathrm{CT}}|R_{\mathrm{DA}}|^2\rho, \qquad (1)$$

where R_{DA} is the distance (Å) between the molecular centers of D and A and $\tilde{\nu}_{\mathrm{CT}}$ is the excitation energy of CT band in the cm^{-1} scale. The oscillator strength is given by[18]

$$f = \frac{4mc}{Ne^2}\int_{\tilde{\nu}_1}^{\tilde{\nu}_2}\sigma(\tilde{\nu})\mathrm{d}\tilde{\nu}\cos^2\theta, \qquad (2)$$

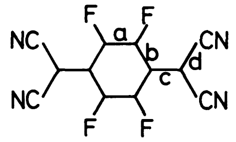
where N is the number of D–A pair per unit volume and θ is the angle between the light polarization and the transition dipole moment. By a numerical integration of the CT band in the conductivity spectrum, f is found to be 0.89. Thus ρ is estimated to be 0.21 from f using $\tilde{\nu}_{\mathrm{CT}}$=11200 cm^{-1} and R_{DA}=3.43 Å.

The degree of CT obtained is 0.21. This value strongly suggests that (BTT)$_2$(TCNQF$_4$) is not an ionic CT complex but a non-ionic (weakly ionized) CT complex. This finding is further checked by the comparison of bond distances of TCNQF$_4$ in (BTT)$_2$(TCNQF$_4$) with those of neutral TCNQF$_4$[19] and ionic complexes of TCNQF$_4$[20–22] summarized in Table 2. The bond distance c is most sensitive to the ionicity of TCNQF$_4$. As seen in Table 2, c of (BTT)$_2$(TCNQF$_4$) is close to that of neutral TCNQF$_4$. In general, however, bond distances are influenced by the molecular packing even if the molecule has the same ionicity. Kistenmacher et al.[23] proposed a way to determine the degree of CT for the crystal of TCNQ derivatives that consists of mixed stacks of alternating donors and the acceptors. The degree of CT ρ may be related to the ratio $\alpha=c/(b+d)$ by

$$\rho = \frac{\alpha_x - \alpha_0}{\alpha_1 - \alpha_0}, \qquad (3)$$

where α_0, α_1, and α_x are the ratios for TCNQ^0, TCNQ$^-$, and TCNQ^{x-} ($0<x<1$), respectively. We applied the relation to the TCNQF$_4$ complexes to estimate the degree of CT because the ratios obtained for TCNQF$_4$ and TCNQ are very close to each other (0.477 for TCNQF$_4^0$ and 0.476 for TCNQ^0; 0.498 for

Table 2. Comparison of Specific Bond Distances (Å) for the $TCNQF_4$ Molecules



	a/Å	b/Å	c/Å	d/Å	$\alpha=c/(b+d)$	Ref.
$(BTT)_2(TCNQF_4)$	1.338(18)	1.430(10)	1.369(18)	1.411(12)	0.482	This work
$TCNQF_4$	1.334(2)	1.437(4)	1.372(2)	1.437(4)	0.477	17
M_2P-$TCNQF_4$[a]	1.354(6)	1.414(4)	1.415(4)	1.430(6)	0.498	18
DBTTF-$TCNQF_4$[b]	1.351(7)	1.421(7)	1.412(7)	1.425(7)	0.496	19
NBP-$TCNQF_4$[c]	1.350(4)	1.410(4)	1.413(4)	1.419(5)	0.499	20

a) M_2P: *N,N′*-dimethylphenazinium. b) DBTTF: dibenzotetrathiafulvalene. c) NBP: *N*-butylphenazinium.

$TCNQF_4^-$ and 0.500 for $TCNQ^-$). By using Eq.3 and the ratio 0.482 obtained for $(BTT)_2(TCNQF_4)$, ρ is found to be 0.24. This value agrees reasonably with that estimated from the conductivity spectra.

Electric and Magnetic Properties

Although BTT and $TCNQF_4$ molecules are essentially in non-ionic states as shown in the preceding section, charge transport may occur passing through the crystal. We examined the temperature dependence of electrical conductivity of the single crystal. The conductivity at room temperature along the stacking direction is found to be 1.0×10^{-8} S cm^{-1} and the activation energy 0.27 eV (1 eV=1.602×10^{-19} J). The conductivity is smaller than that (6×10^{-8} S cm^{-1}) reported for the 1:1 complex by Cowan et al., for which the degree of CT is estimated to be 0.60 from the CN stretching frequency.[4)]

The activation energy is small for non-ionic CT complexes. The energy gap E_g (i.e., the energy required for the intrinsic carrier formation) for a CT complex can be estimated by the following relation;

$$E_g = I(\mathrm{D}) - A(\mathrm{A}) - \{P(\mathrm{D}^+) + P(\mathrm{A}^-)\} \qquad (4)$$

where I(D) is the ionization potential of the donor D and A(A) is the electron affinity of the acceptor A. $P(\mathrm{D}^+)$ and $P(\mathrm{A}^-)$ are the polarization energies associated with the formations of D^+ and A^- ions in the crystal, respectively. The ionization potential of BTT in the solid state is determined experimentally to be 4.9 eV.[24)] This value corresponds to $I(\mathrm{D})-P(\mathrm{D}^+)$. At present, the electron affinity and the polarization energy of $TCNQF_4$ have not been experimentally determined. The electron affinity A(A) of TCNQ is, however, estimated to be 2.8 eV.[25)] $P(\mathrm{A}^-)$ of TCNQ could reasonably be assumed to be 1.5—2 eV. If we put these figures into Eq.4, the energy gap is estimated to be in the range of 0.1—0.6 eV, into which the twice the activation energy (i.e., energy gap) actually observed for $(BTT)_2(TCNQF_4)$ falls. The agreement between estimated and observed values would be further improved by using the parameters proper to $TCNQF_4$. It is therefore suggested that the observed conductivity in $(BTT)_2(TCNQF_4)$ is due to the intrinsic carrier formation.

The suggestion mentioned above is further supported by the results of static magnetic susceptibility measurements. The paramagnetic susceptibility was evaluated by subtracting the diamagnetic contribution $\chi_d=-418\times10^{-6}$ emu mol^{-1} (1 emu mol^{-1}=4π cm^3 mol^{-1}) which is the sum of the diamagnetic susceptibilities of the components $\chi_d=-134\times10^{-6}$ emu mol^{-1} for $TCNQF_4$ and -142×10^{-6} emu mol^{-1} for BTT). The paramagnetic susceptibility follows the Curie-Weiss law over the entire temperature range with a small Weiss constant -2.9 K. The Curie constant 4.7×10^{-4} emu K mol^{-1} is very small and corresponds to only 0.05% of unpaired electrons per formula unit. Therefore, there are essentially no unpaired electrons carrying charges and spins in the ground state, while the degree of CT is estimated to be 0.21—0.24. Thus the charge carriers are produced intrinsically by the excitation across the energy gap.

Conclusion

Benzo[1,2-*c*:3,4-*c′*:5,6-*c″*]trithiophene (BTT) gives a weakly ionized 2:1 charge-transfer (CT) complex with tetrafluorotetracyanoquinodimethan ($TCNQF_4$). The crystal structure of $(BTT)_2(TCNQF_4)$ consists of stacking columns of alternating donor dyads and acceptor monads, extending along the b axis. The degree of CT from BTT to $TCNQF_4$ is estimated to be 0.21 from the conductivity spectra and 0.24 from the molecular geometry of $TCNQF_4$. Semiconducting charge transport passing through the crystal occurs with intrinsic carrier formation due to the CT interaction between BTT and $TCNQF_4$. Side-by-side sulfur-sulfur contacts shorter than the sum of the van der Waals radii are found between the BTT molecules as expected from its molecular structure. However, the effects of the contacts on the physical properties of the crystal remains unclear because of the non-ionic ground state. It is therefore of interest to search ionic complexes and salts of BTT in order to elucidate the transverse interchain interaction through the side-by-side contacts provided by the sulfur atoms at the periphery of the BTT molecule.

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2) TCNE: tetracyanoethylene. TCNQ: tetracyanoquinodimethan; 2.2′-(2,5-cyclohexadiene-1,4-diylidene)bis[propanedinitrile]. DDQ: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Chloranil: 2,3,5,6-tetrachloro-*p*-benzoquinone.

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