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Structural and Electrical Properties of Novel Molecular Conductors Based on Extended-TTF Donors BDT-TTP and I^- Anions

HengBo Cui, Takeo Otsuka, Akiko Kobayashi,* Yohji Misaki,† and Hayao Kobayashi††

Research Centre for Spectrochemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033

†Department of Molecular Engineering, Kyoto University, Yoshida, Kyoto 606-8501

††Institute for Molecular Science, Okazaki 444-8585

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With the aim of developing organic conductors with new types of molecular arrangements, some organic conductors composed of elongated π donors BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) and simple I^- anions were prepared by electrocystallization. The crystal of (BDT-TTP)$_3$I has a very unique three-dimensional donor arrangement, where six BDT-TTP molecules are crystallographically independent. Despite the three-dimensional intermolecular short S···S network, the examination of C=C bond lengths of six BDT-TTP molecules indicates an inhomogeneous charge distribution, which is unfavorable for the formation of metallic bands. The resistivity measurements showed the system to be a semiconductor with a very small activation energy. On the other hand, the needle-shaped crystal has β-type donor arrangement and 2 : 1 stoichiometry. The crystal of β-(BDT-TTP)$_2$I retains its metallic state down to 2 K. Though an open Fermi surface was obtained by tight-binding band calculation, the fairly strong two-dimensionality of the electronic structure was suggested.

The first organic superconductor, Bechgaard salt was reported in 1980;[1] it has exerted an extremely large influence on the development of organic conductors in the last two decades. Though some molecular metals consisting of single-component molecules were recently discovered,[2,3] almost all the molecular conductors currently studied are composed of more than two chemical species because the charge transfer between the molecules forming conduction band and the other chemical species had long been believed to be indispensable for the generation of the charge carriers. In the case of Bechgaard salt with the chemical composition of D_2X, the crystal consists of π donors (D) forming a conduction band and inorganic anions (X^-) generating hole carriers in the conduction band by extracting one electron from two D molecules. Consequently, the various types of molecular conductors can be developed by the suitable choice of π donors and inorganic anions. Since the donor molecules are responsible for the transport properties, the discovery of new types of donor arrangements such as β- and κ-type arrangements was of key importance to develop the field of organic conductors.[4–6] In this sense, the trials to obtain new types of molecular arrangements by the rare combination of the donor molecules such as BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) with elongated π system and small size anions such as halogen ions (X^-) might be interesting because BDT-TTP is a very good π donor to construct the organic conductors with stable metallic states.[7,8] Due to the elongated π donors and small anions, the number of the strong intermolecular contacts can be expected to increase between donor molecules. In order to reduce the Coulomb repulsion between the positively charged donor molecules, the multi-dimensional molecular conductors with new packing motif might be expected. Here we present the crystal structures and electrical properties of two kinds of BDT-TTP salts with I^- anions.

Though a number of studies have been made on the organic conductors with I_3^- anions, the reports on the systems with I^- anions are still very rare. This seems to be mainly due to the difficulty in the preparation of good crystals. The I^- ions tend to be easily oxidized into the I_x^- polyiodide (I^-) ion during electrochemical oxidation and to give the crystals with disordered anion sites, which prevents any further studies. One of the old famous examples of TTF complexes with I^- ions is TTF$_7$(I)$_n$ ($n \approx 5$) reported 25 years ago.[9–11] Since then, several compounds composed of TTF-like donors and I^- anions have been reported.[12–18]

Experimental

Synthesis. All the chemical procedures were performed under an inert atmosphere. The solvents were reagent grade and were freshly distilled. Black plate crystals of (BDT-TTP)$_3$I and black needle crystals of (BDT-TTP)$_2$I were grown by electrochemical oxidation from the mixed solution of 90% chlorobenzene and 10% ethanol (10 mL) containing BDT-TTP (1.5–2 mg) and tetrabutylammonium salt of I^- (30–40 mg) under an argon atmosphere at room temperature. Special H-shaped glass cells with electrodes of 1 mm diameter platinum wires were used. A constant current of 0.1 μA was supplied for 15–20 days.

Crystal Structure Determination. The crystal structures of (BDT-TTP)$_3$I and (BDT-TTP)$_2$I were determined on a RIGAKU MERCURY CCD X-ray system at room temperature. The crystal of (BDT-TTP)$_3$I with the size of $0.30 \times 0.10 \times 0.05$ mm^3 and that of (BDT-TTP)$_2$I with the size of $0.20 \times 0.05 \times 0.05$ mm^3 were

Table 1. Crystallographic Data of $(BDT\text{-}TTP)_3I$ and $(BDT\text{-}TTP)_2I$

	$(BDT\text{-}TTP)_3I$	$(BDT\text{-}TTP)_2I$
Formular	$C_{45}S_{36}H_{18}I_{1.5}$	$C_{20}S_{16}H_8I_1$
Formula weight	1903.15	888.15
Crystal System	$P\bar{1}$	$P\bar{1}$
Space Group	Triclinic	Triclinic
a/Å	10.218(3)	6.357(4)
b/Å	17.597(6)	6.946(4)
c/Å	19.423(7)	16.979(11)
α/°	72.398(12)	83.49(2)
β/°	74.917(13)	80.47(2)
γ/°	75.58(1)	79.61(2)
V/Å^3	3159.9(19)	725.5(8)
Z	2	1
ρ(calcd)/g cm^{-1}	2.001	2.035
μ(Mo Kα)/cm^{-1}	19.80	22.74
R	0.050	0.045
$Rw^{a)}$	0.058	0.053
GOF	0.92	1.08

a) $w = 1$

used. The structures were solved by direct methods (SIR97),[19] and expanded using Fourier techniques (DIRDIF99).[20] The non-hydrogen atoms were refined anisotropically. The full-matrix least-squares refinement on F was made on $(BDT\text{-}TTP)_3I$ based on 6580 reflections ($I > 3.00\ \sigma(I)$), which converged to $R = 0.050$, $Rw = 0.058$, GOF = 0.92. The structure refinement of $(BDT\text{-}TTP)_2I$ converged to $R = 0.045$, $Rw = 0.053$, GOF = 1.08 (see Table 1). All calculations were performed using the crystallographic software package Crystal Structure.[21,22] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 194313 and 194314.

Electrical Resistivity Measurements. The electrical resistivities were measured by the conventional four-probe method from room temperature to 2 K. Four gold wires (0.015 mm diameter) bonded to the crystals with conducting gold paste were used as current and voltage terminals.

Band Structure Calculation. The overlap integrals, tight-binding band structure and Femi surface of $(BDT\text{-}TTP)_2I$ were calculated on the basis of an extended Hückel approximation. Slater type atomic orbitals were used. The parameters of the atomic orbitals are the same as those used in $(BDT\text{-}TTP)_5\text{-}[(Ln(NO_3)_5)]$.[23] The exponent ζ and the ionization potential (Ryd) are: S 3s, 2.122, −1.47; S 3p, 1.827, −0.808; S 3d, 1.500, −0.4; C 2s, 1.625, −1.573; C2p, 1.625, −0.838; H 1s 1.0, −1.0.

Results and Discussion

Electrical Properties. The temperature dependences of resistivities of $(BDT\text{-}TTP)_3I$ and $(BDT\text{-}TTP)_2I$ are shown in Fig. 1. The temperature dependence of the resistivities of $(BDT\text{-}TTP)_3I$ showed the system to be semiconducting with a very small activation energy of 0.014 eV, while $(BDT\text{-}TTP)_2I$ retains the stable metallic state down to 2 K. The room-temperature conductivity of $(BDT\text{-}TTP)_3I$ was 0.4 S cm^{-1} and that of $(BDT\text{-}TTP)_2I$ was 206 S cm^{-1}.

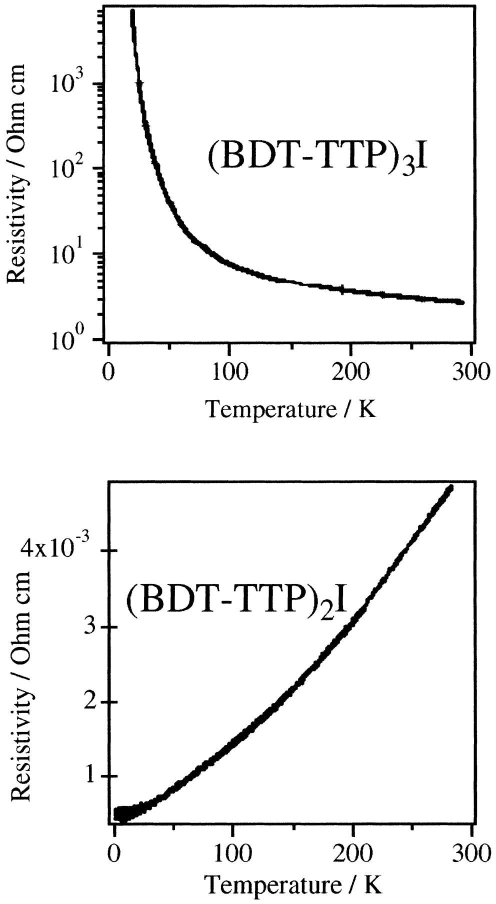

Fig. 1. Temperature dependence of the resistivities of $(BDT\text{-}TTP)_3I$ and $(BDT\text{-}TTP)_2I$.

Crystal Structure of $(BDT\text{-}TTP)_3I$ Salt. The atomic coordinates are listed in Table 2. The crystal structure of $(BDT\text{-}TTP)_3I$ is shown in Fig. 2. The atomic numbering scheme of the BDT-TTP is shown in Fig. 2(a). There were six crystallographically independent BDT-TTP molecules. The molecules A, B, C, B′, and A′ form a periodic unit of the BDT-TTP column along the *b* axis where the molecule A′ (B′) is related to A (B) by the inversion symmetry and molecule C is on the inversion center. These molecules are almost planar and are stacked face-to-face. The deviations of the atoms from the least-squares planes are within 0.01 Å. The dihedral angle between planes A and B is 2.22° and that of planes A and C is 1.57°. The interplanar distances are 3.353 Å (A···A′), 3.380 Å (A···B), and 3.400 Å (B···C). The molecules D and E are located between the BDT-TTP columns and are arranged side-by-side along the [−1,0,1] direction (see Fig. 2(b)). The I^- anions are located between the side-by-side array of the molecules D and E. The D and E molecules are almost perpendicular to the molecules A, B, and C: e.g., the dihedral angle between planes A and D is 84.6°, and that between planes A and E is 89.7°. The remaining molecule F is located on the inversion center between BDT-TTP pentads (see Fig. 2(c)). The molecular plane F is almost perpendicular to the planes D and E: the dihedral angle between planes D and F is 78.7°, and that between planes E and F is 85.7°. On the other hand, the dihedral angle between planes A and F is 66.7°. The S atoms of

Table 2. Atomic Parameters ($\times 10^4$) of $(BDT\text{-}TTP)_3I$

Atom	x	y	z	$B_{eq}/Å^2$	Atom	x	y	z	$B_{eq}/Å^2$
I(1)	5000	5000	5000	1.24(2)	C(4)	8411(11)	4185(6)	6825(6)	1.3(2)
I(2)	7590(1)	5110(1)	1359(1)	2.60(2)	C(5)	8765(11)	4219(6)	5474(6)	1.0(2)
S(1)	6068(3)	4559(2)	7835(2)	1.45(6)	C(6)	10026(11)	3941(7)	5650(6)	1.3(2)
S(2)	8826(3)	3948(2)	8215(2)	1.57(6)	C(7)	10411(11)	3983(7)	4295(6)	1.3(2)
S(3)	7371(3)	4459(2)	6161(2)	1.12(5)	C(8)	10967(11)	3922(6)	3605(6)	1.4(2)
S(4)	10160(3)	3847(2)	6545(1)	1.11(5)	C(9)	11370(10)	3951(8)	2232(7)	2.4(3)
S(5)	8626(3)	4305(2)	4580(1)	1.13(5)	C(10)	12592(12)	3688(7)	2397(6)	1.4(2)
S(6)	11419(3)	3711(2)	4972(1)	1.04(5)	C(11)	6266(13)	2516(7)	8305(6)	1.9(3)
S(7)	9970(3)	4177(2)	2927(2)	1.50(6)	C(12)	7462(12)	2243(7)	8522(6)	1.5(2)
S(8)	12731(3)	3597(2)	3298(2)	1.41(6)	C(13)	7976(11)	2243(7)	7146(6)	1.4(2)
S(9)	6209(3)	2621(2)	7397(1)	1.22(5)	C(14)	8570(11)	2153(6)	6457(6)	1.1(2)
S(10)	8906(3)	2022(2)	7843(1)	1.22(5)	C(15)	9123(10)	2137(6)	5100(6)	1.0(2)
S(11)	7644(3)	2366(2)	5756(1)	1.05(5)	C(16)	10338(11)	1901(6)	5323(6)	1.2(2)
S(12)	10364(3)	1830(2)	6227(1)	1.05(5)	C(17)	10898(10)	1901(6)	3973(6)	0.9(2)
S(13)	9100(3)	2228(2)	4194(1)	1.03(5)	C(18)	11561(11)	1815(6)	3288(6)	1.2(2)
S(14)	11823(3)	1725(2)	4664(1)	1.00(5)	C(19)	12225(11)	1764(7)	1930(6)	1.4(2)
S(15)	10706(3)	1983(2)	2563(1)	1.18(5)	C(20)	13431(10)	1540(7)	2152(6)	1.3(2)
S(16)	13359(3)	1518(2)	3068(2)	1.19(5)	C(21)	6262(11)	554(6)	8018(5)	1.0(2)
S(17)	6313(3)	590(2)	7113(1)	1.24(5)	C(22)	7439(12)	318(7)	8253(6)	1.7(2)
S(18)	8938(3)	44(2)	7638(1)	1.17(5)	C(23)	8099(9)	249(6)	6892(5)	0.7(2)
S(19)	7887(3)	316(2)	5517(1)	1.05(5)	C(24)	8771(10)	145(6)	6229(6)	1.0(2)
S(20)	10560(3)	−199(2)	6036(1)	0.98(5)	C(25)	10583(10)	−109(7)	5121(6)	1.2(2)
S(21)	13656(3)	2972(2)	6219(2)	1.24(5)	C(26)	13352(10)	3621(6)	6803(6)	0.8(2)
S(22)	12592(3)	2357(2)	7812(1)	1.36(5)	C(27)	12866(12)	3350(6)	7512(6)	1.4(2)
S(23)	13755(3)	1187(2)	5977(1)	1.08(5)	C(28)	13165(10)	2145(7)	6940(6)	1.1(2)
S(24)	12716(3)	600(2)	7601(1)	1.21(5)	C(29)	13207(10)	1406(7)	6863(6)	1.3(2)
S(25)	14001(3)	−532(2)	5797(1)	1.13(5)	C(30)	13623(10)	171(7)	6341(6)	1.3(2)
S(26)	12958(3)	−1108(2)	7429(1)	1.30(5)	C(31)	13139(10)	−95(6)	7065(5)	0.7(2)
S(27)	14370(3)	−2377(2)	5660(2)	1.40(5)	C(32)	13566(10)	−1335(6)	6562(6)	1.1(2)
S(28)	13331(3)	−2917(2)	7266(2)	1.56(6)	C(33)	13738(11)	−2101(8)	6505(6)	1.7(2)
S(29)	10669(3)	2839(2)	9565(2)	1.41(5)	C(34)	14214(11)	−3385(7)	6033(6)	1.4(2)
S(30)	9280(3)	2291(2)	11118(2)	1.38(6)	C(35)	13715(11)	−3634(7)	6752(7)	1.7(2)
S(31)	10811(3)	1061(2)	9325(1)	1.23(5)	C(36)	10120(10)	3539(7)	10096(8)	2.7(3)
S(32)	9534(3)	512(2)	10927(1)	1.19(5)	C(37)	9510(10)	3293(8)	10781(8)	2.8(3)
S(33)	3617(3)	−2198(2)	9376(1)	1.59(6)	C(38)	10015(10)	2044(6)	10278(5)	0.9(2)
S(34)	6222(3)	−2917(2)	9926(2)	1.53(6)	C(39)	10084(10)	1313(6)	10185(6)	1.0(2)
S(35)	3595(3)	−490(2)	9673(2)	1.36(5)	C(40)	9717(10)	−120(7)	10351(6)	1.5(2)
S(36)	6251(3)	−1196(2)	10213(2)	1.52(6)	C(41)	4449(11)	−3158(7)	9266(6)	1.4(2)
					C(42)	5619(12)	−3476(8)	9511(6)	1.8(3)
C(1)	6185(13)	4407(8)	8740(6)	2.1(3)	C(43)	4942(11)	−2053(7)	9723(6)	1.3(2)
C(2)	7435(12)	4125(7)	8915(6)	1.8(3)	C(44)	4941(11)	−1334(7)	9841(6)	1.4(2)
C(3)	7844(11)	4238(6)	7531(6)	1.2(2)	C(45)	5591(10)	−143(6)	10118(5)	0.9(2)

$$B_{eq} = 8/3\,\pi^2\,(U_{11}\,(aa^*)^2 + U_{22}\,(bb^*)^2 + U_{33}\,(cc^*)^2 + 2U_{12}\,(aa^*bb^*)\cos\gamma + 2U_{13}\,(aa^*cc^*)\cos\beta + 2U_{23}\,(bb^*cc^*)\cos\alpha)$$

BDT-TTP form a three-dimensional S···S network. There exist many intermolecular shortest S···S distances between adjacent BDT-TTP molecules. For example: S14···S24 = 3.394(3) Å, S12···S23 = 3.319(3) Å, S20···S25 = 3.345(3) Å etc.

As expected, $(BDT\text{-}TTP)_3I$ has the characteristic three-dimensional donor arrangement. However, the resistivity exhibiting a non-metallic behavior suggests the possibility that the excess charges in donor molecules tend to be localized inhomogeneously. In order to examine this possibility, the bond lengths of BDT-TTP molecules in $(BDT\text{-}TTP)_3I$ were compared with those of neutral BDT-TTP molecule[24] and $BDT\text{-}TTP^{1/2+}$ semication[25] (see Table 3). Since the HOMO has nodes on all S–C bonds, the S–C bonds are expected to become shorter in the charged states. In contrast, the C=C bonds are expected to become longer than the corresponding bonds of neutral molecule due to the bonding character of HOMO on the C=C bonds. Though the changes in S-C bonds were not large enough for discussion, the bonds C(5)=C(6), C(3)=C(4), and C(7)=C(8) allowed us to estimate the degree of charge transfer. The short C=C bond lengths of molecules C and E suggest the neutral state of the molecules. On the other hand, the C=C bond lengths of the other molecules (A, B, D, F) are approximately equal to those of the donor molecule in $(BDT\text{-}TTP)_2I$, indicating the semi-cation states of these molecules. Such results are consistent with the requirement of the charge neutralization of the crystal $((D^{1/2+})_4(D^0)_2(I^-)_2)$. Since the

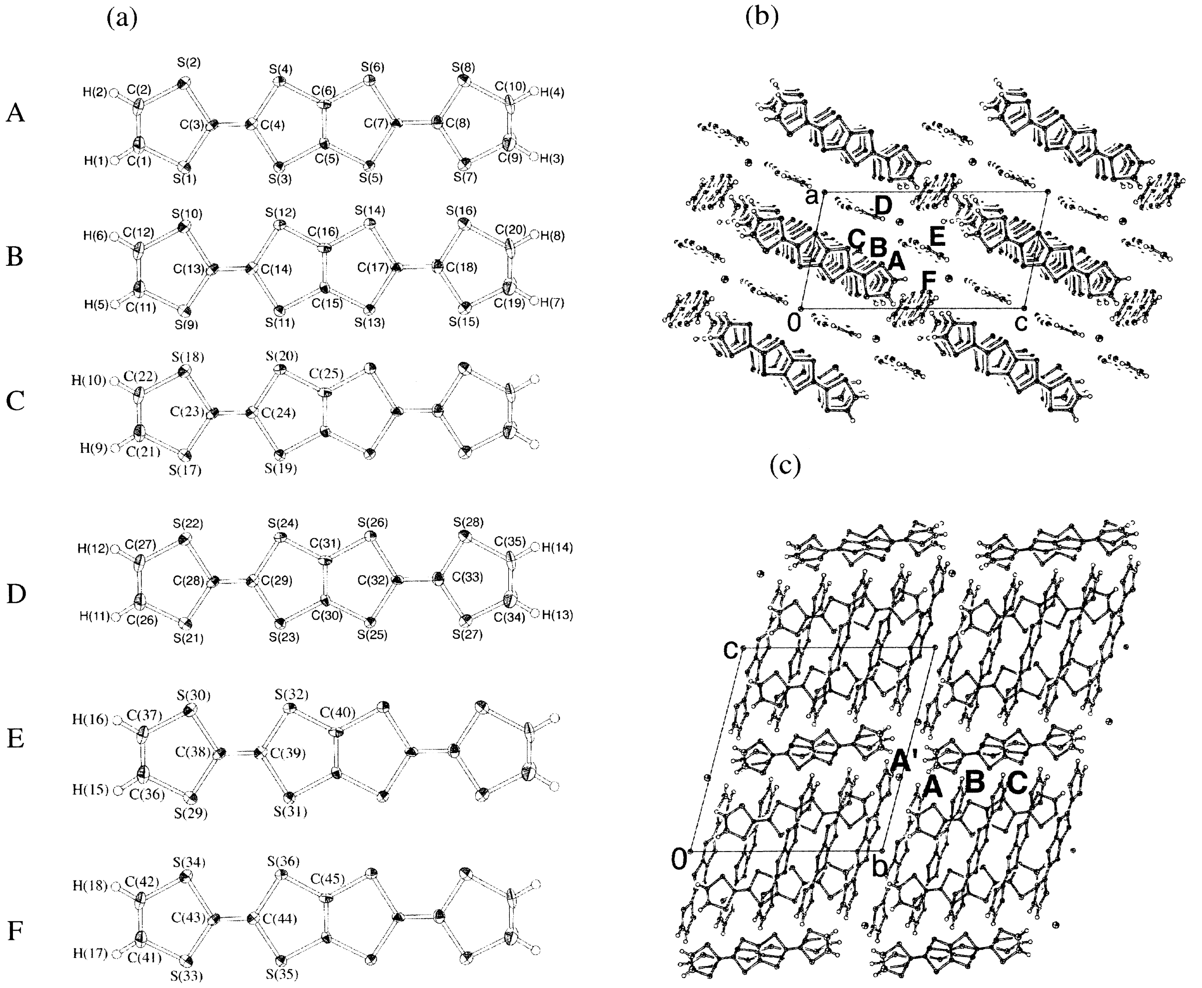

Fig. 2. The structure of $(BDT\text{-}TTP)_3I$ salt. (a) The atomic numbering scheme of BDT-TTP. (b) The crystal structure projected along the *a* axis. (c) The crystal structure projected along the *b* axis.

Table 3. Intramolecular C=C Bond Length (Å) of BDT-TTP

Compound	$l_a = L_{C5\text{-}C6}$	$l_b = (L_{C3\text{-}C4} + L_{C7\text{-}C8})/2$	$l_c = (L_{C1\text{-}C2} + L_{C9\text{-}C10})/2$
BDT-TTP[a]	1.327(5)	1.336(5)	1.332(6)
$(BDT\text{-}TTP)_2ClO_4$[b]	1.35(2)	1.36(2)	1.35(2)
$(BDT\text{-}TTP)_2I$	1.343(13)	1.36(2)	1.32(2)
$(BDT\text{-}TTP)_3I$ salt			
A	1.35(2)	1.35(2)	1.32(2)
B	1.35(2)	1.36(1)	1.33(2)
C	1.32(2)	1.34(1)	1.32(2)
D	1.34(1)	1.35(2)	1.33(2)
E	1.32(2)	1.33(2)	1.30(2)
F	1.33(2)	1.35(1)	1.33(2)

a) The bond length of neutral molecule are taken from Ref. 24.
b) The bond length of semi-cation molecule are taken from Ref. 25.

neutral molecules will tend to terminate the current flow, the inhomegeneous charge distribution will be responsible for the non-metallic properties of $(BDP\text{-}TTP)_3I$.

Crystal Structure of $(BDT\text{-}TTP)_2I$ Salt. The atomic coordinates and the equivalent isotropic thermal parameters of $(BDT\text{-}TTP)_2I$ are listed in Table 4. Figure 3 shows the crystal structure of $(BDT\text{-}TTP)_2I$, which has a typical β-type donor arrangement.[5] The atomic numbering scheme of BDT-TTP is shown in Fig. 3(a). BDT-TTP molecule is almost planar except for one terminal group: the large atomic deviations from least-squares plane are 0.164 Å (C9) and 0.118 Å (C10). The interplanar distance along the dyadic column of BDT-TTP is

Table 4. Atomic Coordinates ($\times 10^4$) and $B_{\mathrm{iso}}/B_{\mathrm{eq}}$ of (BDT-TTP)$_2$I

Atom	*x*	*y*	*z*	$B_{\mathrm{eq}}/\text{Å}^2$
I(1)	0	0	0	4.57(4)
S(1)	8022(5)	1424(5)	7099(2)	2.37(8)
S(2)	3309(5)	2136(5)	7543(2)	2.33(7)
S(3)	7520(4)	1964(5)	5218(2)	1.95(7)
S(4)	2703(4)	2730(5)	5668(2)	1.91(7)
S(5)	6991(5)	2606(5)	3441(2)	1.98(7)
S(6)	2190(4)	3383(5)	3898(2)	2.02(7)
S(7)	6408(5)	3016(5)	1579(2)	2.58(8)
S(8)	1679(5)	3874(5)	2011(2)	2.41(8)
C(1)	6980(20)	1320(20)	8122(7)	2.4(3)
C(2)	4820(20)	1610(20)	8321(8)	2.9(3)
C(3)	5490(20)	1960(20)	6770(6)	1.4(2)
C(4)	5290(20)	2200(20)	5982(7)	1.7(3)
C(5)	5920(20)	2500(20)	4446(6)	1.3(2)
C(6)	3760(20)	2830(20)	4661(6)	1.4(3)
C(7)	4390(20)	3140(20)	3124(6)	1.7(3)
C(8)	4210(20)	3350(20)	2332(7)	2.1(3)
C(9)	4810(20)	3270(20)	805(8)	3.1(3)
C(10)	2730(20)	3670(20)	1009(8)	3.3(3)

$$B_{\mathrm{eq}} = 8/3\,\pi^2\,(U_{11}\,(aa^*)^2 + U_{22}\,(bb^*)^2 + U_{33}\,(cc^*)^2 + 2U_{12}\,(aa^*bb^*)\cos\gamma + 2U_{13}\,(aa^*cc^*)\cos\beta + 2U_{23}\,(bb^*cc^*)\cos\alpha)$$

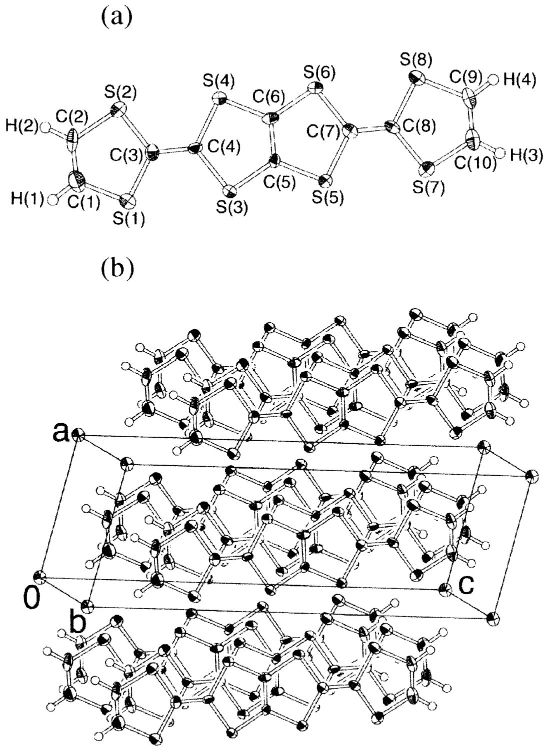

Fig. 3. The structure of β-(BDT-TTP)$_2$I salt. (a) The atomic numbering scheme of BDT-TTP. (b) The crystal structure projected along the *b* axis.

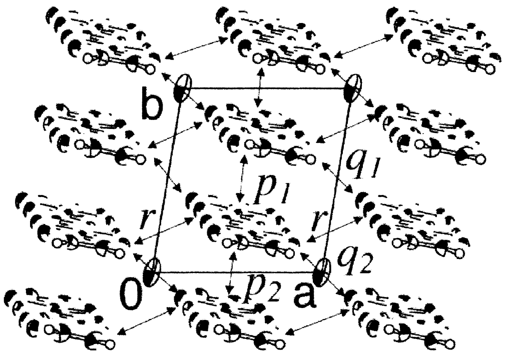

Fig. 4. The donor arrangement of β-(BDT-TTP)$_2$I viewed along the long axis of BDT-TTP.

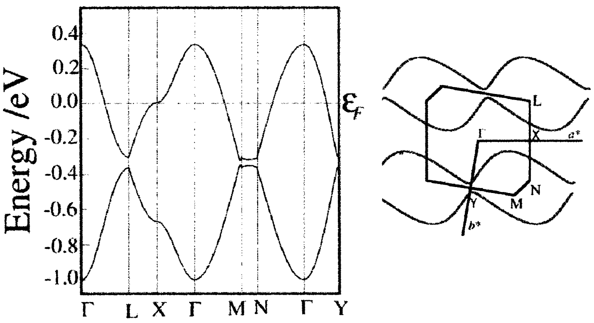

Fig. 5. The band structure and Femi surface of β-(BDT-TTP)$_2$I calculated using tight-binding approximation.

3.503 Å and 3.440 Å. The I^- anion is on the origin of the unit cell. Since every BDT-TTP molecule is crystallographically equivalent, BDT-TTP must have a formal charge of +1/2. The C=C bond lengths listed in Table 3 suggest that the terminal C=C bond length hardly reflects the formal charge of the molecule. This is probably due to the fact that the bond lengths of the terminal part of large molecule are apparently shortened by the librational motion of the molecule. Except for the terminal bond, the C=C bond lengths of (BDT-TTP)$_2$I are approximately equal to those of (BDT-TTP)$_2$ClO$_4$.

Band Structure of (BDT-TTP)$_2$I Salt. The overlap integrals of the highest occupied molecular orbital of BDT-TTP of (BDT-TTP)$_2$I were calculated (see Fig. 4): p1 = 25.4×10^{-3}, p2 = 24.8×10^{-3} in the stack, $r = -0.08 \times 10^{-3}$, q1 = 9.4×10^{-3}, q2 = 7.1×10^{-3}. The intra-stack overlaps p1 and p2 are of course larger than the other interactions but interstack interactions are also fairly strong. Therefore, as shown in Fig. 5, the tight-binding energy band calculation gave an open but nearly two-dimensionally closed Femi surface.

The band structure examination was not made on (BDT-TTP)$_3$I because the charge localization was suggested by the examination of the bond lengths of BDT-TTP molecules, which means that the simple tight-binding band examination requires more information on the site potential of each donor site.

Conclusion

Two types of crystals of BDT-TTP conductors containing I^- anions were prepared by electrocrystallization. The crystal structure analysis of the plate crystal of (BDT-TTP)$_3$I revealed the characteristic three-dimensional donor arrangement, where six BDT-TTP molecules are crystallographically independent. Despite a three-dimensional intermolecular short S···S network, the examination of bond lengths showed an inhomogeneous charge distribution on BDT-TTP molecules, which is unfavorable for the realization of a metallic state. In fact, the resistivity measurements revealed the system to be a semiconductor with a very small activation energy. The other needle-shaped crystal of $(\text{BDT-TTP})_2\text{I}$ has a β-type donor arrangement and retained metallic behavior down to 2 K. Though tight-binding band calculations gave an open Fermi surface, the fairly strong two-dimensionality of the electronic structure was suggested.

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