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THE CRYSTAL STRUCTURE AND ELECTRICAL RESISTIVITY OF $(BPDT\text{-}TTF)_2I_3$

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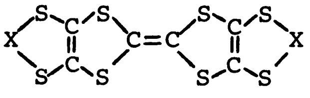
The crystal of $(BPDT\text{-}TTF)_2I_3$ belongs to triclinic system with the lattice constants of a=16.350(4), b=9.246(3), c=6.843(2) Å, α=111.11(2), β=93.21(2), γ=91.39(2)°. The structure is isomorphic with the organic superconductor, β-$(BEDT\text{-}TTF)_2I_3$. The resistivity decreases with increasing the pressure and reaches 0.05 Ω cm at 10 kbar, though $(BPDT\text{-}TTF)_2I_3$ remains semiconductive up to at least 10 kbar.

Recently Yagubskii et al. have found the superconducitvity of β-$(BEDT\text{-}TTF)_2I_3$ at ambient pressure (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene).1) Unlike the first organic superconductors $(TMTSF)_2X$ ($X=ClO_4$, PF_6···), which have one-dimensional(1-D) bands along the stacking axes of the TMTSF molecules,2) the examination of the intermolecular overlap integrals of the highest occupied molecular orbital (HOMO) of BEDT-TTF has revealed the 2-D character of the conduction band of β-$(BEDT\text{-}TTF)_2I_3$. The simple tight-binding approximation gave a 2-D closed Fermi-surface.3)

We have pointed out that the transverse intermolecular interaction is important in the BEDT-TTF compounds.4) Although the HOMO has pπ character and is considered to be weakly dependent on the group X, the mode of molecular arrangement is strongly dependent on it.4-6) Therefore, the intermolecular interaction may be controlled to some extent by changing X.


; $X=C_2H_4$(BEDT-TTF), C_3H_6(BPDT-TTF), CH_2(BMDT-TTF)

Crystals of $(BPDT\text{-}TTF)_2I_3$ were electrochemically synthesized as black plates in a 1,1,2-trichloroethane solution of BPDT-TTF (=bis(propylenedithio)tetrathiafulvalene) and $(n\text{-}C_4H_9)_4NI_3$. The crystal data are: $(C_{12}H_{12}S_8)_2I_3$, triclinic, $P\bar{1}$, a=16.350(4), b=9.246(3), c=6.843(2) Å, α=111.11(2), β=93.21(2), γ=91.39(2)°, V=962.3(4) $Å^3$, Z=1. Intensities were measured on a Rigaku automated diffractometer with Mo Kα radiation. The number of the independent reflections ($2\theta<60°$, $|F_o|>3\sigma(|F_o|)$) is 4650. The structure was solved by the heavy atom method. The final R value was 0.053. The positional parameters are listed in Table 1.

The crystal structure is shown in Fig. 1. The unit cell contains two BPDT-TTF molecules which are interrelated by the inversion symmetry. Although the lattice constants a, b, and c are slightly larger than those of β-$(BEDT\text{-}TTF)_2I_3$, owing to the bulky propylene groups, $(BPDT\text{-}TTF)_2I_3$ is almost isomorphous with β-$(BEDT\text{-}TTF)_2I_3$.[3,7] The BPDT-TTF molecules are stacked along [011]. The mode of molecular stacking is shown in Fig. 2. A similar stacking mode of BPDT-TTF has been found in $(BPDT\text{-}TTF)_3(PF_6)_2$.[5] Usually, the stacking axis is parallel to the direction of the highest electrical conductivity. However, the anisotropy of the intermolecular overlap integrals of the HOMO of BEDT-TTF in β-$(BEDT\text{-}TTF)_2I_3$ showed that the intermolecular interactions along the stacking direction [011] are not necessarily larger than those along [010].[3] This is due to the long intermolecular S···S distance along [011] (3.75 Å (A···B); 4.03 Å (A···C) (Fig. 3)).[3] Contrary to β-$(BEDT\text{-}TTF)_2I_3$, $(BPDT\text{-}TTF)_2I_3$ has short intermolecular contacts along [011] (Fig. 2). In addition, short S···S contacts are also observed along the transverse direction; the shortest S···S distance is 3.44 Å.

Table 1. Fractional atomic coordinates. The e.s.d.'s are given in parentheses

	x(x10^5)	y(x10^4)	z(x10^4)
I1	0	0	0
I2	1190(4)	7666(1)	5832(1)
S1	53944(10)	2654(2)	5299(3)
S2	55790(10)	1566(2)	8808(3)
S3	38183(10)	4568(2)	7388(3)
S4	40334(10)	3488(2)	873(3)
S5	65260(11)	496(2)	2665(3)
S6	67875(12)	-753(2)	6898(3)
S7	23257(12)	6278(2)	8943(3)
S8	26052(12)	5014(2)	3035(3)
C1	50279(36)	2659(7)	7637(10)
C2	43859(37)	3492(7)	8547(10)
C3	61069(36)	1230(7)	5091(10)
C4	61905(36)	735(7)	6718(10)
C5	31062(38)	5109(7)	9284(10)
C6	32060(36)	4600(7)	895(10)
C7	76380(44)	650(9)	3286(13)
C8	79639(46)	-564(9)	4088(14)
C9	78183(44)	-253(9)	6372(13)
C10	14168(48)	5019(10)	8659(15)
C11	11222(50)	4941(12)	679(18)
C12	16234(49)	4068(11)	1769(16)

Although the intermolecular contacts along [011] in $(BPDT\text{-}TTF)_2I_3$ are much closer than those in the zero-pressure superconductor, β-$(BEDT\text{-}TTF)_2I_3$, $(BPDT\text{-}TTF)_2I_3$ is less conductive. The anisotropy of the electrical resistivities in the (100) plane was measured over the temperature range 300-180 K (Fig. 4). The resistivity along the c axis ($\rho(R.T.)_{//c}$) is about 0.5 Ω cm. The measurements were made also under high pressure.[8] The room-temperature resistivity along [011] ($\rho_{//(b+c)}$) is 0.6 Ω cm at ambient pressure and that along the direction perpendicular to [011] ($\rho_{\perp(b+c)}$) is 3.5 Ω cm. The anisotropy and the

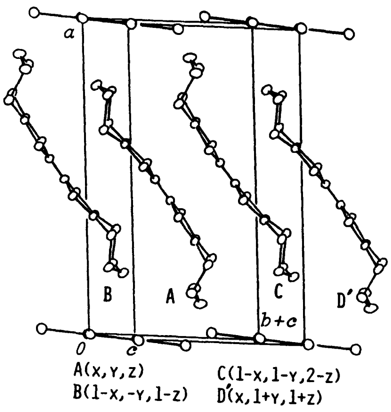
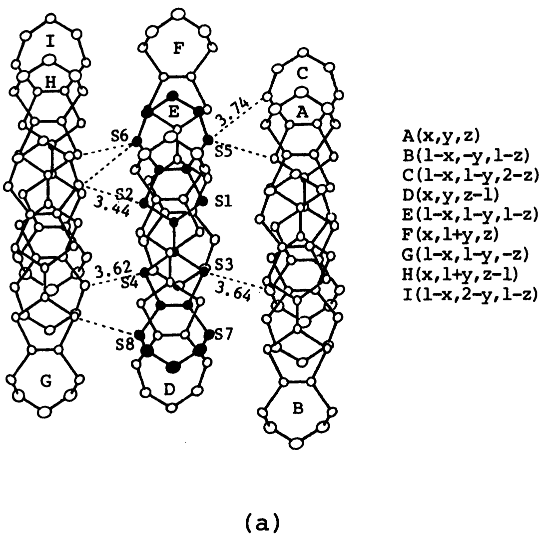
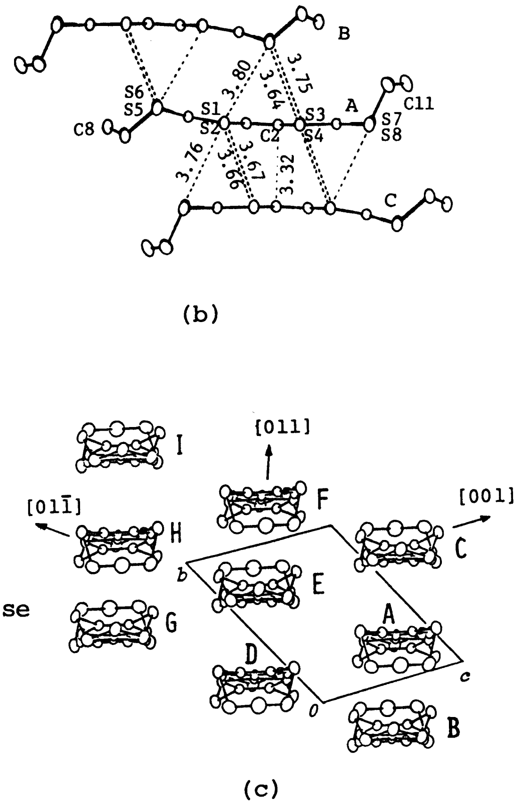


Fig. 1. Crystal structure of $(BPDT\text{-}TTF)_2I_3$.



(a)



(b)

(c)

Fig. 2. Molecular arrangement of BPDT-TTF. (a) Mode of molecular overlapping and transverse S···S contacts. (b) Intermolecular S···S contacts(<3.8 Å) and the shortest C···C distance(3.32 Å) along [011]. (c) Molecular arrangement in the (100) plane.

activation energy decrease with increasing the pressure (Fig. 5). The resistivity also decreases with increasing the pressure. The room-temperature value of $\rho_{//(b+c)}$ at 10 kbar (10^9 Pa) is about 0.05 Ω cm, which is the same order of the resistivity of β-(BEDT-TTF)$_2$I$_3$ (0.03 Ω cm). These facts suggest the possibility that (BPDT-TTF)$_2$I$_3$ becomes a 2-D metal at the pressure much higher than 10 kbar.

In conclusion, despite of the apparent resemblance of the crystal structures between (BPDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$, their conductive properties show a marked difference. (BPDT-TTF)$_2$I$_3$ remains semiconductive up to at least 10 kbar, indicating that the system with close intermolecular contacts along the stacking axis is not always highly conductive. The examination of the anisotropy of the intermolecular interactions will be required to interpret the conduction properties of (BPDT-TTF)$_2$I$_3$.

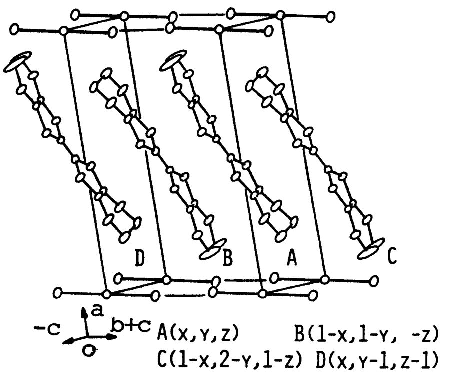


Fig. 3. Crystal structure of β-(BEDT-TTF)$_2$I$_3$.[3,7]

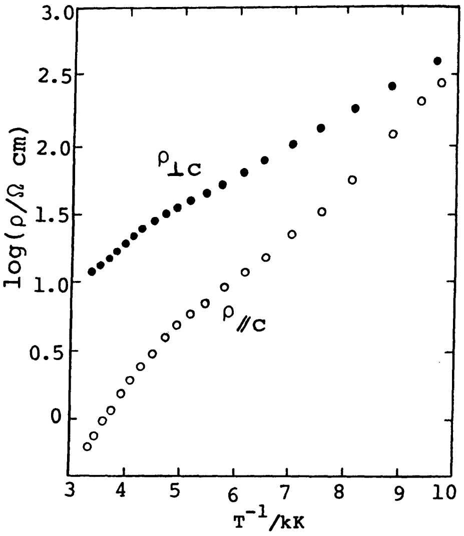


Fig. 4. Electrical resistivities of $(BPDT-TTF)_3I_2$ (at ambient pressure).

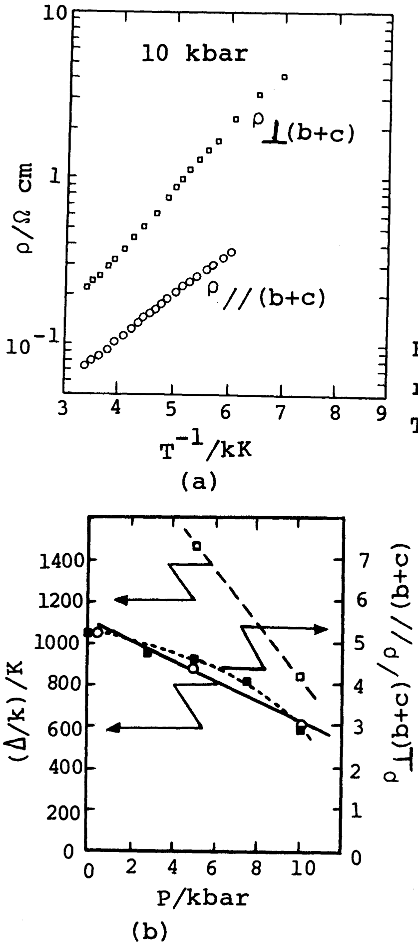


Fig. 5. (a) Electrical resistivities of $(BPDT-TTF)_2I_3$ at ca. 10 kbar

(b) Pressure dependence of the activation energy (Δ/K) and the anisotropy of the resistivity ($\rho_{\perp(b+c)}/\rho_{//(b+c)}$). The activation energy of $\rho_{//(b+c)}$ is denoted by circle and that of $\rho_{\perp(b+c)}$ is denoted by open square.

References

1) E. B. Yagubskii, I. F. Schegolev, V. N. Laukin, P. A. Kononovich, M. V. Kartosovnic, A. V. Zvarykina, and L. I. Buravov, Pis'ma Zh. Eksp. Teor. Fiz., 39, 12 (1984).
2) P. M. Grant, Phys. Rev. Lett., 50, 1006 (1983); M. H. Wangho, W. M. Walsh, Jr., R. C. Haddon, and F. Wudl, Solid State Commun., 43, 637 (1982); T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 1982, 1923.
3) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett., in press.
4) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, Chem. Lett., 1983, 581; ibid., 1983, 759; ibid., 1984, 179; H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, J. Am. Chem. Soc., 105, 207 (1983).
5) R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 1984, 781.
6) R. Kato, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 1984, 993.
7) V. F. Kaminskii, T. G. Prokhoroea, R. P. Shivaeva, and E. B. Yagubskii, Pis'ma Zh. Eksp. Teor. Fiz., 39, 15 (1984).
8) Details of the high pressure cell will be reported elsewhere.

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