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THE CRYSTAL AND ELECTRONIC STRUCTURES OF BEDT-TTF$_2$I$_2$Br

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The crystal structure of BEDT-TTF$_2$I$_2$Br is isomorphous to the well-known superconductor, β-BEDT-TTF$_2$I$_3$. The suppression of the superconductivity in BEDT-TTF$_2$I$_2$Br down to at least 0.5 K, will be ascribed to the orientational disorder of the I$_2$Br anions. Examination of the intermolecular overlap integrals indicates that the system has a two-dimensional closed Fermi surface.

The recent report on a new superconducting phase of β-BEDT-TTF$_2$I$_3$ with extraordinarily high transition temperature ($T_c \approx 8$ K at 1.3×10^8 Pa)$^{1)}$ compared with those of organic superconductors ever known is very interesting because the pressure of 1.3×10^8 Pa is considered to be too small to produce any large change of the molecular arrangement of BEDT-TTF. Besides this report, somewhat ambiguous but similar findings concerning the high T_c organic superconductors have been also made (β-BEDT-TTF$_2$I$_3$,$^{2)}$ β-BEDT-TTF$_2$IBr$_2$$^{3)}$). These reports suggest that the superconducting transition temperature of the BEDT-TTF polyhalide system is very sensitive to the condition of the measurements.

In this report, the crystal and electronic structure of BEDT-TTF$_2$I$_2$Br will be presented. The room-temperature conductivity of this salt is about 20 S cm^{-1}, comparable to that of β-BEDT-TTF$_2$I$_3$.$^{4)}$ However, unlike the I$_3$ and IBr$_2$ compounds, the I$_2$Br salt does not show superconducting behavior down to at least 0.5 K.$^{4)}$ In addition, the temperature dependence of the resistivity is weaker than those of the other polyhalide systems (ρ(300 K)/ρ(4.2 K)=250(I$_2$Br), 1250(IBr$_2$), 700(I$_3$)).$^{4)}$

The crystals of BEDT-TTF$_2$I$_2$Br were obtained electrochemically. The unit cell dimensions determined by a Rigaku automated diffactometer showed that BEDT-TTF$_2$-I$_2$Br is isomorphous to β-BEDT-TTF$_2$I$_3$ and β-BEDT-TTF$_2$IBr$_2$. The crystal data are: (C$_{10}$H$_8$S$_8$)$_2$I$_2$Br, M.W.=1103.1, triclinic, $P\bar{1}$, a=15.178(5), b=9.026(2), c=6.611(2) Å, α=110.12(2), β=95.26(2), γ=94.11(2)°, V=841.6(4) Å^3, Z=1. The unit cell volume is intermediate between those of the I$_3$(853 Å^3), and IBr$_2$(829 Å^3)salts.$^{5,6)}$ The statistical analysis of the intensity distribution indicates that the crystal structure has an inversion symmetry. By tentatively assuming the centrosymmetric structure of I_2Br anion (i.e. I-Br-I), the structure was refined anisotropically. But the R-factor obtained was fairly large (R=0.124). The temperature factor of the central Br atom became too small compared with that of I atom. Then the noncentrosymmetric molecular structure of I_2Br (I-I-Br) was assumed. Since the I_2Br anion is located on the origin of the unit cell, the orientation of the $(I\text{-}I\text{-}Br)^-$ anion must be randomly disordered. The block-diaginal least-squares refinement was performed successfully. Considering the positional disorder of the heavy halogen atoms, the R-value of 0.073 is fairly satisfactory. The final atomic parameters are listed in Table 1. The crystal structure is shown in Fig. 1.

Besides the positional disorder of the anions, the structure of BEDT-TTF_2I_2Br is quite similar to that of β-BEDT-TTF_2I_3. The non-centrosymmetric structure of I_2Br has been found in CsI_2Br.[7] Based on the fact that the I-I bond length (2.78 Å) is longer than I-Br(2.91 Å), the negative charge in I_2Br^- has been considered to be distributed mainly on Br atom. This asymmetry will produce the random potential on BEDT-TTF sites, which is consistent with the relatively large residual resistivity of the I_2Br salt. The bond length of I-X(X=(I+Br)/2), 2.811 Å is almost equal to the mean value of the I-I (2.904 Å(β-BEDT-TTF_2I_3)) and I-Br (2.702 Å(β-BEDT-TTF_2IBr_2)) distances.

The bond lengths and angles of BEDT-TTF are shown in Fig. 2. The bond lengths are intermediate between those of the corresponding bonds of the neutral (BEDT-TTF^0) and monocation(BEDT-TTF^+) molecules. The molecular arrangement of BEDT-TTFs is shown in Figs. 3 and 4. Although the BEDT-TTF molecules appear to stack along [011], there is no intermolecular S···S contact shorter than the v. d. Waals distance of S···S(3.70 Å). Contrary to this, there are many interstack short contacts. The intermolecular overlap integrals of the highest occupied

Table 1. Atomic coordinates ($\times 10^4$) of BEDT-TTF_2I_2Br

	X	Y	Z	$B_{eq}/Å^2$
I	0	0	0	4.3
IBr	141(1)	7470(1)	6153(2)	5.6
S(1)	4480(1)	7394(3)	4640(4)	3.2
S(2)	4287(1)	8537(3)	992(4)	3.3
S(3)	6205(1)	5701(3)	2809(4)	3.0
S(4)	5993(1)	6880(3)	-816(4)	3.0
S(5)	2870(2)	8624(3)	6439(4)	4.4
S(6)	2659(2)	10036(4)	2129(5)	4.7
S(7)	7964(2)	4619(3)	1975(4)	3.8
S(8)	7703(2)	6038(3)	-2361(4)	3.8
C(1)	4887(5)	7464(10)	2279(14)	2.6
C(2)	5586(5)	6746(10)	1525(14)	2.4
C(3)	3572(8)	8409(10)	4423(14)	2.7
C(4)	3471(5)	8947(10)	2758(14)	2.6
C(5)	7075(5)	5503(10)	1189(14)	2.3
C(6)	6972(5)	6030(10)	-491(13)	2.5
C(7)	2314(8)	10265(14)	6304(18)	4.7
C(8)	1941(8)	10203(16)	4170(20)	5.2
C(9)	8770(7)	5015(22)	339(24)	7.5
C(10)	8485(9)	4812(21)	-1833(24)	6.9

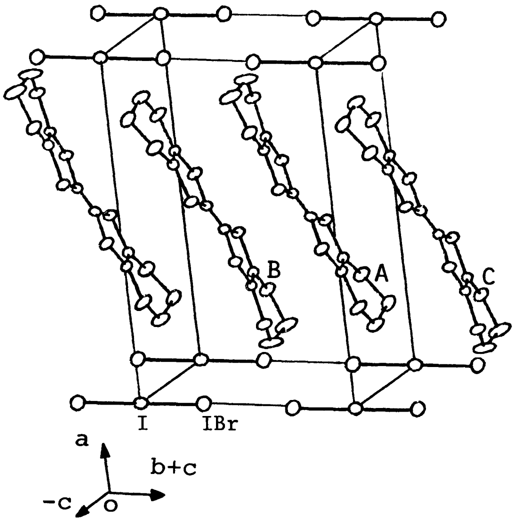

Fig. 1. Crystal structure of BEDT-TTF_2I_2Br.

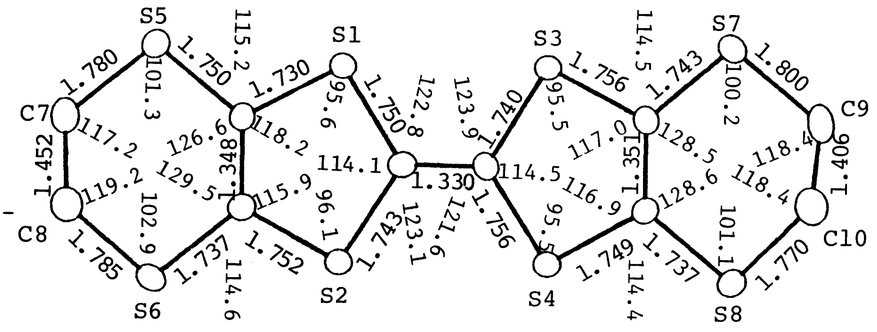

Fig. 2. Bond lengths and angles of BEDT-TTF. The standard deviations of the bond lengths are 0.009-0.025 Å and those of bond angles are 0.4-1.5°.

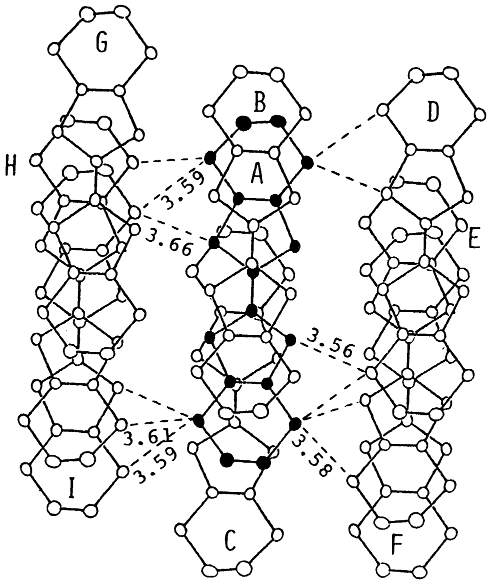

Fig. 3. Intermolecular overlaps and short S···S contacts of BEDT-TTF.

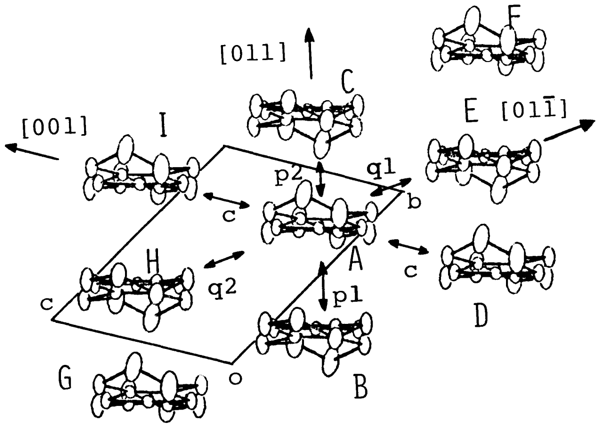

Fig. 4. Intermolecular interactions (see Table 2).

molecular orbital (HOMO) of BEDT-TTFs are given in Table 2. These values are almost equal to those of β-BEDT-TTF_2I_3 salt.[7] Since there is no significant intermolecular interaction along the a axis, the electronic structure becomes two-dimensional(2-D). Using the approximate relation of t=-ES (S is the intermolecular overlap integral of HOMO and E is a constant of the order of the energy of HOMO (∿10 eV)),[9] the simple tight-binding band was calculated.[10]

$$E(k)=2t_c\cos\mathbf{kc} \pm D^{1/2}$$

$$D=[(t_{p1}+t_{p2})\cos(\mathbf{kb}+\mathbf{kc})/2 + (t_{q1}+t_{q2})\cos(\mathbf{kb}-\mathbf{kc})/2]^2 + [(t_{p1}-t_{p2})\sin(\mathbf{kb}+\mathbf{kc})/2 - (t_{q1}-t_{q2})\sin(\mathbf{kb}-\mathbf{kc})/2]^2,$$

where t_c, t_{p1}, t_{p2}, t_{q1}, and t_{q2} are the transfer integrals. The 2-D closed Fermi surface almost identical to that of β-BEDT-TTF_2I_3[7] was obtained (Fig. 5).

As described before, despite of the close resemblance of the molecular arrangements and electronic structures between the polyhalide anion salts of BEDT-TTF, the superconducting state of BEDT-TTF_2I_2Br is suppressed down to at least 0.5 K. The largest difference between the supeerconducting salts (I_3, IBr_2) and nonsuperconducting salt (I_2Br) can be found in the orderness of the polyhalide anions. The random potential due to the positional disorder of I_2Br appears to play an important role to suppress the superconducting transition.

Table 2. Overlap integrals of HOMO in BEDT-TTF$_2$I$_2$Br. The values in the parentheses are those of β-BEDT-TTF$_2$I$_3$.

	Direction		10^{-3} S	
A - B	p1	[011]	-23.9	(-24.5)
A - C	p2	[100]	-8.9	(-8.4)
A - E	q1	[011]	-12.5	(-12.7)
A - H	q2	[011]	-6.7	(-6.8)
A - D, A - I	c	[001]	-5.2	(-5.0)

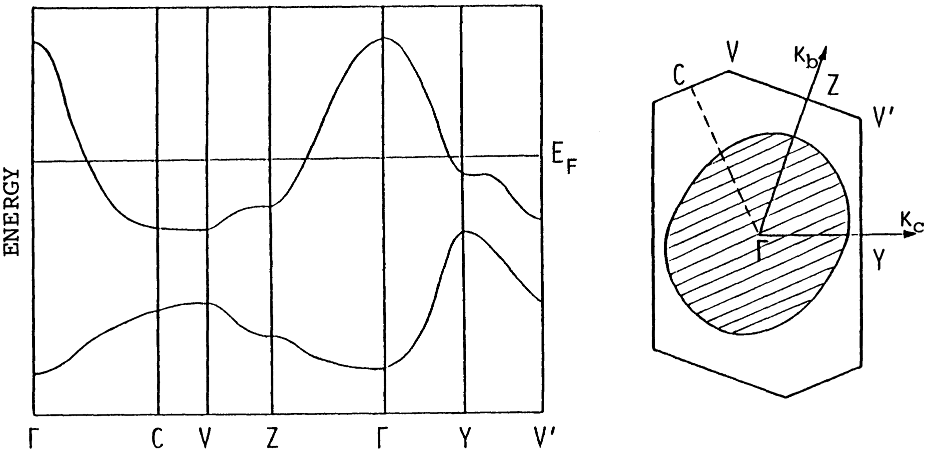

Fig. 5. The energy band structure and the Fermi surface of BEDT-TTF$_2$I$_2$Br. Energy is in arbitrary units. The shaded region indicates hole-like part.

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5) The unit cell adopted in this report is identical to that adopted by T. Mori et al. in the analysis of β-BEDT-TTF$_2$I$_3$$^{7)}$ but is not identical to those by Kamminskii et al.$^{11)}$ and Leung et al.$^{12)}$
6) The volume of β-BEDT-TTF$_2$I$_2$Br determined by T. J. Emge et al. , whose paper (Inorg$_{8\,3}$Chem., 24, 1738 (1985)) appeared after submission of this paper, is 842.3 A^{3} at 298 K.
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