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BAND STRUCTURES OF TWO TYPES OF (BEDT-TTF)$_2$I$_3$

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On the basis of the extended Hückel molecular orbital calculation, the intermolecular overlaps of the highest occupied molecular orbitals are calculated for α-(BEDT-TTF)$_2$I$_3$ reported by Bender et al., and for superconducting β-(BEDT-TTF)$_2$I$_3$ reported by Yagubskii et al. (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene). α-(BEDT-TTF)$_2$I$_3$ is a two-dimensional semimetal or a narrow gap semiconductor. β-(BEDT-TTF)$_2$I$_3$ is a two-dimensional metal which has an almost isotropic closed Fermi surface.

Recently the superconductivity of β-(BEDT-TTF)$_2$I$_3$ at ambient pressure (T_c=1.4 -1.5 K) has been observed by Yagubskii et al.,[1)] which has followed the observation of the superconductivity in (BEDT-TTF)$_2$ReO$_4$ under pressure.[2)] It is characteristic of BEDT-TTF compounds that the steric effect of the ethylene groups prevents the infinite face-to-face stacking of the molecules.[3)] The side-by-side interaction is very important and comparable to the face-to-face interaction. For the interpretation of physical properties of these organic molecular conductors, the calculation of intermolecular overlaps of the highest occupied molecular orbitals (HOMO) is useful.[3,4)] In the present investigation, the intermolecular overlaps of the HOMO are calculated for two types of (BEDT-TTF)$_2$I$_3$; one is reported by Bender et al. (α-type),[5)] and the other is superconducting as is reported by Yagubskii et al. (β-type).[1)]

The crystal structure of α-(BEDT-TTF)$_2$I$_3$ is shown in Fig. 1 (space group P$\bar{1}$).[5)] The organic cations form sheets parallel to the ab-plane. Electronic interaction between the different sheets is negligible. The molecular orbitals of crystallographically independent three molecules (A, B, and C) are calculated by means of the extended Hückel method. The Slater exponents and the ionization potentials (including sulfur 3d orbitals) are the same as those used in a previous report.[4)] The intermolecular overlaps S of the HOMO are calculated as shown in Table 1. Table 1 also shows φ: the angle between the molecular planes and the direction of the interaction, and D: the slipping of the molecules along the

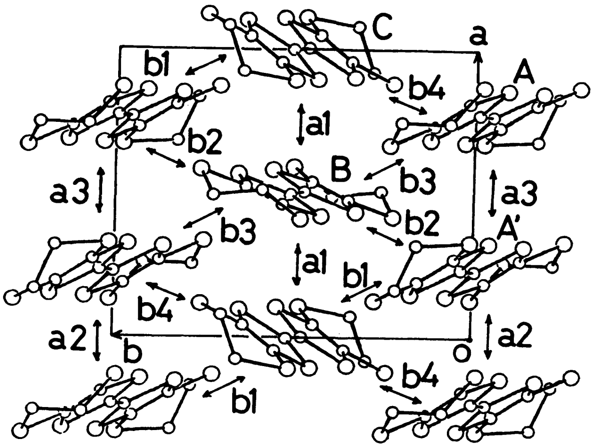

Fig. 1. Intermolecular overlaps in α-$(BEDT\text{-}TTF)_2I_3$.

Table 1. Overlap integrals of the HOMO in α-$(BEDT\text{-}TTF)_2I_3$

Direction	S /$\times10^{-3}$	φ	D /Å
a1	3.0	(64°	0.1)
a2	4.9	62°	0.2
a3	-1.8	52°	0.1
b1	-12.3		
b2	-14.2		
b3	-6.2		
b4	-2.3		

Table 2. Atomic parameters ($\times10^4$) of β-$(BEDT\text{-}TTF)_2I_3$

	X	Y	Z
I(1)	0	0	0
I(2)	148(1)	7473(1)	5978(2)
S(1)	4480(2)	7385(4)	4620(5)
S(2)	4305(2)	8530(4)	969(5)
S(3)	6192(2)	5691(4)	2803(5)
S(4)	5982(2)	6868(4)	-819(5)
S(5)	2889(3)	8629(5)	6394(6)
S(6)	2705(3)	10059(5)	2095(6)
S(7)	7931(2)	4592(4)	1985(5)
S(8)	7680(2)	6038(4)	-2343(5)
C(1)	4877(7)	7451(13)	2266(16)
C(2)	5593(7)	6734(13)	1508(16)
C(3)	3587(8)	8421(14)	4398(18)
C(4)	3509(7)	8961(13)	2728(18)
C(5)	7147(7)	5485(12)	1184(16)
C(6)	6954(7)	6039(12)	-485(16)
C(7)	2360(11)	10280(17)	6282(22)
C(8)	1945(11)	10179(21)	4068(25)
C(9)	8695(15)	4786(44)	170(38)
C(10)	8577(18)	5169(42)	-1397(56)

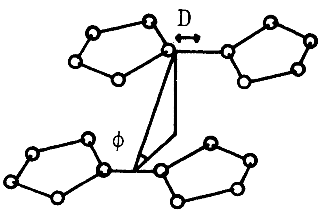

Fig. 2. Relative orientation of the inner rings of two parallel BEDT-TTF molecules.

molecular long axis; these parameters describing the configuration of the neighbor molecules have been defined in Ref. 4 (Fig. 2). The overlap shows that the anisotropy in the ab-plane is not large. Since a unit cell contains four molecules, there appear four energy levels from the HOMO. From the stoichiometry, $(BEDT\text{-}TTF)_2^+\cdot I_3^-$, 3/4 of this band is occupied. Therefore, the band structure becomes either semiconductive or semimetallic, according to whether or not there opens a gap between the third and the fourth energy levels. The calculation on the basis of the standard tight-binding method and the overlaps in Table 1, gives a semimetallic band structure. However, in the molecular orbital calculation of each molecule, the energy level of the HOMO obtained from the geometry of the A molecule is about 0.1 eV higher than those of B and C. It is also suggested from the examination of the bond lengths of A, B, and C, that the cations are ionized as $A^+A^+B^0C^0$.[3,5] In the ground state, the holes should be localized on the A molecules. They are easily activated around room temperature. Therefore, α-$(BEDT\text{-}TTF)_2I_3$ is regarded as a narrow-gap semiconductor, which acts as a two-dimensional semimetal at high temperatures.

The crystal structure of β-$(BEDT\text{-}TTF)_2I_3$ was independently determined by

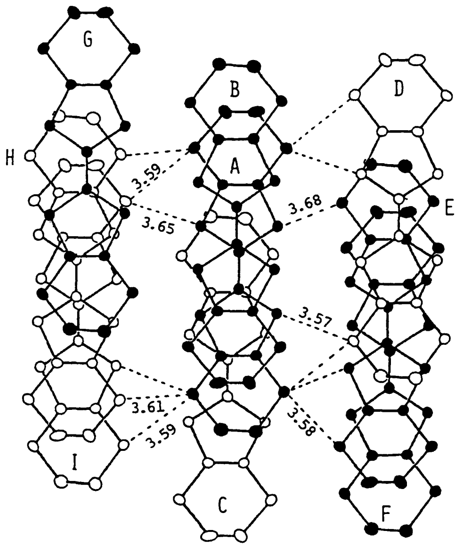

Fig. 3. Intermolecular overlaps and short S•••S contacts in β-$(BEDT\text{-}TTF)_2I_3$.

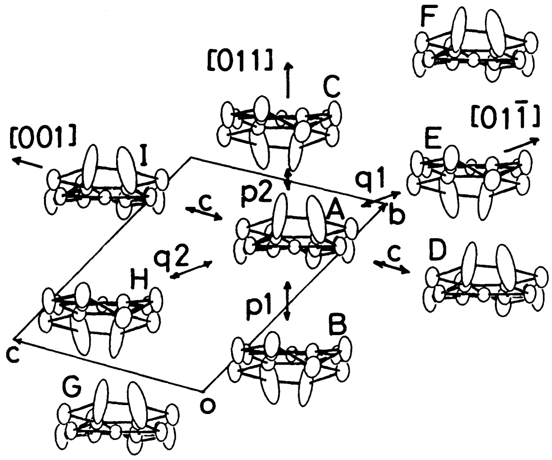

Fig. 4. Intermolecular overlaps in β-$(BEDT\text{-}TTF)_2I_3$.

Table 3. Overlap integrals of the HOMO in β-$(BEDT\text{-}TTF)_2I_3$

	Direction	$S\ /\times10^{-3}$	ϕ	D /Å
A - B	p1 [011]	-24.5	87°	1.5
A - C	p2 [011]	-8.4	84°	3.8
A - E	q1 [01$\bar{1}$]	-12.7	22°	2.0
A - H	q2 [01$\bar{1}$]	-6.8	18°	0.3
A - D, A - I	c [001]	-5.0	14°	1.8

Kaminskii et al.[6] The crystal data are: triclinic, space group P$\bar{1}$, a=15.243(2) b=9.070(2), c=6.597(1) Å, α=109.73(2), β=95.56(2), γ=94.33(2)°, V=848.9 Å^3, and Z=2. Using 3788 independent reflections ($|F_o|>3\sigma(|F_o|)$), the structure was refined to conventional R value of 0.052. The atomic parameters are shown in Table 2. Figures 3 and 4 show the intermolecular short contacts and the mode of the molecular overlap. The intermolecular overlaps S of the HOMO are, as before, calculated as shown in Table 3. The BEDT-TTF molecules are stacked face-to-face ($\phi\sim90°$) to form a column along the [011] direction. However, there is no short S•••S contact between A and B (>3.75 Å) and between A and C (>4.03 Å). The intrastack overlap p1 is the largest overlap, but p2 is much smaller. It may be said that the molecules are slightly dimerized in the stack. There are many S•••S contacts shorter than the van der Waals distance (3.7 Å) along the c and q directions. The second largest overlap is q1, and the large overlaps, p1 and q1, are aligned as p1-q1-p1-q1--- along the b axis. However, the anisotropy of the interaction is not large in the bc-plane.

The band structure calculated by the standard tight-binding method is shown in Fig. 5. Since a unit cell contains two molecules and the conduction band is 3/4 filled, the band structure is inevitably metallic; this is the same as the well-known organic superconductor, $(TMTSF)_2X$. However, in β-$(BEDT\text{-}TTF)_2I_3$, since

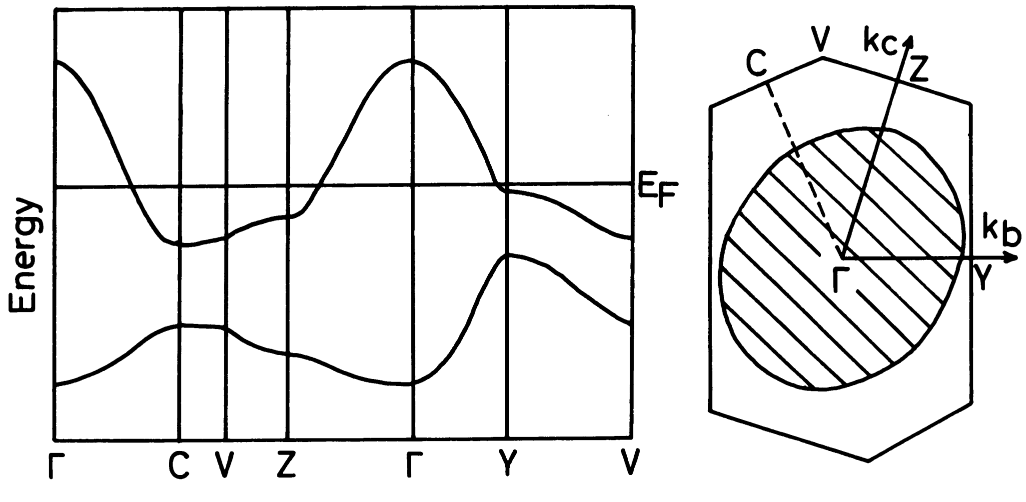

Fig. 5. The energy band structure and the Fermi surface of β-$(BEDT\text{-}TTF)_2I_3$. Energy in arbitrary units. The shaded region indicates hole-like part.

the interaction is rather isotropic, the Fermi surface is a closed circle in the bc-plane. This is the first example of organic conductors with an isotropic two-dimensional metal band.

Compared with the calculations and the experiments of other organic conductors,4) the overall bandwidths of α- and β-$(BEDT\text{-}TTF)_2I_3$ are estimated as about 0.35 eV and 0.5 eV respectively. These values are rather smaller than those of other organic metals and probably cause their relatively low conductivities; 60-250 $\Omega^{-1}cm^{-1}$ for α-type and 30 $\Omega^{-1}cm^{-1}$ for β-type. Although our calculation elucidates two-dimensional nature of $(BEDT\text{-}TTF)_2I_3$, it should be noted that the effect of electron correlation is considered to be comparable to their bandwidths and the above simple band calculation must be improved for the detailed interpretation of some sorts of physical properties.

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