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THE CRYSTAL STRUCTURE OF β'-(BEDT-TTF)$_2$ICl$_2$. A MODIFICATION OF THE ORGANIC SUPERCONDUCTOR, β-(BEDT-TTF)$_2$I$_3$

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The crystal of β'-(BEDT-TTF)$_2$ICl$_2$ has a modified structure of organic superconductor, β-(BEDT-TTF)$_2$I$_3$. Unlike the β-type salt with a two-dimensional(2D) electronic structure, the anisotropy of the intermolecular overlap integrals of HOMO of BEDT-TTF in β'-(BEDT-TTF)$_2$ICl$_2$ suggests the 1D character of the electronic structure.

Recent discoveries of the superconductivity of BEDT-TTF polyhalide systems[1,2] have attracted a considerable physical and chemical interest. The multi-dimensionality is the most remarkable structural feature of BEDT-TTF compounds.[3] However, it should be noted that the two-dimensional(2D) molecular array does not always lead to 2D electronic structure because the magnitude of the intermolecular interaction depends on not only intermolecular distance but also the anisotropy of the molecular orbital.[4,5] In this letter, we will report a new structure type of the BEDT-TTF polyhalide.

The crystals of β'-(BEDT-TTF)$_2$ICl$_2$ were obtained electrochemically. The crystal data are: $(C_{10}H_8S_8)_2ICl_2$, triclinic, $P\bar{1}$, a=12.937 (3), b=9.778(2), c=6.636(1) Å, α=98.59(2), β=100.98(2), γ=87.19(2)°, V=814.6(3) Å^3, Z=1. The structure was solved by the Patterson method and refined by the block-diagonal least-squares method. The final R value was 0.044. The atomic coordinates are listed in Table 1. The crystal structure is shown in Fig. 1. The centrosymmetric anion ICl_2^- is on the origin of the unit cell. The I-Cl bond length is 2.57(2) Å, which is 5% shorter than I-Br distance in β-(BEDT-TTF)$_2$IBr$_2$.[2] While the Cl···Cl distance between the neighbouring ICl_2^- anions(5.15(6) Å) is much longer than the corresponding distance in β-type salt (4,21 Å(I···I)(I_3)[7], 4.16 (I···Br)(I_2Br)[10]). The bond lengths of BEDT-TTF are in good agreement with those of BEDT-TTF$^{+1/2}$.[11] The mode of intermolecular overlapping is shown in Fig. 2. There is a large difference in the stacking mode between β'-(BEDT-TTF)$_2$ICl$_2$ and β-(BEDT-TTF)$_2$I$_3$. The terminal ethylene groups of BEDT-TTF in the crystals of BEDT-TTF salts frequently exhibit the positional disorder(or large thermal motion). But

the thermal motions of the terminal ethylene groups of BEDT-TTF in the ICl_2 salt are not large (B_{eq}=3.7-4.8 Å^2). All the hydrogen atoms could be located by difference synthesis. The cell volume is considered to be an important factor for determining the superconducting transition temperature of β-type salts.[12] The unit cell volum of β'-(BEDT-TTF)$_2ICl_2$ is smaller than those of any β-type salts whose crystal structures have been determined. This is consistent with the small size of the ICl_2^- anion: V=853 Å^3(I_3),[6,7] 845 (AuI_2),[8] 842(I_2Br),[9,10] 829(IBr_2),[2]. The structure change β↔β' indicates that the crystal cannot retain the β-type structure when the anion size becomes small. In this connection, it should be noted that (BPDT-TTF)$_2I_3$ with the cell volume of 962 Å^3 has β-type structure.[13]

The intermolecular overlap integrals (S) of the highest occupied molecular orbital (HOMO) of BEDT-TTF, from which the conduction band is formed, were calculated and compared with those of the β-type salts (Table 2). Based on the simple approximation of t=-ES, the tight-binding energy band was calculated, where t is the transfer integral and E is a constant (≈10 eV) of the order of the orbital energy of HOMO. Although the absolute value of S depends on the adopted atomic orbital (A.O.) parameters (Table 2), the anisotropy of S and therefore the form of the Fermi surface do not depend heavily on them (Fig. 4). Unlike β-type salt with 2D closed Fermi surface, β'-(BEDT-TTF)$_2ICl_2$ has a 1D plane-like Fermi surface. This difference comes from the large anisotropy of S of the ICl_2 salt, where the interaction is largest along [010]. The conductivity measurement shows that β'-(BEDT-TTF)$_2ICl_2$ is a semiconductor.[16] This may be due to the effect of Coulomb interaction neglected in this calculation. Similar situation has been observed in $TMTTF_2X$ (X=ClO_4, IO_4,...)[17] and β-(BPDT-TTF)$_2I_3$.[13] The band calculation of $TMTTF_2X$ gives 1D Fermi surface closely similar to that of the organic superconductor, $TMTSF_2ClO_4$.[5] However, the conducting behavior of $TMTTF_2X$ is not always metallic. In addition, β-(BPDT-TTF)$_2I_3$ is a semiconductor and the electronic structure is

Table 1. Atomic coordinates(x 10^4) of β'-(BEDT-TTF)$_2ICl_2$. Those of hydrogen atoms are omitted

	X	Y	Z
I	0	0	0
Cl	-906(1)	2358(1)	883(2)
S(1)	4626(1)	2686(1)	5901(2)
S(2)	4463(1)	1779(1)	9849(2)
S(3)	6527(1)	4702(1)	8283(2)
S(4)	6304(1)	3859(1)	12239(2)
S(5)	2980(1)	832(2)	3376(2)
S(6)	2769(1)	-189(2)	8113(2)
S(7)	8409(1)	6396(2)	10016(2)
S(8)	8101(1)	5378(2)	14748(2)
C(1)	5082(4)	2832(5)	8563(7)
C(2)	5867(4)	3698(5)	9578(7)
C(3)	3696(4)	1432(5)	5829(8)
C(4)	3606(4)	1027(5)	7643(8)
C(5)	7450(4)	5331(5)	10479(7)
C(6)	7341(4)	4956(5)	12286(7)
C(7)	2702(5)	-871(6)	3869(9)
C(8)	2075(5)	-842(6)	5537(9)
C(9)	9377(6)	6353(8)	12384(10)
C(10)	8932(6)	6689(8)	14291(10)

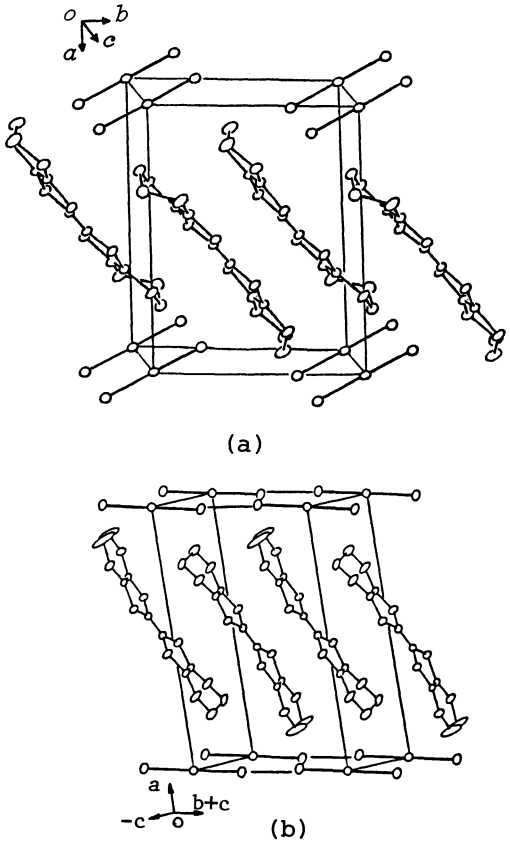
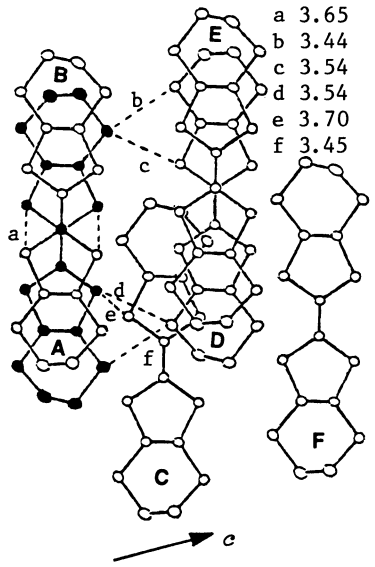


Fig. 1. (a) Crystal structure of β'-(BEDT-TTF)$_2ICl_2$.
(b) Structure of β-(BEDT-TTF)$_2I_3$ presented for comparison.

not 2D but 1D along [011] (Table 2 and Fig. 4), in spite of the apparent structural resemblance between β-$(BEDT\text{-}TTF)_2I_3$ and β-$(BPDT\text{-}TTF)_2I_3$. These facts suggest that in the organic system with 3/4 filled band, which is separated into upper and lower bands by the energy gap at the middle of the band energy, the 1D Fermi surface obtained by the simple band calculation becomes frequently artificial. However, this discrepancy does not deny the validity of S for the evaluation of the dimensionality of the electronic structure.[18)]



(a)

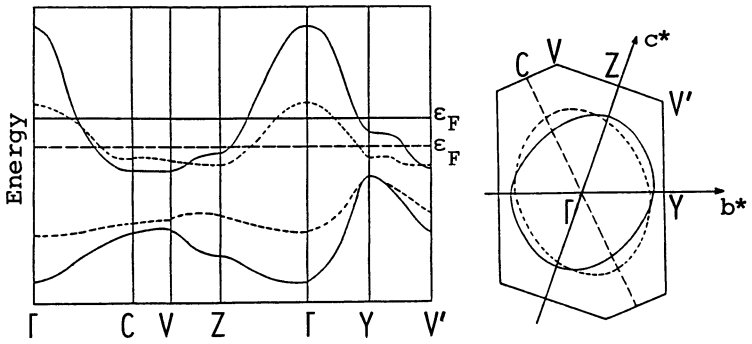
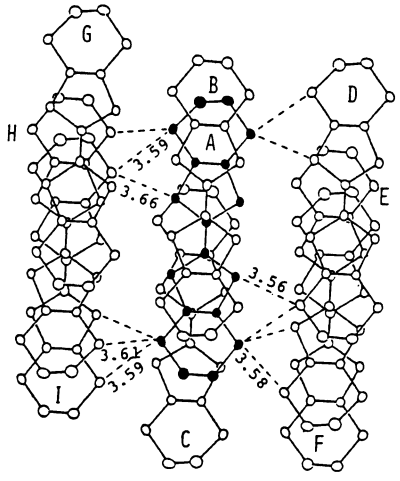
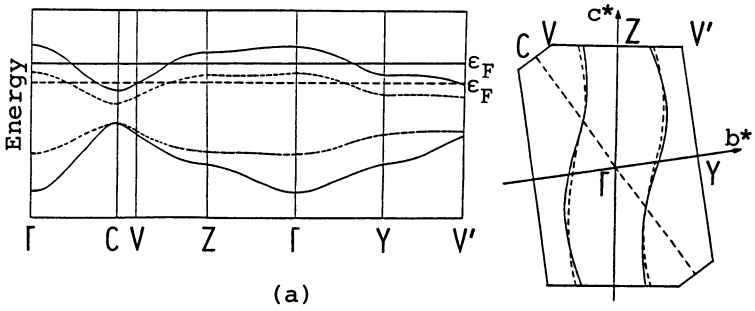


Fig. 3. Energy band and 2D Fermi surface of β-$(BEDT\text{-}TTF)_2I_3$. The solid and broken lines are those obtained by using the overlap integrals M and C (see Table 2), respectively (see also Ref. 7).

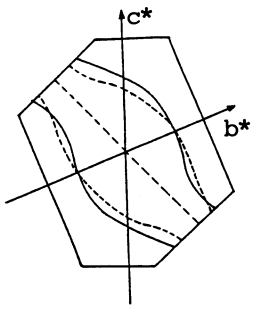


(b)

Fig. 2. Comparison of the modes of intermolecular overlapping.
(a) β'-$(BEDT\text{-}TTF)_2ICl_2$.
(b) β-$(BEDT\text{-}TTF)_2I_3$ (Ref. 7).



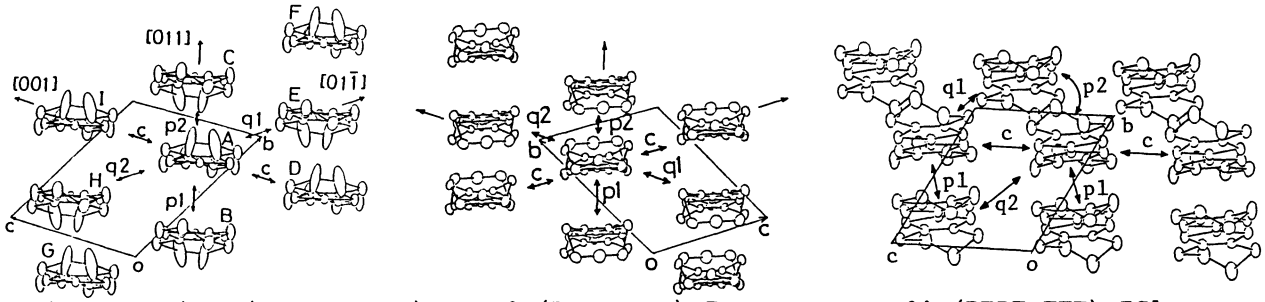
(a)



(b)

Fig. 4. (a) Energy band and Fermi surface of β'-$(BEDT\text{-}TTF)_2ICl_2$. (b) Fermi surface of β-$(BPDT\text{-}TTF)_2I_3$.

Table 2. Intermolecular overlap integrals (S x 10^3) of HOMO of β-(BEDT-TTF)$_2$X (X=I_3, I_2Br), β-(BPDT-TTF)$_2I_3$ and β'-(BEDT-TTF)$_2ICl_2$.



β-(BEDT-TTF)$_2$X (X=I_3, I_2Br) β-(BPDT-TTF)$_2I_3$ β'-(BEDT-TTF)$_2ICl_2$

	β-(BEDT-TTF)$_2I_3$			β-(BEDT-TTF)$_2I_2$Br		β-(BPDT-TTF)$_2I_3$		β'-(BEDT-TTF)$_2ICl_2$	
	M	C	T	M	C	M	C	M	C
p1[011]	24.5	15.4	24.5	23.9	13.3	21.2	12.9	27.2	15.4
p2[011]	8.4	5.6	6.4	8.9	6.2	12.7	8.0	-1.6	-1.7
q1[01$\bar{1}$]	12.7	4.7	6.4	12.5	4.7	6.4	0.9	6.6	1.7
q2[01$\bar{1}$]	6.8	1.8	3.4	6.7	1.8	3.3	1.9	10.0	7.2
c [001]	-5.0	-2.0	-2.5	-5.2	-2.3	1.6	0.6	1.6	0.1

M and C are those calculated based on the A.O. parameters reported in Refs. 5 and 14, respectively. T is that determined by Tajima et al. from the optical studies.[15)]

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