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

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The crystal of $\beta'$-(BEDT-TTF)$_2$ICl$_2$ has a modified structure of
organic superconductor, $\beta$-(BEDT-TTF)$_2$I$_3$. Unlike the $\beta$-type salt with
a two-dimensional(2D) electronic structure, the anisotropy of the
intermolecular overlap integrals of HOMO of BEDT-TTF in $\beta'$-(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 $\beta'$-(BEDT-TTF)$_2$ICl$_2$ were obtained electrochemically. The
crystal data are: (C$_{10}$H$_8$S)$_2$ICl$_2$, triclinic, P$\overline{1}$, a=12.937(3), b=9.778(2),
c=6.636(1) Å, $\alpha$=98.59(2), $\beta$=100.98(2), $\gamma$=87.19(2)$^o$, 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$$^-$ is on the origin of the unit cell. The I-Cl bond
length is 2.57(2) Å, which is 5% shorter than I-Br distance in $\beta$-(BEDT-TTF)$_2$IBr$_2$.$^2$
While the Cl···Cl distance between the neighbouring ICl$_2$$^-$ anions(5.15(6) Å) is much
longer than the corresponding distance in $\beta$-type salt (4.21 Å(I···I)(I$_3$)$^7$), 4.16
(I···Br)(I$_2$Br)$^{10}$). 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 $\beta'$-(BEDT-TTF)$_2$ICl$_2$ and $\beta$-
(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 ICl₂ salt are not large
\(B_{eq}=3.7-4.8 \text{ Å}^2\). 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)$_2$ICl$_2$ 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: \(v=853 \text{ Å}^3\) (I$_3$)⁶,⁷
845 (AuI$_2$)⁸, 842(I$_2$Br)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)$_2$I$_3$ with the cell volume
of 962 Å³ 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 \(E_t=ES\), the tight-binding energy
band was calculated, where \(t\) is the transfer
integral and \(E\) is a constant (\(\text{eV}\)) 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)$_2$ICl$_2$ 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)$_2$ICl$_2$ 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$_2$X (X=ClO$_4$, IO$_4$,...)¹⁷) and β-
(BPDT-TTF)$_2$I$_3$.¹³) The band calculation of TMTTF$_2$X
gives 1D Fermi surface closely similar to that of
the organic superconductor, TMTSF$_2$ClO$_4$⁵). However,
the conducting behavior of TMTTF$_2$X is not
always metallic. In addition, β-(BPDT-TTF)$_2$I$_3$ is
a semiconductor and the electronic structure is

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Table 1. Atomic coordinates (x \(10^4\)) of \(\beta'-(BEDT-TTF) \_2\)ICl$_2$. Those of hydrogen atoms are omitted.

Fig. 1. (a) Crystal structure of \(\beta'-(BEDT-TTF) \_2\)ICl$_2$.

(b) Structure of \(\beta-(BEDT-TTF) \_2\)I$_3$ presented for comparison.
not 2D but 1D along [011] (Table 2 and Fig. 4), in spite of the apparent structural resemblance between \( \beta-(\text{BEDT-TTF})_2I_3 \) and \( \beta-(\text{BPDT-TTF})_2I_3 \). 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)

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

Fig. 4. (a) Energy band and Fermi surface of \( \beta'-(\text{BEDT-TTF})_2ICl_2 \). (b) Fermi surface of \( \beta-(\text{BPDT-TTF})_2I_3 \).
Table 2. Intermolecular overlap integrals ($S \times 10^3$) of HOMO of $\beta\-(BEDT-TTF)_2X$ ($X=I_2$, $I_2Br$), $\beta\-(BPDFT-TTF)_2I_3$ and $\beta'\-(BEDT-TTF)_2ICl_2$.

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$M$ 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

References


15) H. Tajima et al., private communications.

16) M. Tokumoto et al., to be published.

17) K. Takeuchi et al., to be published.


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