

Crystal and Electronic Structures of a New
Molecular Superconductor, κ -(BEDT-TTF) $_2$ I $_3$

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The crystal of a new ambient-pressure superconductor, κ -(BEDT-TTF) $_2$ I $_3$ belongs to the monoclinic system with space group P2 $_1$ /c and $a=16.387$, $b=8.466$, $c=12.832$ Å and $\beta=108.56^\circ$. The 2-dimensional(2D) metal sheets composed of paired BEDT-TTF molecules and the I $_3$ anion sheets are arranged alternately along the a direction. The orientation of the neighbouring paired molecules is almost perpendicular to each other.

To date, three types of the ambient-pressure superconductors based on BEDT-TTF(bis(ethylenedithio)tetrathiafulvalene, abbreviated hereafter as ET) have been reported.¹⁻³⁾ It is well-known that β -(ET) $_2$ I $_3$ salt shows a drastic enhancement of the superconducting transition temperature(T_c) by applying so-called soft pressure.⁴⁾ However under the usual condition, T_c is reduced to about 1.5 K. Since T_c of β -(ET) $_2$ I $_3$ salt is considered to be reduced by the onset of the incommensurate lattice distortion wave developed at low temperatures, we tried to control the growth of the modulation wave by introducing the disorder in the anion sites. For this purpose, ET salts were prepared by the electrochemical method from the tetrahydrofuran solution of ET and the mixed supporting electrolytes of (n-C $_4$ H $_9$) $_4$ NI $_3$ and (n-C $_4$ H $_9$) $_4$ NAuI $_2$. The constant current of 1.0 μ A was applied. Besides the β -type salt, we obtained various types of ET crystals, α , γ' , δ , θ and κ . When the content of (n-C $_4$ H $_9$) $_4$ NAuI $_2$ is small, the main product is the α -type crystals and when (n-C $_4$ H $_9$) $_4$ NAuI $_2$ content is large, the δ -type salt is the main product. It was very difficult to distinguish the type of the crystal form by its shape. We have already reported the superconducting transition and crystal and electronic structures of the θ -type salt.³⁾ Very recently, we have found another superconducting phase (κ -phase, $T_c=3.6$ K).⁵⁾ X-ray microanalyses were made on the two crystals. Both of them showed that the AuI $_2$ content is less than detectable limit (κ -(ET) $_2$ (I $_3$) $_{1-x}$ (AuI $_2$) $_x$, $x<0.006$), so that the κ -type salt is essentially I $_3$

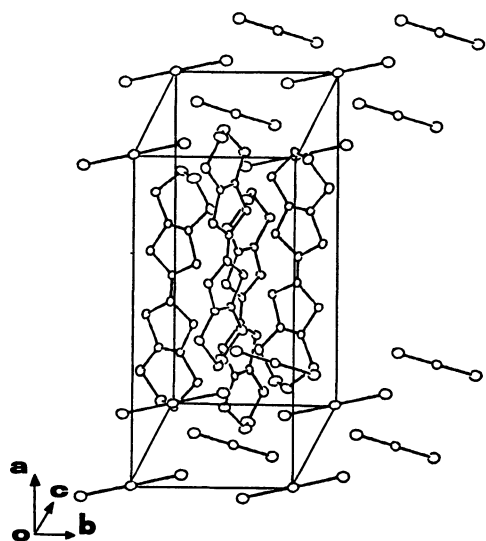
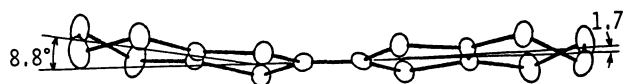
Fig. 1. Crystal structure of κ -(ET)₂I₃.

Fig. 2. Side view of the ET molecule.

salt(κ -(ET)₂I₃). In this paper, we report the crystal and electronic structures of this ambient-pressure superconductor, κ -(ET)₂I₃.

Black thick plates of the κ -type salt were examined by X-ray oscillation and Weissenberg photographs. The κ -type salt belongs to the monoclinic system with cell volume of approximately equal to those of the α -type salt and the average structure of the θ -type salt. Almost all the crystals of the κ -type salt ever obtained are twinned. The determination of the lattice constants and the collection of the X-ray intensity data were made on the weakly twinned crystal by the use of a Rigaku four-circle diffractometer. The crystal data are: monoclinic, $P2_1/c$, $a=16.387(4)$, $b=8.466(2)$, $c=12.832(8)$ Å, $\beta=108.56(3)^\circ$, $V=1687.6$ Å³, $Z=2$. Of the 5154 independent reflections, the 3067 significant reflections ($|F_O| > 3\sigma(|F_O|)$) were obtained ($2\theta < 60^\circ$ (Mo K α)). The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R-value is 0.081.

The structure of κ -(ET)₂I₃ is shown in Fig. 1. Only one ET is crystallographically independent and I₃ anions are on the inversion centers. In contrast to the β -(ET)₂I₃ salt with a conformational disorder of ethylene group, ethylene conformation in the κ -type salt is ordered.

The bond length of the central C=C double bond of ET is 1.34(2) Å, which is intermediate between the bond length of neutral molecule (1.31 Å) and that of monocation of ET⁺ (1.38 Å). The other C=C double bonds (1.31, 1.32 Å) are slightly shorter than the central C=C bond. The C-C bond lengths of two ethylene groups are 1.51 and 1.46 Å. Somewhat short C-C length of 1.46 Å suggests a relatively large thermal motion of one of the two ethylene groups. The average S-C bond length in the C₆S₈ skeleton is 1.744 Å and the S-C(ethylene) is 1.790 Å. The ET molecule is slightly bent. The dihedral angles between the least-squares planes of three tetrathio-substituted ethylene moieties are 8.8° and 1.7° (Fig. 2). The corresponding dihedral angles of the neutral ET molecules are 14.7° and 12.3°. ⁶⁾

The crystal structure is quite different from the structures of the traditional 1D molecular metals. The ET molecules form 2D sheets parallel to the bc-plane. The dihedral angle between the neighbouring molecules interrelated by

the screw axis symmetry is 87° , that is, almost rectangular. The I_3 anions are located between the donor sheets. The donor sheets and anion sheets are arranged alternately along the a direction (Fig. 3). Similar to the θ -type salt, the κ -type salt can be regarded as a layered metal. The interatomic distances between I...H atoms are longer than 3.2 \AA .

The molecular arrangement in the metal layer is shown in Fig. 4. The metal sheet is composed of the paired molecules. The shortest S...S contact in the paired molecules is 3.66 \AA . The orientation of the neighbouring paired molecules is almost perpendicular to each other and the paired molecules with different orientations are arranged alternately to form 2D sheet (Fig. 4). The κ -type salt is the first organic superconductor composed of paired molecules. This structural feature requires the structure concept of the organic conductors based on the molecular stacking to be renewed.

Since the conduction band is formed by the intermolecular overlapping of the highest occupied molecular orbital (HOMO) of ET, the intermolecular overlap

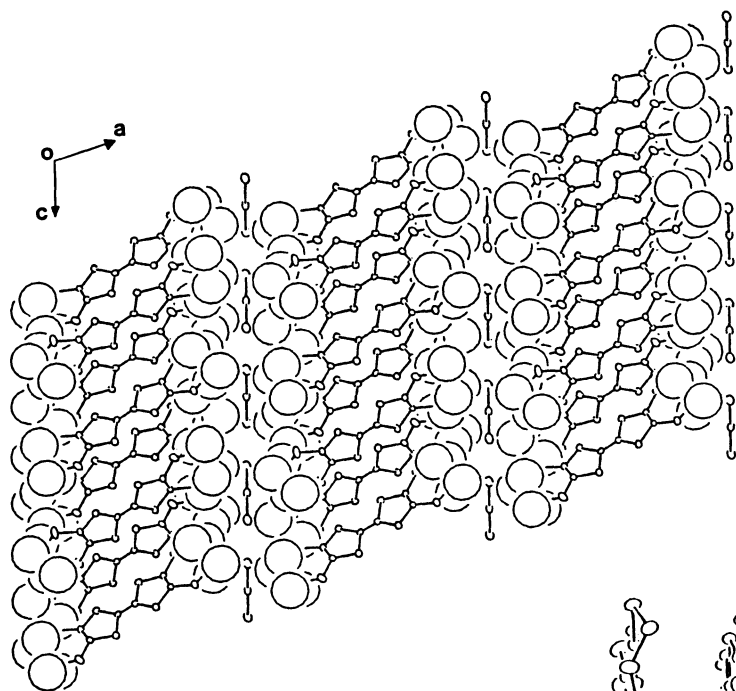
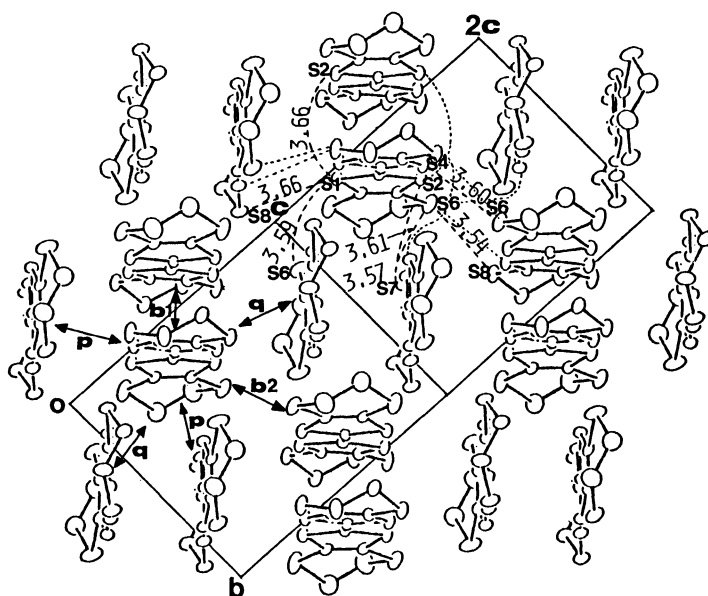


Fig. 3. The arrangement of the ET layers and the anion sheets in κ -(ET) $_2$ I $_3$. The large circles are the van der Waals spheres of the hydrogen atoms.

Overlap integrals ($\times 10^{-3}$)

b1	10.92
b2	2.46
p	5.05
q	-1.85

Fig. 4. Molecular arrangement and the intermolecular overlap integrals ($\times 10^{-3}$).



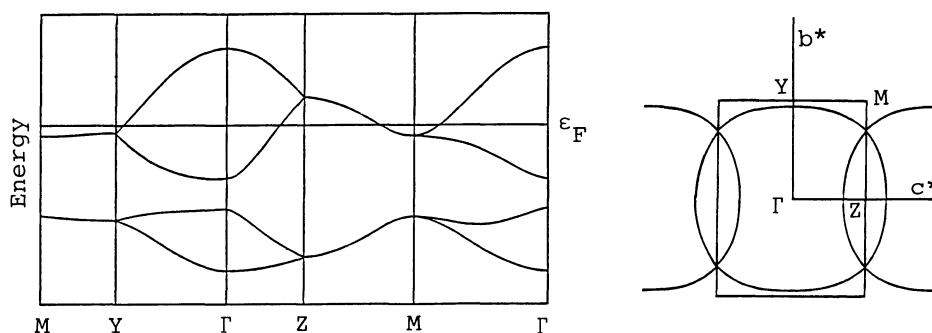


Fig. 5. Tight-binding band and Fermi surface of κ -(ET)₂I₃.

integrals of HOMO(S) were calculated (Fig. 4). The interaction between the paired molecules is largest but the other interactions are also large. The tight-binding band calculated using the simple approximation, $t=ES$ (t is transfer integral, E is orbital energy of HOMO (≈ -10 eV)) gave nearly isotropic round Fermi surface, similar to that of the θ -type salt (Fig. 5). The 2D packing motif based on paired molecules will give a hint to design new layered molecular superconductors.

The large anisotropy of the coherence lengths in the superconducting state was observed.⁷⁾ This is consistent with the 2D crystal and electronic structures of κ -(ET)₂I₃. Recently, an anomalously large magnetoresistance of the κ -type salt has been found, when the magnetic field is applied to the direction parallel to the metal layer, which will be reported in the near future.⁷⁾

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