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CRYSTAL STRUCTURES AND ELECTRICAL PROPERTIES OF BEDT-TTF COMPOUNDS

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Abstract The crystal structure and the electrical resistivities of BEDT-TTF compounds are reported. The most prominent feature of the crystal structure is the side-by-side array of BEDT-TTF molecules. The steric effects of the ethylene groups prevent the infinite stacking of the molecules. The electrical properties and the change in the X-ray diffraction patterns of β-$(BEDT\text{-}TTF)_2PF_6$ suggest that β-$(BEDT\text{-}TTF)_2PF_6$ is a one-dimensional conductor along the transverse direction. A simple band calculation indicates that $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ is a two-dimensional semimetal. $(BEDT\text{-}TTF)_3(ClO_4)_2$ shows a metal-insulator transition at 170 K, which is consistent with the one-dimensional band structure of this compound.

INTRODUCTION

Since the superconductivity of BEDT-TTF compounds has been reported, the BEDT-TTF salts have become one of the better studied organic conductors.1) In other molecular conductors, planar donor and/or acceptor molecules are stacked face-to-face to form columns. The molecular stacking is essential to the formation of a one-dimensional (1-D) band, because the highest occupied molecular orbital (HOMO) is composed of π-electrons, which are distributed along the stacking direction. For the formation of the conduction band, the intermolecular spacing must be small. If the molecules are not planar, it may be impossible to stack the molecules face-to-face. Then the band width becomes narrow and electrons will be localized. Therefore, it is quite natural that the stacking of the planar molecules has been always found in the crystals of the molecular conductors.

However, the electronic properties and the crystal structures of BEDT-TTF compounds show that such a stacking structure is not an indispensable condition for high conductivity.

CRYSTAL AND MOLECULAR STRUCTURE

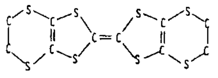
We have made crystal structure analyses and conduction measurements of BEDT-TTF compounds and the compounds of analogous molecules, which are listed in Table I.

$(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ is 2-D (semi)metal.[2-4) The room-temperature conductivity is 25 S cm^{-1}. The solvent molecule TCE(trichloroethane) is included in the crystal. Solvent inclusion is frequently observed in BEDT-TTF compounds. $(BEDT\text{-}TTF)_3(ClO_4)_2$ shows a metal-insulator(M-I) transition at 170 K.[5) $(BEDT\text{-}TTF)_2ReO_4$ is the first organic sulfur donor superconductor.[1) β-$(BEDT\text{-}TTF)_2PF_6$ is a 1-D conductor along the transverse direction.[6) Among the crystals of the monocationic salts, the BEDT-TTF^+ ions form a strongly distorted dimeric chain, which is consistent with the semiconductive properties of the salts.$^{7)}$ The last two compounds are prepared from the similar donors BPDT-TTF and BMDT-TTF.

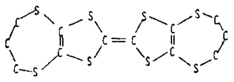
TABLE I Stoichiometries and electrical conductivities of the compound of BEDT-TTF and the related molecules.

Compound	Stoichiometry	R.T. Conductivity(Scm^{-1})
1) BEDT-TTF		
2) (BEDT-TTF)$_2$ClO$_4$(TCE)$_{0.5}$	4:2:1	25 (2-D semimetal)
3) (BEDT-TTF)$_3$(ClO$_4$)$_2$	3:2	50 (1-D metal ? (>170K))
4) (BEDT-TTF)$_2$ClO$_4$(C$_4$H$_8$O$_2$)	2:1:1	10^{-2}(2-D semiconductor)
5)*(BEDT-TTF)$_2$ReO$_4$	2:1	200(superconductor(>4Kb)
6) (BEDT-TTF)ReO$_4$(THF)$_{0.5}$	2:2:1	10^{-2}(semiconductor)
7) (BEDT-TTF)IO$_4$(THF)$_{0.5}$	2:2:1	10^{-5}(semiconductor)
8) α-(BEDT-TTF)$_2$PF$_6$	2:1	1 (semiconductor)
9) β-(BEDT-TTF)$_2$PF$_6$	2:1	10 (1-D metal(>297 K))
10) (BPDT-TTF)$_3$(PF$_6$)$_2$	3:2	1 (semiconductor(?))
11) (BMDT-TTF)$_3$PF$_6$(DCE)	3:1:1	10 (2-D conductor(?))

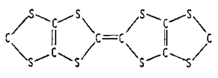
* Parkin, Engler, Schumaker, Lagier, Lee, Scott, & Greene, Phys. Rev. Lett., 50, 270 (1983).



BEDT-TTF



BPDT-TTF



BMDT-TTF

TCE: Trichloroethane DCE: Dichloroethane

THF: Tetrahydrofuran

The lattice constants are given in Table II. The crystal symmetry differs from compound to compound. This is a marked contrast to the isomorphism of the well-known superconducting salts (TMTSF)$_2$X (X=ClO$_4^-$, PF$_6^-$,...).$^{8)}$ The most prominent feature of the crystal structures of the BEDT-TTF compounds is the side-by-side array of the molecules (see Fig. 1), which has been found in the 2:1

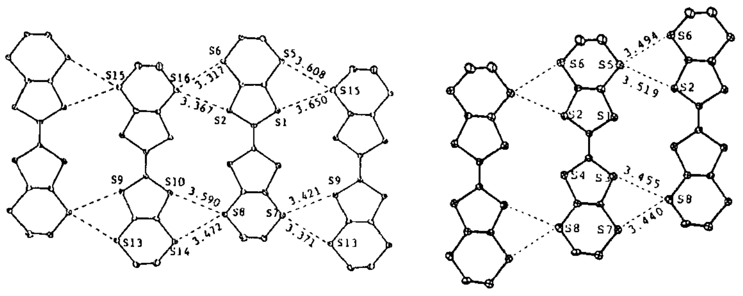
(BEDT-TTF:X) and also in the 3:2 compounds. The sulfur atoms in the six-membered rings play an important role in forming this transverse array of BEDT-TTFs. The crystals of the neutral molecules9) and the 1:1 compounds11) are composed of dimeric units of BEDT-TTF (see Fig. 2). Because of the steric effects of the ethylene group, the nonplanar BEDT-TTFs do not form face-to-face infinite stacks. In some cases, BEDT-TTFs take "twist-type" overlapping to avoid the steric repulsion (see Fig. 3).6,10)

TABLE II Lattice constants.

Compound	Symmetry	a(Å)	b	c	α(°)	β	γ
1)[a]	M[b] $P2_1/c$	6.614	13.985	16.646		109.55	
2)	T $P\bar{1}$	12.966	18.602	7.740	79.32	104.80	110.85
3)	T $P\bar{1}$	16.463	9.498	7.613	95.91	87.17	90.84
4)	M $P2/c$	8.242	6.677	32.998		92.71	
5)	T $P\bar{1}$	7.78	12.59	16.97	73.01	79.89	89.06
6)	M $P2/c$	12.679	8.037	19.292		97.69	
7)	M $P2/c$	12.692	8.036	19.285		97.66	
8)	T $P\bar{1}$	14.711	8.597	6.462	95.71	97.64	98.87
9)	O Pnna	14.960	32.643	6.664			
10)	M $C2/m$	13.156	12.802	16.865		93.94	
11)	T $P\bar{1}$	16.841	9.998	7.776	113.64	99.79	100.03

[a] The number 1)-11) corresponds to the compound listed in Table I.
[b] M: monoclinic, T: triclinic, O: orthorhombic.

The bond lengths of BEDT-TTF are given in Table III. The C-S bond lengths, b and c become shorter and the C=C bonds, a and d become longer with increasing formal charge of BEDT-TTF (BEDT-TTF$^{+\rho}$). This is consistent with the



(a) (BEDT-TTF)$ClO_4(TCE)_{0.5}$ (b) β-$(BEDT\text{-}TTF)_2PF_6$

FIGURE 1. Transverse array of BEDT-TTF.

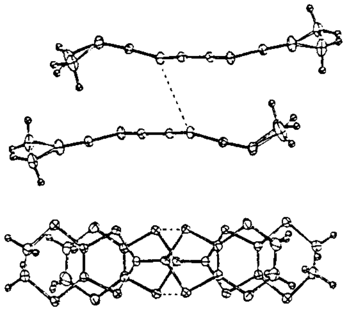


FIGURE 2. Dimeric arrangement of BEDT-TTF found in the crystal of BEDT-TTF molecule.

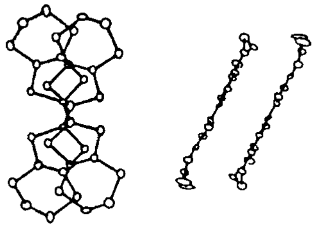


FIGURE 3."Twist-type overlapping" found in the crystal of $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$.

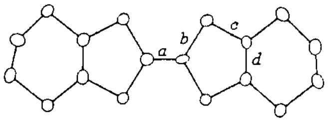
results of an extended Hückel molecular orbital calculation: the HOMO has nodal planes on every C-S bond. Since the HOMO has pπ character, the conduction band of BEDT-TTF compound is considered to be composed of π electrons.

ELECTRICAL CONDUCTION AND BAND STRUCTURE

The crystal structure of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ is shown in Fig. 4. The mode of the molecular arrangement of BEDT-TTF shows that there is no intermolecular short contact

TABLE III Bond lengths of BEDT-TTF$^{+\rho}$
The bond lengths are averaged by assuming D_{2h} symmetry.

Formal charge (ρ)		Bond length (Å)*			
ρ	(compound)	*a*	*b*	*c*	*d*
0	neutral molecule	1.31	1.757	1.754	1.332
1/2	α-(BEDT-TTF)$_2$PF$_6$	1.365	1.740	1.750	1.345
2/3	(BEDT-TTF)$_3$(ClO$_4$)$_2$	1.366	1.731	1.743	1.345
1	(BEDT-TTF)ReO$_4$(THF)$_{0.5}$	1.38	1.72	1.73	1.37



* The bond lengths in the six-membered rings are less accurate because of the large thermal motion of the ethylene groups. They are not included in this Table.

along [102], the direction of best overlap (see Fig. 5). Much closer contacts along the a axis([100]) establish the side-by-side array of BEDT-TTF (Fig. 1). Some short S···S contacts are also found along [$\bar{1}$02]. The electrical resistivity and its anisotropy indicate that the 2-D metallic state of this system is stable down to low temperature. Since the energy level of the HOMO is far from the other energy levels, the approximate band structure can be derived from the intermolecular overlap integrals of the HOMO.$^{3)}$ The intermolecular overlap integral along [100] (S[100]) is smaller than S[$\bar{1}$02] (S[$\bar{1}$02]/S[100]≒4). This is due to the pπ character of HOMO. Since the magnitudes of the overlap integrals are of the same order in two directions, the band structure is quite different from that of typical 1-D metals (see Fig. 6). The small areas of electrons and holes in the Fermi surface suggest 2-D semimetallic properties.

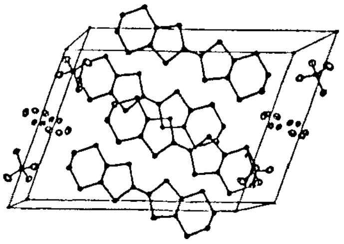


FIGURE 4. Crystal structure of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$.

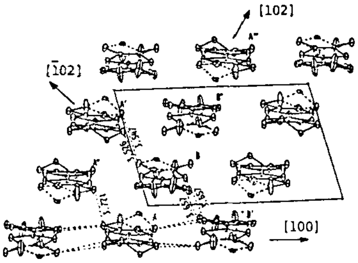


FIGURE 5. Molecular arrangement in $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$.

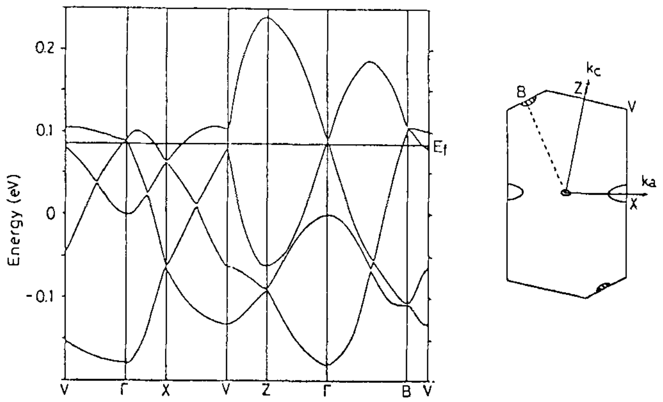


FIGURE 6. Band structure of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$.

The 2-D nature of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ suggests that some other compounds may exist, where the transverse intermolecular interaction is much larger than the parallel interaction. Indeed, in $\beta\text{-}(BEDT\text{-}TTF)_2PF_6$, the conductivity is largest along the transverse direction (c axis) (Figs. 1 and 7). The electrical resistivity shows a M-I transition at 297 K(T_c) (Fig. 8). Above T_c, the anisotropy of

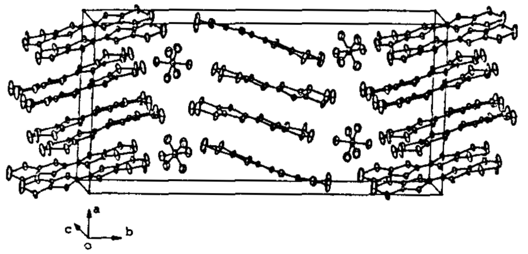


FIGURE 7. Crystal structure of β-$(BEDT\text{-}TTF)_2PF_6$.

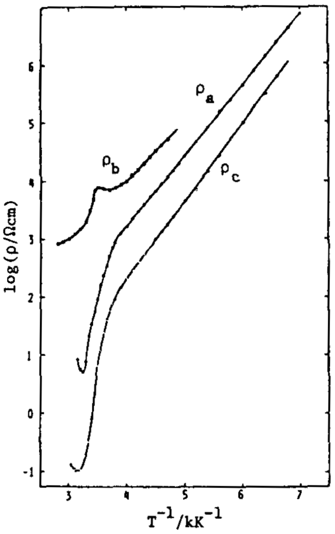


FIGURE 8. Electrical resistivities of β-$(BEDT\text{-}TTF)_2PF_6$.

conductivity is considerably large, and the thermoelectric power tends to saturate to a value of 60 μV/K, which indicates a highly correlated band. X-ray diffraction patterns show that the lattice constant c is doubled below T_c, suggesting that the side-by-side array of BEDT-TTFs is modulated by a $4k_F$-wave.[11] Thus, β-$(BEDT\text{-}TTF)_2PF_6$ is the first example of a 1-D conductor along the transverse direction.

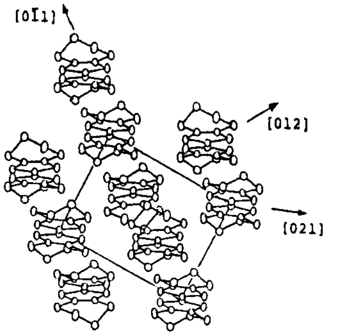


FIGURE 9. The arrangement of BEDT-TTF in $(BEDT\text{-}TTF)_3(ClO_4)_2$.

Unlike $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$, $(BEDT\text{-}TTF)_3(ClO_4)_2$ undergoes a sharp M-I transition at 170 K. The molecular arrangements in these two compounds are similar (Figs. 5 and 9). If the simple band picture described before is valid, the difference in the conduction properties of these systems may be explained by an examination of the intermolecular overlap integrals. Two independent overlap integrals along [012] are almost equal to each other, and are much larger than those along the other directions. Thus, the HOMO forms a 1-D band along [012]. Since three BEDT-TTFs form a repeating unit along [012], the system can transform to an insulating state without any change of the lattice periodicity, which is consistent with the result of X-ray diffraction experiments: the lattice constants gave no evidence of superlattices below the M-I transition temperature.

As mentioned before, the steric effects of the ethylene groups of BEDT-TTF prevent the infinite face-to-face stacking of the molecules. However, the crystal structure analyses of $(BPDT\text{-}TTF)_3(PF_6)_2$ and $(BMDT\text{-}TTF)_3PF_6$ (DCE) (see Table I) show that the molecular arrangement is not the same as for the BEDT-TTF compounds. In the crystal of $(BPDT\text{-}TTF)_3(PF_6)_2$, the BPDT-TTF are arranged face-to-face to form columns,[12] while $(BMDT\text{-}TTF)_3PF_6(DCE)$ has a 2-D network of S atoms.[13] The molecular planes of the two crystallographically independent BMDT-TTF molecules are nearly perpendicular to each other (≑100°).

In summary, the crystal structure analyses of the compounds of BEDT-TTF and analogous molecules show that the molecular stacking is not an indispensable condition for high conductivity. Moreover, molecular conductors can be metallic along the transverse direction. A simple band picture based on the calculation of the intermolecular overlap integrals of the HOMO is valid for the interpretation of the organic molecular conductors.

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