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Dimensionality Examination of Cation Radical Salts Based on EDT-TTF (EDT-TTF = Ethylenedithiotetrathiafulvalene)

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Crystal and electronic structures of organic conductors, (EDT-TTF)$_2$X (EDT-TTF = ethylenedithiotetrathiafulvalene; X = PF_6, AsF_6, TaF_6, BF_4, ClO_4, ReO_4, $Au(CN)_2$), have been studied. In all these compounds, the donor molecules exhibit face-to-face stacking. Simple tight-binding band calculations indicate quasi-one-dimensional electronic structures.

The interest in molecular metals based on organic sulfur or selenium containing π-donors has been enhanced by the observation of superconductivity in the cation radical salts of TMTSF (tetramethyltetraselenafulvalene),[1)] BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene),[2)] DMET (dimethyl(ethylenedithio)-diselenadithiafulvalene),[3)] and MDT-TTF (methylenedithiotetrathiafulvalene).[4)] Metal state stabilization in these compounds is believed to depend on increase in dimensionality of their electronic structures represented by the warped or closed Fermi surface. Therefore, the dimensionality examination is of special importance, in the characterization of the new system. In this paper, we have examined the dimensionality of a new series of cation radical salts based on EDT-TTF (ethylenedithiotetrathiafulvalene) with TaF_6^-, AsF_6^-, PF_6^-, ReO_4^-, ClO_4^-, BF_4^-, and $Au(CN)_2^-$. EDT-TTF is a hybrid between TTF and BEDT-TTF molecules, and its homolog, MDT-TTF, has provided the superconducting salt.[4)]

EDT-TTF was obtained by cross-coupling of the appropriate 1,3-dithiole-2-thione (1) and 1,3-dithiole-2-one (2) in triethyl phosphite. Separation of the desired cross-coupling product from the symmetrical self-coupling co-products was accomplished by HPLC (silica gel, CS_2). The product distribution was TTF : EDT-TTF : BEDT-TTF = 1 : 29 : 18. Cation radical salts of EDT-TTF were prepared by electrochemical oxidation in presence of $(n\text{-}Bu)_4NX$ (X = PF_6, AsF_6, TaF_6, BF_4, ClO_4, ReO_4, $Au(CN)_2$) in 1,1,2-trichloroethane using a constant current (1 μA).

Crystal data of (EDT-TTF)$_2$X are summarized in Table 1. Intensity data were collected on a Rigaku automatic four-circle diffractometer with monochromated Mo-

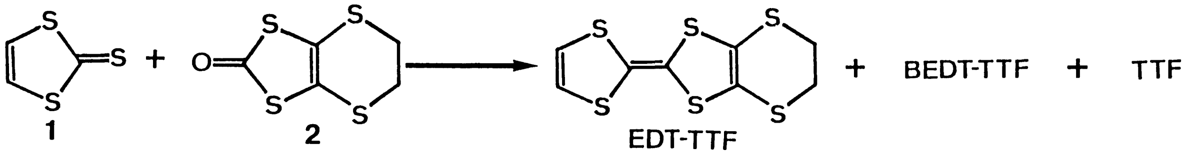

Table 1. Crystal data and electrical properties of $(EDT\text{-}TTF)_2X$

X	$Au(CN)_2$	TaF_6	$AsF_6(\alpha)$	$AsF_6(\beta)$	PF_6	ReO_4	ClO_4	BF_4
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Pccn	Pccn	C2/c	C2/c	C2/c
a/Å	14.752	15.213	14.855	28.303	28.014	29.720	29.283	29.133
b/Å	7.225	7.049	7.043	7.120	7.122	7.185	7.145	7.134
c/Å	6.388	6.463	6.457	12.706	12.650	12.416	12.417	12.379
α/°	106.15	102.22	102.38					
β/°	101.56	102.57	96.15			110.56	111.54	111.85
γ/°	90.50	98.77	101.68					
Z	1	1	1	4	4	4	4	4
$V/Å^3$	639.2	646.7	638.1	2560.5	2523.9	2482.4	2416.5	2388.0
R	0.074	0.088	0.037	0.090	0.063	0.115	0.129	0.064
$\sigma_{R.T.}$/ S cm^{-1}	5	10^2	50	30	10^2	10	10^2	10
T_{M-I}/K	semicon.	57	50	ca.50	42	150	ca.100	170

Kα radiation. The structures were solved by the direct method and refined by the block-diagonal least-squares method using reflections with $|F_o|>3\sigma(|F_o|)$. The final R values are listed in Table 1.

In all these compounds, the asymmetric EDT-TTF molecules stack alternately to form almost uniform columns (Figs. 1-3). The EDT-TTF molecule is almost planar except the ethylenedithio-fragment. Conformational disorder of the ethylene group is not observed in each case. From crystallographic point of view, these salts are classified into three almost isostructural groups.

The triclinic group contains the $Au(CN)_2$, TaF_6, and AsF_6(α form) salts. The molecular packing in the triclinic group is similar to that of the Bechgaard salt, $(TMTSF)_2X$ (Fig. 1). The mode of molecular overlapping in the column of the $Au(CN)_2$ salt is slightly different from those of other salts. The anion is on the center of inversion. Along the c axis, short intermolecular S•••S contacts based on the ethylenedithio-fragment are observed.

The orthorhombic group includes AsF_6 (β form) and PF_6 salts (Fig. 2). The unit cell contains one crystallographically independent EDT-TTF molecule and four equivalent donor columns running along the b axis. In the bc plane, there are short intermolecular S•••S contacts. Along the a axis, the donor molecules are prevented from close contact by the anions.

The monoclinic group contains the salts with tetrahedral anions (BF_4^-, ClO_4^-, and ReO_4^-). The packing motif of the donors in the monoclinic group is quite similar to that in the orthorhombic group (Fig. 3). The tetrahedral anions do not exhibit the orientational disorder.

We examined the electronic structures of α-$(EDT\text{-}TTF)_2AsF_6$ (triclinic), β-$(EDT\text{-}TTF)_2AsF_6$ (orthorhombic), and $(EDT\text{-}TTF)_2ReO_4$ (monoclinic) by the simple tight-binding band calculations. When the extended Hückel approximation is adopted, the electronic band structure can be easily obtained from the anisotropy of the intermolecular overlap integrals of HOMO's in EDT-TTF (Table 2). Then the

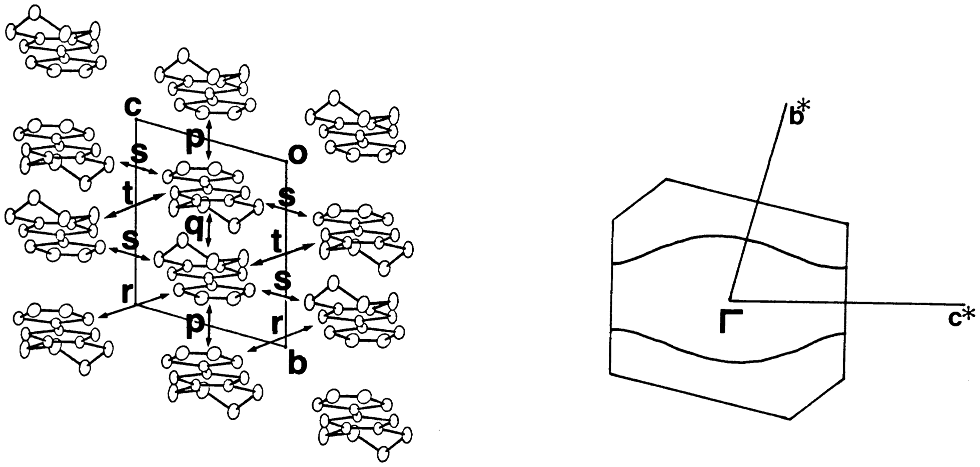

Fig. 1. Molecular arrangement and calculated Fermi surface of α-$(EDT\text{-}TTF)_2AsF_6$.

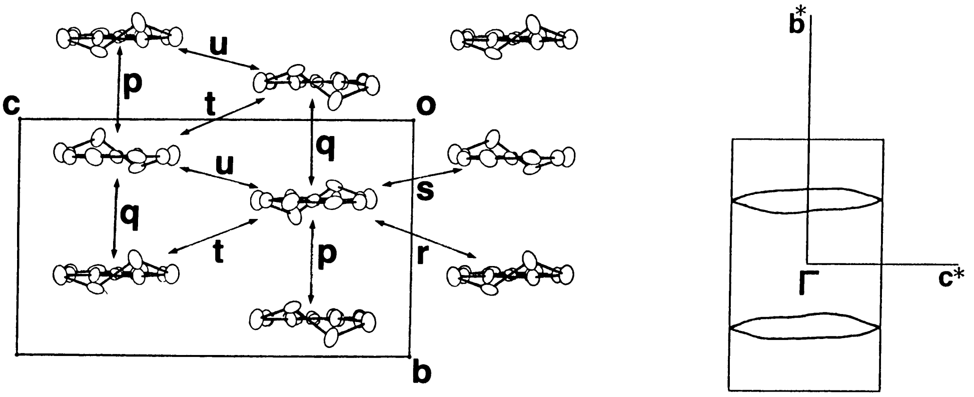

Fig. 2. Molecular arrangement and calculated Fermi surface of β-$(EDT\text{-}TTF)_2AsF_6$.

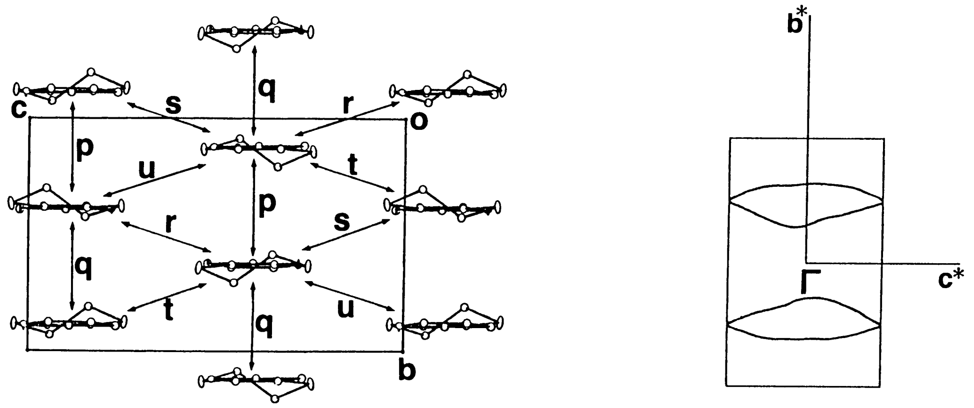

Fig. 3. Molecular arrangement and calculated Fermi surface of $(EDT\text{-}TTF)_2ReO_4$.

Table 2. Intermolecular overlap integrals (× 10^3) of HOMO's in $(EDT\text{-}TTF)_2X$

X	p	q	r	s	t	u
AsF_6(α)	17.13	18.88	2.15	-0.74	2.74	
AsF_6(β)	-15.74	-15.74	2.14	0.40	2.05	0.40
ReO_4	-19.42	-19.42	1.90	1.90	3.06	1.79

dimensionality of the electronic structure can be judged from the curvature of the Fermi surface. The term "one-(two-)dimensionality" is explained to mean the "flat(cylindrical) Fermi surface". This criterion on the dimensionality would still retain the meaning even in the case where the system is not really metallic, because the Fermi surface thus obtained is regarded as a visual expression of the anisotropy of the intermolecular interactions through frontier orbitals.

The calculated Fermi surface of α-(EDT-TTF)$_2$AsF$_6$ (Fig. 1) is very similar to that of (TMTSF)$_2$X.$^{5)}$ In β-(EDT-TTF)$_2$AsF$_6$ and (EDT-TTF)$_2$ReO$_4$, the Fermi surface consists of two pairs of warped planes (Figs. 2 and 3). The quasi-one-dimensional character of the band structures indicates that the gap formation by the CDW or SDW tends to occur. Resistivity measurements at ambient pressure showed that almost all these salts are highly conductive (10-10^2 S cm^{-1}) at room temperature but semiconductive at low temperature. The room temperature conductivity ($\sigma_{R.T.}$) and the metal-insulator transition temperature (T_{M-I}) are listed in Table 1.

BEDT-TTF molecules with two ethylenedithio-fragments prefer the extensive two-dimensional arrangements to the face-to-face stacking.$^{2)}$ In the EDT-TTF salts, lack of one ethylenedithio-fragment makes the one-dimensional face-to-face stacking more preferable. Further survey of the EDT-TTF salts should be required, because the molecular arrangement of the cation radical with the significant transverse interaction is sensitive to the counter anion,$^{2-4)}$ and there remains a possibility of the two-dimensional stable metal system based on EDT-TTF.

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