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Crystal Structure and Physical Properties of (BMDT-TTF)SbF_6

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In a crystal of (BMDT-TTF)SbF_6, quasi two-dimensional(2D) intermolecular interactions of BMDT-TTF molecules are observed. This compound was a semiconductor with fairly high room temperature conductivity (ca. 1 S cm^{-1}), and would be a simple model compound for the consideration of electron-electron interaction in quasi 2D half-filled band system.

In the molecular conductor, the 1:1 salt comprised of one electron (hole) for every molecule has been considered low conductive. For example, Rb•TCNQ-II with a one-dimensional uniform TCNQ column is not metallic, in contrast to TTF•TCNQ and NMP•TCNQ containing similar TCNQ column.1) This indicates that a simple band picture with a half-filled conduction band should be affected by the electron-electron interaction. It is well-known that there exists antiferromagnetic interaction between adjacent sites in the highly correlated band system. Three-dimensional magnetic orderness, however, does not develop usually in the organic conductors because of its strong one-dimensionality. Recent progress of the molecular conductor has provided the multi-dimensional system.2) We are much interested in the possibily of the magnetic orderness in the multi-dimensional system with the half-filled band. In this paper, we report crystal structure of (BMDT-TTF)SbF_6 (BMDT-TTF;bis(methylenedithio)tetrathiafulvalene) and indicate that this compound has very simple half-filled band with weak one-dimensionality (quasi two-dimensional character).

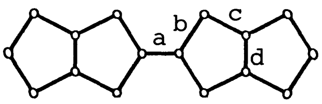
Black elongated plates of (BMDT-TTF)SbF_6 were obtained by the electrochemical oxidation of a 1,1,2-trichloroethane solution containing BMDT-TTF and $(n\text{-}C_4H_9)_4N$ SbF_6 at a constant current of 1 μA. Crystal data: $C_8H_4S_8SbF_6$, triclinic, space group $P\bar{1}$, a=9.573(3), b=7.500(2), c=5.633(2) Å, α=100.20(3), β=91.61(3), γ=90.96(2)°, V=397.7 $Å^3$, Z=1. Intensities were measured on a Rigaku automated four-circle diffractometer with Mo Kα radiation up to 2θ=60°. Independent 2892 reflections ($|F_o|>3\sigma(|F_o|)$) were used for calculations. The structure was solved by the direct method and refined to the conventional R value of 0.039. The final atomic coordinates are given in Table 1.

The crystal structure of (BMDT-TTF)SbF_6 is shown in Fig. 1. The BMDT-TTF

Table 1. Fractional atomic coordinates (× 10^3 for H atoms; × 10^4 for others) with their estimated standard deviations

Atom	x	y	z
Sb	0	0	0
F(1)	1854(3)	-567(5)	764(7)
F(2)	634(4)	2261(4)	-656(7)
F(3)	247(5)	-1115(5)	-3235(7)
S(1)	3276(1)	1581(1)	6583(2)
S(2)	5009(1)	1869(1)	2457(2)
S(3)	1816(1)	5090(2)	6023(2)
S(4)	3524(1)	5331(2)	1771(2)
C(1)	4637(4)	733(5)	4794(8)
C(2)	2983(4)	3381(6)	5131(8)
C(3)	3782(5)	3509(5)	3229(8)
C(4)	1844(6)	5828(7)	3123(10)
H(1)	78(8)	501(10)	207(15)
H(2)	173(9)	745(10)	357(17)

Table 2. Comparison of bond lengths (Å) of BMDT-TTF(neutral) and BMDT-TTF$^+$ The bond lengths b, c, and d are average values, with an approximated D_{2h} symmetry.



	neutral	BMDT-TTF$^+$
a	1.327	1.361
b	1.766	1.730
c	1.738	1.722
d	1.334	1.350

Table 3. Overlap integrals S_v (× 10^3) of the HOMO in (BMDT-TTF)SbF_6

S_b	-5.10
S_c	-12.48
S_{b+c}	0
S_{b-c}	0.81
S_{-a+b}	0.23

S_v indicates the overlap integral between molecules interrelated by the translation vector v.

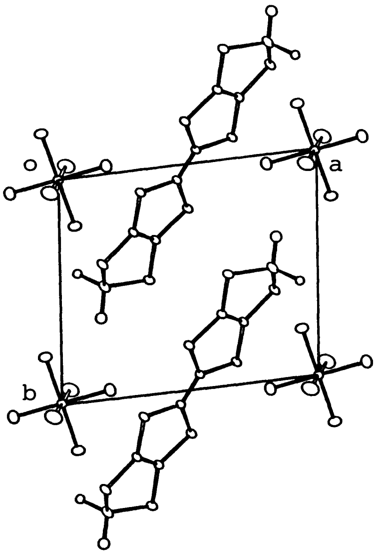


Fig. 1. Crystal structure of (BMDT-TTF)SbF_6.

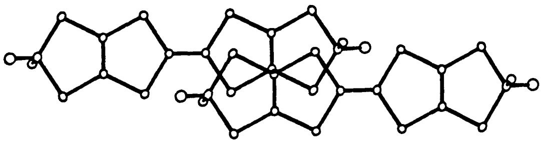


Fig. 2. Mode of intermolecular overlapping.

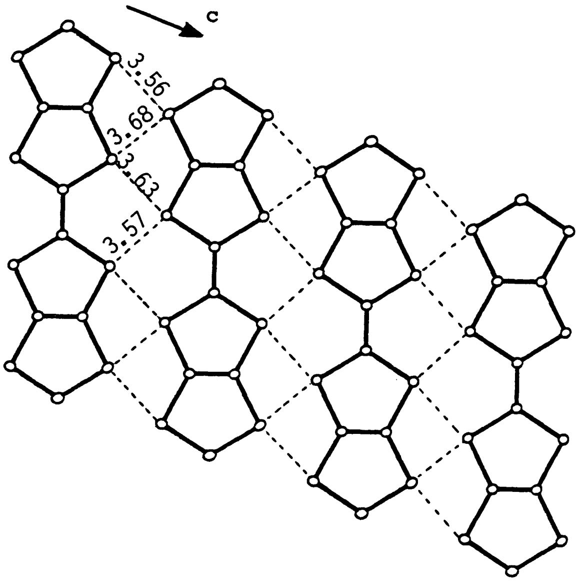


Fig. 3. Side-by-side arrangement of BMDT-TTF molecules.

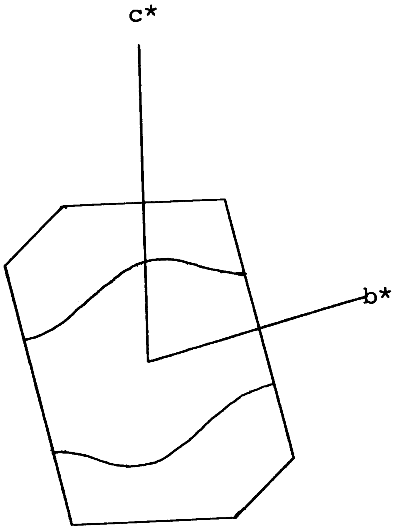


Fig. 4. "Artificial" Fermi surface of (BMDT-TTF)SbF_6 obtained by a simple tight-binding approximation.

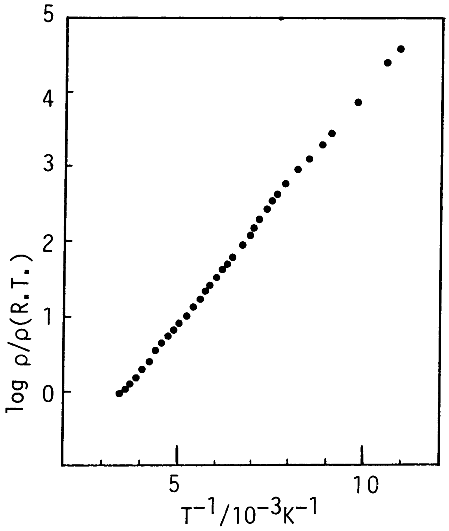


Fig. 5. Electrical resistivity of (BMDT-TTF)SbF_6 along the c axis.

molecule lies on an inversion center, and almost planar. Lengthened C=C distances (a, d; in Table 2) and shortened C-S distances (b, c) of BMDT-TTF^+ compared with those of neutral BMDT-TTF[3] are in good agreement with the result of the molecular orbital calculation; the HOMO (highest occupied molecular orbital) has nodal planes on every C-S bond. This is just the same as we can see in the BEDT-TTF compound.[4] The BMDT-TTF units are repeated along the b axis in a face-to-face manner. In this direction, an adjacent molecule is largely shifted along the long axis (Fig. 2) and there is no short intermolecular S•••S distance (<3.70 Å; van der Waals distance), in spite of rather short interplanar distance (3.45 Å). On the other hand, the BMDT-TTF molecules interrelated by the unit translation along the c axis are connected to each other by many short intermolecular S•••S contacts (Fig. 3). Such a side-by-side arrangement is frequently observed in the crystals of molecular conductors based on the BEDT-TTF type donor or the dmit(dimercaptoisotrithione) complexes.[2] In addition to these intermolecular interaction parallel to the bc plane, we observe a short intermolecular S(3)•••S(3) distance (3.62 Å) between molecules interrelated by the translation vector **a-b** (and -a+b). All these structural features indicate that in this crystal there exist two-dimensional donor sheets which are parallel to the bc plane and weakly interrelated to each other along the a axis. Such a multi-dimensional molecular arrangement, which is not based on the conventional column formation, is the most characteristic feature of the BMDT-TTF compounds.

In order to investigate the electronic structure, we first calculated the intermolecular overlap integrals (S) of HOMO of BMDT-TTF (Table 3).[5] The strongest interaction is observed along the side-by-side arrangement (S_c). The S_c value is larger than the corresponding S value in β-(BEDT-TTF)$_2PF_6$,[6] which is the first one-dimensional organic conductor along the side-by-side array. On the other hand, the S_b value ($p\sigma$-$p\sigma$ type overlap) is rather small, as a result of the insufficient face-to-face overlapping (Fig. 2). The anisotropy $S_b/S_c \simeq 0.4$ is much larger than that in the Bechgaard salt $(TMTSF)_2X$ ($\simeq 0.1$). The S_{-a+b} value indicates weak interaction among the donor sheets along the a axis.

The tight-binding approximation gives a simple two-dimensional energy band,

$$E(k)=2t_b\cos(kb)+2t_c\cos(kc),$$

where we neglect the weak interactions, S_{-b+c} and S_{-a+b}. This energy band is half-filled and the Fermi surface contains largely distorted planes (Fig. 4).7) This simple band picture predicts that this compound behaves as a metal. The resistivity measurement along the c axis, however, shows that this compound is a semiconductor (E_a= 0.12 eV) although the room-temperature conductivity (ca. 1 S cm^{-1}) is very high as a 1:1 salt (Fig. 5).

These results indicate that a simple band picture of non-interacting electrons does not suffice for the full understanding of the electronic structure. The introduction of on-site Coulomb repulsion would lead the system to the non-metallic state. This has been shown by preliminary ESR measurements.8) (BMDT-TTF)SbF_6 exhibits a broad ESR signal (linewidth ΔB=21 G) at room temperature when the static magnetic field is applied perpendicular to the c axis. The intensity decreases monotonously only by a factor of 0.5 from 300 K to 5 K, although the intensity for a semiconductor of a simple band model is expected to tend to vanish at low temperature.

In conclusion, (BMDT-TTF)SbF_6 is not a simple non-magnetic semiconductor. In any case, (BMDT-TTF)SbF_6 would be a prototype for the examination of the theory of the electron-electron interaction. Detailed ESR study will be reported elsewhere.

References

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7) The band energy calculations were based on the approximation that the transfer integral(t_v) is proportional to the overlap integral(S_v).
8) M. Kinoshita, private communication. We are much grateful to Dr. T. Sugano, and Prof. M. Kinoshita, the Institute for Solid State Physics, the University of Tokyo, for permitting us to use their ESR data.

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