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CRYSTAL AND BAND STRUCTURES OF AN ORGANIC CONDUCTOR β''-(BEDT-TTF)$_2$AuBr$_2$

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A novel organic conductor β''-(BEDT-TTF)$_2$AuBr$_2$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene, $C_{10}H_8S_8$) crystallizes in the triclinic space group $P\bar{1}$, with cell constants: a=9.027(1), b=16.372(2), c=5.712(1) Å, α=97.60(1), β=102.94(1), γ=92.09(1) °, V=813.7(2) Å^3, and Z=1. A band structure calculation indicates that its intermolecular interaction is largest along the transverse molecular array.

The discoveries of the superconductivity in β-(BEDT-TTF)$_2$X (X=I_3^-, IBr_2^-, and AuI_2^-) have aroused much interest in BEDT-TTF salts with polyhalide and metal halide anions.[1-3] In contrast to these β-phases, the small anions, ICl_2^- and $IBrCl^-$, have been known to produce semiconducting β'-phases, which are structurally a little different from the β-phases.[4,5] Recently Beno et al. have reported a series of monoclinic salts, α'-(BEDT-TTF)$_2$X (X=$Ag(CN)_2^-$, $Au(CN)_2^-$, and $AuBr_2^-$);[6] in spite of its naming, these salts seem to bear some resemblance to the salts of β-(BEDT-TTF)$_2$$PF_6$ series rather than the α-phase trihalide.[7,8] In the present paper, we report another $AuBr_2^-$ salt, β''-(BEDT-TTF)$_2$AuBr$_2$, with a new type of crystal structure.

Crystals were grown by electrochemical crystallization of BEDT-TTF in 1,1,2-trichloroethane using tetra-n-butylammonium dibromoaurate(I) as a supporting electrolyte. Intensities were measured by the θ-2θ scan technique on a Rigaku automated four-circle diffractometer with graphite monochromatized Mo Kα radiation (2θ<60°). The crystal size was 0.2×0.2×0.02 mm^3. Lorentz and polarization effects, and absorption corrections were performed. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares procedure (R=0.058) by using 3224 reflections ($|F_o|>3\sigma(F)$). The hydrogen atoms were not included in the final refinement, and anisotropic thermal parameters were adopted for all other atoms. The atomic coodinates are given in Table 1. The anisotropic thermal parameters and the list of the structure factors are available upon request.

The crystal structure is shown in Fig. 1. There is one independent BEDT-TTF molecule in an asymmetric unit, and the $AuBr_2^-$ anion lies on an inversion center. The molecular packing apparently resembles the β-phase structure; the triclinic

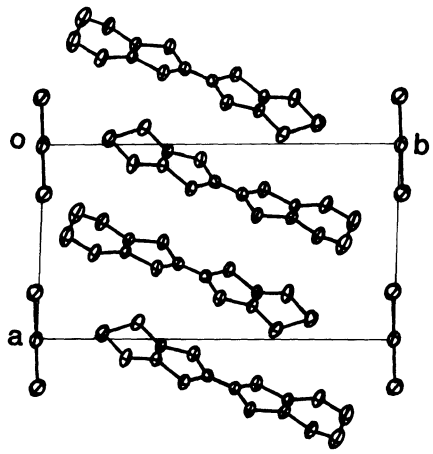

Fig. 1. Crystal structure of β''-$(BEDT\text{-}TTF)_2AuBr_2$, projected on the ab plane.

Table 1. Atomic parameters ($\times 10^4$) and equivalent thermal factors $B_{eq}=(4/3)\Sigma\Sigma\beta_{ij}\, a_i \cdot a_j$ ($\AA^2$)

Atom	X	Y	Z	B_{eq}
Au	0	0	0	3.5
Br	2252(1)	7(1)	-1503(2)	4.8
S(1)	7403(2)	3687(1)	7715(3)	2.7
S(2)	8873(2)	5448(1)	7244(3)	2.8
S(3)	5377(2)	3604(1)	2887(3)	2.8
S(4)	6743(2)	5447(1)	2538(3)	2.7
S(5)	6718(2)	1966(1)	8323(4)	3.5
S(6)	10510(2)	7037(1)	7188(4)	3.3
S(7)	4275(2)	1857(1)	2549(4)	3.3
S(8)	7857(3)	7060(1)	1693(4)	3.5
C(1)	6811(7)	4160(4)	5160(13)	2.3
C(2)	7420(7)	4918(4)	4972(12)	2.2
C(3)	6386(8)	2738(4)	6460(13)	2.3
C(4)	9053(8)	6286(4)	5712(13)	2.4
C(5)	5458(8)	2709(4)	4256(13)	2.4
C(6)	8071(8)	6302(4)	3594(12)	2.3
C(7)	5594(11)	1074(5)	6471(18)	5.0
C(8)	9748(9)	7936(5)	5920(16)	3.6
C(9)	4165(11)	1255(6)	4945(18)	5.2
C(10)	9405(9)	7816(5)	3174(16)	3.8

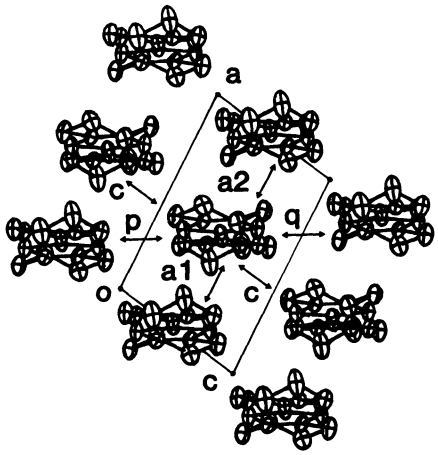

Fig. 2. Intermolecular overlaps in the donor sheet, viewed along the molecular long axis.

unit cell contains two parallel donor molecules. The donors form a sheet parallel to the ac plane, and the sheets are separated from each other by $AuBr_2^-$ anions. The molecular arrangement within the donor sheet is depicted in Fig. 2. The Au-Br bond length is 2.377(1) $\AA$. Figure 3 shows the intramolecular bond lengths of BEDT-TTF; these bond lengths are typical of $BEDT\text{-}TTF^{1/2+}$ [9] The intermolecular S···S contacts are summarized in Table 2. The interactions p and q possess some short S···S contacts, whereas the interactions a1 and a2 have no S···S contacts shorter than twice of the van der Waals radius (3.7 $\AA$).

In order to afford a better understanding of the intermolecular interaction, the intermolecular overlap integrals of the highest occupied molecular orbitals of BEDT-TTF, from which the conduction band is formed, were estimated on the basis of the extended Hückel molecular orbital calculation (Table 3). The Slater exponents and the ionization potentials (including sulfur 3d orbitals) are the same as those used in a previous report.[10] The parameter ϕ in Table 3 is the angle between the molecular plane and the interaction direction, and D is the slip distance along the

Table 2. Intermolecular S···S contacts shorter than 4 Å. The symbols of the interactions a1, a2, etc. are shown in Fig. 2

a1	S(1)-S(6)	3.801(3)	c	S(7)-S(5)	3.632(3)	p	S(7)-S(8)	3.467(3)
	S(3)-S(4)	3.781(3)		S(3)-S(5)	3.906(3)		S(3)-S(8)	3.485(3)
a2	S(2)-S(2)	3.798(3)		S(3)-S(1)	3.821(3)		S(3)-S(4)	3.810(3)
	S(6)-S(3)	3.902(3)		S(4)-S(1)	3.875(3)		S(4)-S(4)	3.862(3)
				S(4)-S(2)	3.930(3)	q	S(5)-S(6)	3.351(2)
				S(8)-S(2)	3.703(3)		S(1)-S(6)	3.471(3)
				S(8)-S(6)	3.886(3)		S(1)-S(2)	3.980(2)
							S(2)-S(2)	3.843(3)

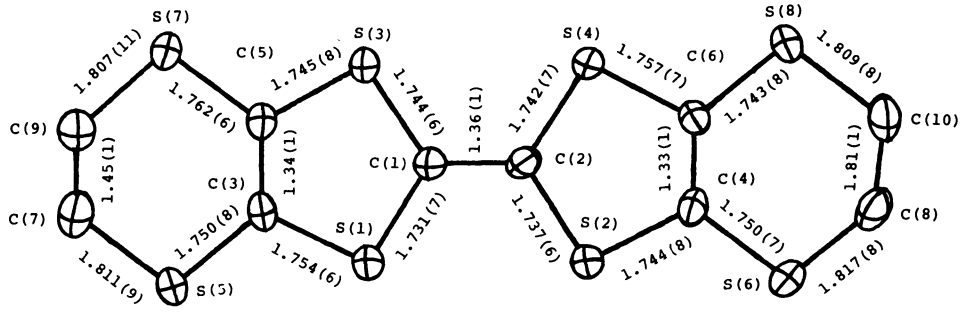

Fig. 3. Intermolecular bond lengths of the BEDT-TTF molecule in β''-(BEDT-TTF)$_2$AuBr$_2$.

Table 3. Overlap integrals of the HOMO and the parameters φ and D, which describe the configuration of the neighbor molecule[10]

Direction	Overlap /10^{-3}	φ /°	D /Å
a1	-1.5	63	0.0
a2	-6.5	60	3.3
c	-15.0	36	1.6
p	-8.7	6	1.6
q	-9.6	3	1.7

molecular long axis.[10] The interactions a1 and a2 are around φ=60° and there is no true face-to-face (φ=90°) interaction. This molecular arrangement contrasts with the dimerized φ=90° stacking in the β-phase,[11] and the alternate 90°-30° arrangement in the β'-phase.[4] The tendency that the face-to-face stacking is favorable in the order, β>β'>β'', is related to the anion size, 9.0 Å (AuI_2^-) > 8.74 Å (ICl_2^-) > 8.65 Å ($AuBr_2^-$). The donor sheet of the β''-phase is composed of three types (0°, 30°, and 60°) of interactions. Such a molecular arrangement is similar to those of (BEDT-TTF)$_2$$ClO_4(C_2H_3Cl_3)_{0.5}$ and (BEDT-TTF)$_3$$(ClO_4)_2$.[10,12] Like these perchlorate salts, the φ=60° interactions a1 and a2 of β''-(BEDT-TTF)$_2$$AuBr_2$ are weaker than the other interactions (Table 3).

By using the overlap integrals in Table 3, the tight-binding band structure is calculated as shown in Fig. 4. Because the dispersion is dominated by the large c interaction, the major part of the Fermi surface consists of open planes parallel to (001), though the small close part around the X point suggests a

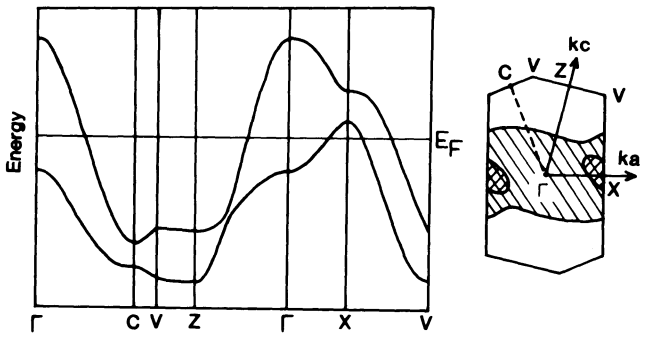

Fig. 4. The energy band structure and the Fermi surface. The shaded regions indicate hole-like parts.

small amount of two-dimensional interaction. Therefore this complex is essentially regarded as one-dimensional along the c direction. Since the β'-phase is one-dimensional approximately along the 'stacking' direction,[4] the β'-phase and the β''-phase exhibit one-dimensionality in the different directions.

A preliminary conductivity measurement shows that β''-(BEDT-TTF)$_2$AuBr$_2$ undergoes a metal-semiconductor transition around 200 K.[13]

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