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CRYSTAL STRUCTURE OF α'-(BEDT-TTF)$_2$BrICl

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Crystal of the semiconducting salt of α'-(BEDT-TTF)$_2$BrICl has a modified structure of metallic α-(BEDT-TTF)$_2$I$_3$. Unlike the molecules in α-(BEDT-TTF)$_2$I$_3$, all the molecules are on the general positions. The average molecular planes of two crystallographically independent BEDT-TTF molecules are not parallel. The dihedral angle between them is 48°. A two-dimensional sulfur network is formed by the intermolecular short S···S contacts.

There are many structural modifications of BEDT-TTF polyhalides. Shibaeva et al. have reported the five structure types of BEDT-TTF polyiodides (α, β, γ, δ, ε).[1] α-(BEDT-TTF)$_2$I$_3$ is the first polyiodide of BEDT-TTF whose novel structural and physical properties have been reported.[2] The subsequent discoveries of the low T_c[3] and high T_c[4,5] superconducting phases of β-(BEDT-TTF)$_2$I$_3$ have refreshed the interest in the organic superconductors. The extraordinary variety of the structures of BEDT-TTF compounds is originated from the multi-dimensional molecular arrangements of BEDT-TTFs.[6] Metallic conduction along the transverse molecular array is one of the most striking feature of the BEDT-TTF compounds.[7] In addition, it may be noteworthy that a slight structural modification leads to a large change of the electronic properties. Anion disorder tends to lower the superconducting transition temperature of the β-type salt.[5] In this paper, we will report a modified α-type structure of BEDT-TTF polyhalide, which is named hereafter as the α'-type structure. Unlike α-(BEDT-TTF)$_2$I$_3$ which is metallic around room temperature,[2] α'-(BEDT-TTF)$_2$BrICl is a semiconductor.[8]

The crystal data are: $(C_{10}H_8S_8)_2$BrICl, triclinic, $P\bar{1}$, a=16.307(5), b=12.373(3), c=8.871(2) Å, α=113.44(2), β=91.50(3), γ=93.60(3)°, V=1636.3 Å^3, Z=2. The unit cell volume is nearly equal to that of α-(BEDT-TTF)$_2$I$_3$ (1717 Å^3 [2]) and is approximately twice the β-type salt. Of the 7584 independent reflections ($2\theta < 55°$ (Mo Kα)), only 2776 significant reflections ($|F_o| > 3\sigma(|F_o|)$) were obtained. This is due to the small size of the crystal used for data collection (ca. 0.3x0.18x0.01 mm^3). The structure was solved by the Patterson method and refined by the block-

diagonal least-squares method to a conventional R value of 0.087. The unit cell structure is shown in Fig. 1. The atomic coordinates are listed in Table 1. All the molecules (BEDT-TTF(A), BEDT-TTF(B), and BrICl) are on the general positions. This is in contrast to the α-type salt where a half of the molecules is on the inversion centers. Very recently, Yagubskii et al. have presented brief structural data of IBr_2 salt of BEDT-TTF.[9] This new semiconducting salt was named as α-(BEDT-TTF)$_2$IBr$_2$ (β-(BEDT-TTF)$_2$IBr$_2$ is a superconductor with considerably high T_c, discovered by Williams et al.[10]). The salt of Yagubskii et al. and α'-(BEDT-TTF)$_2$BrICl appear to be isomorphous to each other. However, we call the structure of the BrICl salt as the α'-type, in order to make clear the structural difference between the BrICl salt and the so-called α-type salt represented by α-(BEDT-TTF)$_2$I$_3$. The $BrICl^-$ anion takes a linear form as $(Br\text{-}I\text{-}Cl)^-$. The thermal parameters of Br and Cl atoms indicate the existence of the orientational disorder. The structure was refined with varying the atomic populations of these atoms. The ratio of the preferred orientation to the inverted orientation is about 0.65:0.36. The coordinates of Br and Cl in Table 1 are those corresponding to the preferred orientation. The mean bond length of I-Br and I-Cl is 2.65 Å, which is shorter than the I-Br length in β-(BEDT-TTF)$_2$IBr$_2$(2.70 Å)[10] but longer than the I-Cl distance in β'-(BEDT-TTF)$_2$ICl$_2$(2.57 Å)[11]. There is no interanionic Br···Cl contact shorter than 4.0 Å, in contrast to the close I···I contact (3.90 Å) observed in α-(BEDT-TTF)$_2$I$_3$.[2] In α-(BEDT-TTF)$_2$I$_3$, the systematic difference in the bond lengths of the three crystallographically independent BEDT-TTF molecules suggests that the positive charges are not distributed uniformly. All the BEDT-TTF molecules on the inversion centers are neutral and only the molecules on the general positions are positively charged.[2,12] However, in α-(BEDT-TTF)$_2$BrICl, the large standard deviations of the bond lengths did not permit to confirm the charge localization. As shown in Fig. 2, the molecules A and B are stacked separately along [001]. However, α'-(BEDT-TTF)$_2$BrICl cannot be regarded as a one-dimensional(1D) system

Table 1. Atomic coordinates (x10^4) of α'-(BEDT-TTF)$_2$BrICl

	X	Y	Z		X	Y	Z
I	-31(1)	2527(2)	129(2)				
Br	-50(2)	3372(3)	-2184(4)				
Cl	-22(2)	1673(4)	2436(5)				
		BEDT-TTF(A)				BEDT-TTF(B)	
S1	6530(4)	6159(5)	3721(8)	S9	6319(4)	1055(5)	4918(8)
S2	6081(4)	3776(5)	3556(8)	S10	6343(4)	-1329(5)	2339(8)
S3	4742(4)	6245(5)	2199(8)	S11	4492(4)	1220(5)	3466(8)
S4	4247(4)	3907(5)	2119(9)	S12	4586(4)	-1131(5)	840(8)
S5	8248(4)	6251(5)	4869(8)	S13	8055(4)	1245(5)	6073(8)
S6	7723(4)	3388(6)	4564(8)	S14	8054(4)	-1646(5)	3059(8)
S7	3171(4)	6598(5)	871(9)	S15	2864(4)	1597(6)	2414(8)
S8	2550(4)	3819(5)	833(8)	S16	2965(4)	-1199(6)	-754(8)
C1	5756(11)	4990(17)	3153(24)	C11	5791(11)	-71(19)	3190(27)
C2	5011(11)	5031(20)	2565(23)	C12	5107(11)	16(18)	2604(25)
C3	7300(13)	5422(19)	4262(26)	C13	7251(11)	381(18)	4770(24)
C4	7085(13)	4342(18)	4177(25)	C14	7254(12)	-733(19)	3557(25)
C5	3746(13)	5671(18)	1496(24)	C15	3665(12)	648(18)	2000(24)
C6	3522(12)	4603(19)	1465(25)	C16	3724(13)	-430(18)	843(25)
C7	8884(15)	5165(28)	4970(62)	C17	8896(15)	356(22)	5290(38)
C8	8706(13)	4166(26)	4901(46)	C18	8733(15)	-909(22)	4790(39)
C9	2132(14)	5976(19)	727(29)	C19	2135(15)	795(21)	647(32)
C10	2036(14)	4614(21)	-160(29)	C20	2038(14)	-460(23)	151(34)

because there is no intermolecular S···S contact shorter than the van der Waals distance (3.70 Å) between the molecules along [001]. In contrast, there are many intermolecular short S···S contacts between the different stacks. Thus, the molecules A and B form 2D sulfur network similar to that of α-(BEDT-TTF)$_2$I$_3$. As pointed out by Kato et al., the "outer sulfur atoms (S_o)" of BEDT-TTF play an important role to form 2D sulfur network.[13] The shortest intermolecular $S_o \cdots S_o$ distance is 3.45 Å. The shortest $S_o \cdots S_i$ (inner sulfur atom) distance is 3.51 Å. There is no $S_i \cdots S_i$ contact less than the van der Waals distance of 3.70 Å. This structural feature is almost identical with that of α-(BEDT-TTF)$_2$I$_3$, where the shortest $S_o \cdots S_o$, $S_o \cdots S_i$ and $S_i \cdots S_i$ distances are 3.50, 3.51 and 3.76 Å, respectively.[2] The mean molecular plane of molecule A is not parallel to that of the molecule B. The dihedral angle between these two planes is 48°. In α-(BEDT-TTF)$_2$I$_3$, the dihedral angles between the molecule on the general position and two crystallographically independent molecules on the inversion centers are 70° and 59°.[2]

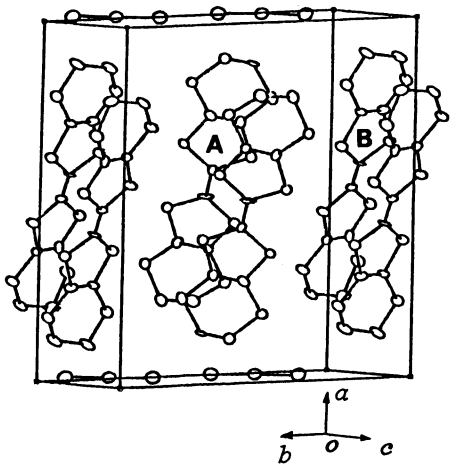


Fig. 1. The crystal structure of α'-(BEDT-TTF)$_2$BrICl. A and B indicate two crystallographically independent molecules of BEDT-TTF.

We calculated intermolecular overlap integrals of the highest occupied molecular orbital (HOMO) of BEDT-TTF, which give a measure of the magnitude and the anisotropy of the intermolecular interaction. The largest overlap integral obtained between the molecules A(1-x,1-y,-z) and B(x,1+y,z) (see Fig. 2) is the same order of the largest one in α-(BEDT-TTF)$_2$I$_3$ and about a half of those of β- and β'-type salts,[11] where A(or B)(x',y',z') denotes the molecule related to the molecule A(or B) defined in Figs. 1 and 2 by the symmetry operation (x',y',z'). The other interactions are very small. It should be recalled that the charge localization frequently observed in multi-dimensional organic conductors plays an important role to determine the electronic structure.[14] In the present work, we can not decide whether charge localization occurs or not in α'-(BEDT-TTF)$_2$BrICl. Nevertheless, the small intermolecular interactions suggest that the metallic state is hardly realized in the α'-type structure.

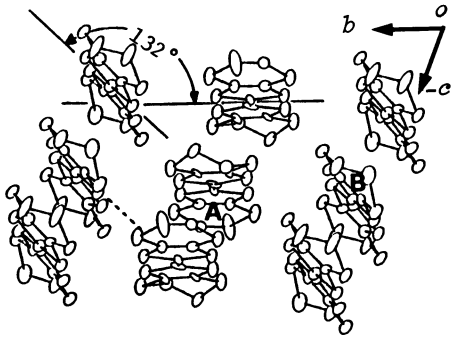
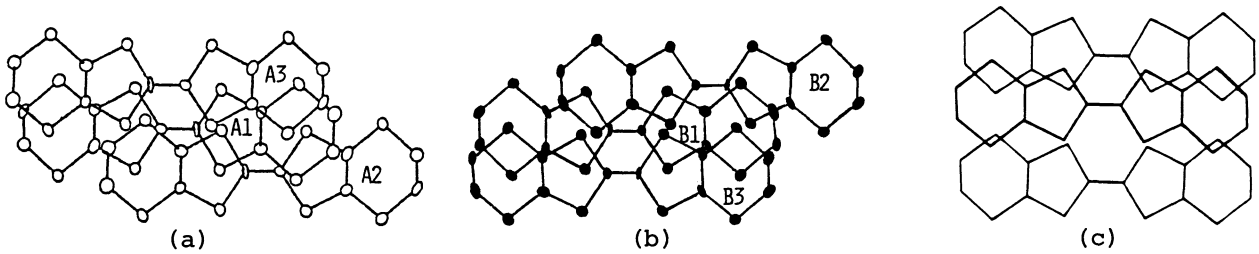


Fig. 2. Molecular arrangement in α'-(BEDT-TTF)$_2$BrICl. The broken line indicates the molecular pair with the largest intermolecular overlap integral.



BEDT-TTF(A):A1(x,y,z), A2(1-x,1-y,-z), A3(1-x,1-y,1-z)
BEDT-TTF(B):B1(x,y,z), B2(1-x, -y,-z), B3(1-x, -y,1-z)

Fig. 3. Modes of intermolecular overlap in α'-$(BEDT\text{-}TTF)_2BrICl$ ((a) and (b)). Overlapping mode in α-$(BEDT\text{-}TTF)_2I_3$ (Refs. 1 and 2) is shown for comparison (c).

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