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TWO-DIMENSIONAL CHARACTER OF CRYSTAL STRUCTURE OF ORGANIC CONDUCTOR, $(BMDT\text{-}TTF)_3PF_6$(1,2-DICHLOROETHANE)

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In the crystal of $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane) (BMDT-TTF= bis(methylenedithio)-tetrathiafulvalene), there are two crystallographically independent BMDT-TTF molecules whose molecular planes are approximately perpendicular to each other. This new type of molecular arrangement achieves the two-dimensional S···S network.

Crystal structures and physical properties of the molecular metals would be controlled by designing the constituent molecule. The organic conductors based on the donor molecule, BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene), have shown various physical properties; two-dimensional metallic properties, superconductivity and quasi-one-dimensional conduction along the transverse direction.[1] The crystal structures of these compounds are characterized by the inter-molecular S···S contacts in the transverse direction.[2] This is considered to arise from the extension of the TTF framework by incorporating the six-membered heterorings in the BEDT-TTF molecule. The structural features of the external heterorings in BEDT-TTF derivatives should be closely related to the mode of inter-molecular S···S contacts. We report here preparation of BMDT-TTF (bis(methylenedithio)-tetrathiafulvalene) where the TTF framework is extended by incorporating five-membered heterorings, and structure determination of its cation radical salt, $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane).

BMDT-TTF was prepared as follows;

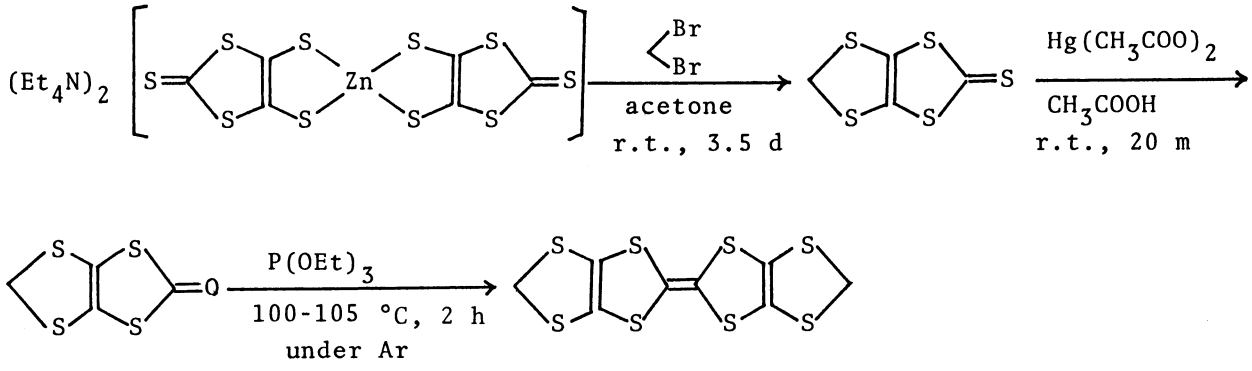


Table 1. Fractional atomic coodinates ($\times 10^4$). The e.s.d.'s are given in parentheses.

	x	y	z
S1	329(1)	6108(2)	7668(2)
S2	788(1)	3265(2)	7081(2)
S3	-1510(1)	4617(2)	7749(2)
S4	-1053(1)	1770(2)	7126(2)
S5	2047(1)	7487(2)	7409(2)
S6	2495(1)	4564(2)	6683(3)
S7	-3305(1)	3113(2)	7512(3)
S8	-2830(1)	300(2)	7049(2)
C1	25(3)	4248(6)	7364(8)
C2	-751(3)	3618(6)	7399(7)
C3	1318(3)	6004(6)	7373(8)
C4	1521(3)	4709(6)	7079(8)
C5	-2281(3)	3084(6)	7417(8)
C6	-2073(3)	1786(6)	7151(8)
C7	2889(4)	6580(8)	7413(12)
C8	-3673(4)	1038(8)	6313(10)
S9	659(1)	-311(2)	-2274(2)
S10	1205(1)	1490(2)	2042(2)
S11	2282(1)	1359(2)	-2600(2)
S12	2832(1)	3188(2)	1694(2)
C9	384(3)	251(5)	-41(8)
C10	1646(3)	974(6)	-1216(8)
C11	1888(3)	1777(6)	684(8)
C12	3186(4)	2431(8)	-498(10)
CL	4725(2)	4239(6)	7037(6)
CS	4944(8)	5681(13)	5258(20)
P	5000	0	0
F1	4850(3)	-1503(5)	260(7)
F2	4178(5)	117(10)	366(18)
F3	5458(8)	835(9)	2033(11)

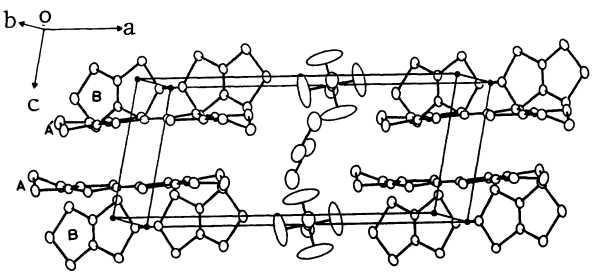


Fig. 1. Crystal structure.

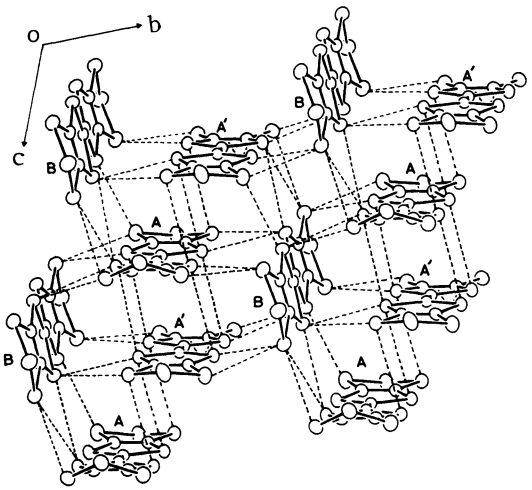
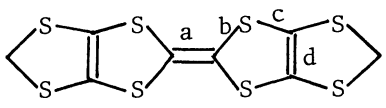


Fig. 2. Two-dimensional S···S network parallel to the bc plane. Short S···S distances (3.35-3.69 Å) are indicated by dotted lines.

Black plates of $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane) were obtained by the electrochemical oxidation (at a constant current of ca. 2 μA) of a solution containing BMDT-TTF (10^{-3} mol dm^{-3}) and $(n\text{-}Bu)_4NPF_6$ (10^{-1} mol dm^{-3}) in 1,2-dichloroethane. The crystal data: Triclinic, $P\bar{1}$, a=16.841(3), b=9.998(3), c=7.776(2) Å, α=113.64(2), β=99.72(2), γ=100.03(2)°, V=1138.6 $Å^3$, Z=1. Intensities were measured on a Rigaku automated diffractometer with Mo Kα radiation. The number of the independent reflections ($2\theta \leq 60°$, $|Fo| > 3\sigma(|Fo|)$) is 4438. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R value was 0.061. Final positional parameters are given in Table 1.

The crystal structure is shown in Fig. 1. The unit cell contains two crystallographically independent BMDT-TTF molecules (molecules A and B). The center of the molecule B is on the inversion center. The molecular arrangement of BMDT-TTF molecules is quite different from that in the conventional one-dimensional organic conductors. The molecular planes of the molecules A and B are nearly perpendicular to each other (a dihedral angle is ca. 100°). This new type of molecular arrangement achieves the two-dimensional S···S networks (Fig.2). These S···S networks are parellel to the bc plane and are separated from each other by PF_6^- anions and 1,2-dichloroethane molecules.

Table 2. Comparison of mean bond lengths of BMDT-TTF. The bond lengths are average values, with an approximated D_{2h} symmetry. The standard deviations are in the parentheses.



	Bond lengths / Å			
	a	b	c	d
Molecule A	1.36(1)	1.74(1)	1.73(2)	1.35(1)
Molecule B	1.32(2)	1.77(3)	1.75(3)	1.31(2)

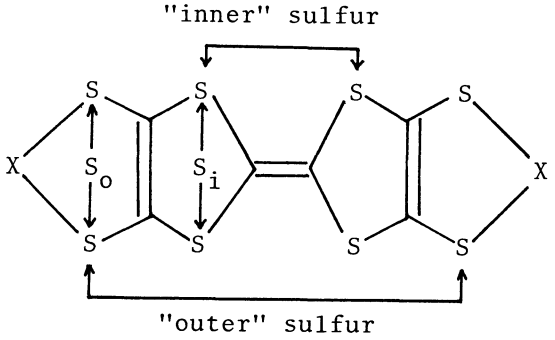
The bond lengths in TTF derivatives vary with their oxidation state. In the case of BEDT-TTF, the C-S distances in the TTF framework become shorter and the C=C distances become longer as the formal charge increases.[3] This is consistent with the result of the extended Hückel molecular orbital calculation; the HOMO has nodal planes on every C-S bond.[4] In the molecule A, the C-S distances in the TTF framework are shorter and the C=C distances are longer than those in the molecule B (Table 2). This suggests that the formal charge of the molecule A is larger than that of the molecule B.

The most prominent structural feature of $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane) is the molecular arrangement of donor molecules which enables "perpendicular" type inter-molecular overlapping of the sulfur orbitals. To investigate the molecular features related to the molecular arrangement and the mode of inter-molecular S···S contacts, we take the spread of sulfur atoms to the transverse direction (S_o and S_i, in Table 3; the sulfur atoms in the incorporated heterorings are named "outer" sulfur atoms and those in the TTF framework "inner" sulfur atoms.). When a donor molecule contains many sulfur atoms which contribute to the HOMO and project far toward the transverse direction, strong inter-molecular interaction through the sulfur atoms will occur in the transverse direction. Let us consider the S_o/S_i ratio of the BEDT-TTF and BMDT-TTF molecules. The S_o/S_i ratio of BEDT-TTF is larger than 1.0, that is, the "outer" sulfur atoms stick out more than the "inner" sulfur atoms. Thus, the transverse S···S contacts between the BEDT-TTF molecules are based on the "outer" sulfur atoms and no mutual transverse contact between the "inner" sulfur atoms cannot be observed (Fig. 3a). Since the contribution of the "outer" sulfur atoms to the HOMO is smaller than that of the "inner" sulfur atoms,[4] the S_o/S_i ratios larger than 1.0 are undesirable for the strong

Table 3. S_o/S_i ratios of BMDT-TTF and BEDT-TTF

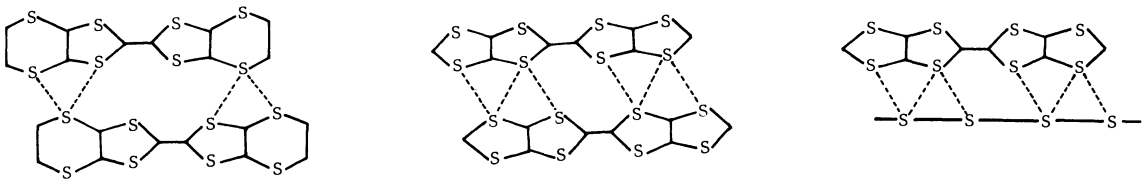
Compound		S_o	S_i	S_o/S_i
$(BMDT\text{-}TTF)_3PF_6(C_2H_4Cl_2)$	A	2.98	2.96	1.01
	B	2.97	2.98	1.00
α-$(BEDT\text{-}TTF)_2PF_6$ [5]		3.43	2.94	1.17
β-$(BEDT\text{-}TTF)_2PF_6$ [1c]		3.48	2.92	1.19

S_o and S_i distances (Å) given are average values.



BMDT-TTF; X=-CH_2-
BEDT-TTF; X=-$(CH_2)_2$-

Fig. 3. Molecular arrangements and possible close S···S contacts.



(a) (b) (c)

transverse S···S interaction. As planar molecules are most preferable for the face-to-face stacking, so molecules whose S_o/S_i ratio is 1.0 are preferred for the strong transverse S···S interaction (Fig. 3b). Furthermore, the change of the dihedral angle between adjacent molecular planes will not affect the number of close S···S contacts (Fig. 3c; dihedral angle 90°). This indicates that the BMDT-TTF molecules will take a wide variety of the molecular arrangement.[6]

In conclusion, the crystal structure of $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane) suggests that the ring size of the external heterorings influences the molecular arrangement in a crystal and dimensionality of a system. A detailed study of its physical properties is in progress.[7]

References

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5) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, T. Sasaki, G. Saito, and H. Inokuchi, Chem. Lett., 1983, 759.

6) Recently, we have prepared the ClO_4 salt of BMDT-TTF. The structure of this compound has the two-dimensional character, but is different from that of the PF_6 salt.

7) The electrical conductivity of $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane) was preliminarily measured along the direction approximately perpendicular to the a axis. The conductivity is thermally activated over the entire temperature range. The activation energy in the 205-115 K range E_a(205-115) is 0.11 eV, and E_a(290-205) is 0.20 eV. The conductivity reaches ca. 10 $(\Omega\ cm)^{-1}$ at room temperature.

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