CHEMISTRY LETTERS, pp. 1693 - 1696, 1984. © The Chemical Society of Japan 1984

CRYSTAL STRUCTURE OF (BMDT-TTF)$_3$ClO$_4$(1,2-DICHLOROETHANE). MOLECULAR DESIGN FOR THE MULTI-DIMENSIONAL MOLECULAR CONDUCTOR

Reizo KATO,* Hayao KOBAYASHI, Akiko KOBAYASHI,† and Yukiyoshi SASAKI†
Department of Chemistry, Faculty of Science, Toho University,
Funabashi, Chiba 274
†Department of Chemistry, Faculty of Science, The University of
Tokyo, Hongo, Bunkyo-ku, Tokyo 113

In the crystal of (BMDT-TTF)$_3$ClO$_4$(1,2-dichloroethane), inclined BMDT-TTF (bis(methylenedithio)TTF) molecules with dihedral angles of 57-58° construct the two-dimensional S···S network parallel to the ac plane. The steric and electronic features of BMDT-TTF suggest that BMDT-TTF will take a wide variety of the molecular arrangement which lead to the multi-dimensional molecular conductors.

The organic donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) has provided the first sulfur-based organic superconductors, (BEDT-TTF)$_2$ReO$_4$($T_c \approx 2$ K, above 4 kbar)$^{1)}$ and β-(BEDT-TTF)$_2$I$_3$($T_c \approx 1.4$-1.5 K, at ambient pressure).$^{2)}$ Recent studies of the crystal structures and the band structures of the BEDT-TTF compounds have revealed the importance of the two-dimensional intermolecular S···S interaction as a mean of the suppression of the Peierls instability.$^{3)}$ These rusults have thrown new light on the molecular design for the ground-state metal. In this paper, taking BMDT-TTF (bis(methylenedithio)tetrathiafulvalene) as an example of modification of the BEDT-TTF molecule, we report the crystal structure of (BMDT-TTF)$_3$ClO$_4$(1,2-dichloroethane) and consider the conditions of donor molecules available for the multi-dimensional molecular conductors.

Black elongated plates of (BMDT-TTF)$_3$ClO$_4$(1,2-dichloroethane) were obtained by the electrochemical oxidation (at a constant current of ca. 0.2 μA) of a solution containing BMDT-TTF (10^{-3} mol dm^{-3}) and (n-C$_4$H$_9$)$_4$NClO$_4$ (10^{-1} mol dm^{-3}) in 1,2-dichloroethane. The crystal data: Orthorhombic, Pnma, a=12.728(1), b=33.302(3), c=10.204(2) Å, V=4325.1 Å^3, Z=4. Intensities were measured on a Rigaku automated diffractometer with Mo Kα radiation. The number of the independent reflections ($2\theta<60°$, $|Fo|>3\sigma(|Fo|)$) is 2265. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R value was 0.093. Final positional parameters are given in Table 1.

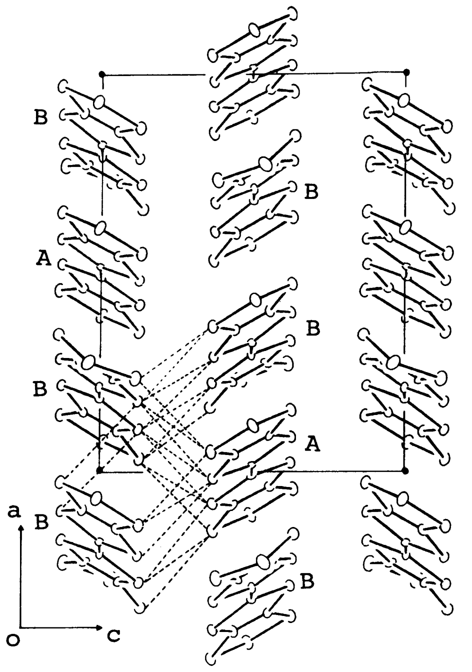


Fig. 1. Crystal structure of $(BMDT\text{-}TTF)_3ClO_4$(1,2-dichloroethane) viewed along the b axis. Short S···S distances (crystallographically independent; 3.423-3.691 Å) are indicated by dotted lines.

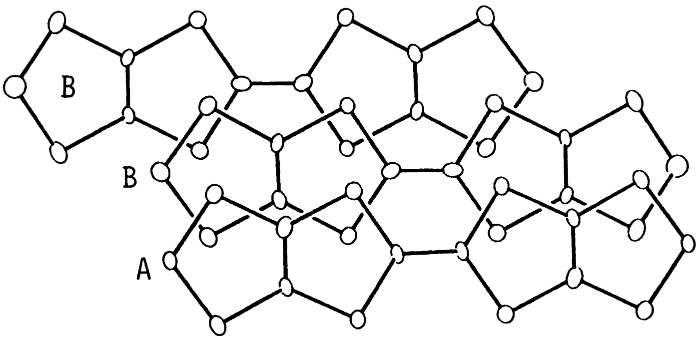


Fig. 2. Mode of intermolecular overlapping of BMDT-TTF molecules arranged along the a axis.

The crystal structure is throughly different from those of the conventional one-dimensional organic conductors (Fig. 1). The unit cell contains two crystallographically independent BMDT-TTF molecules (molecules A and B). The center of the molecule A is on the inversion center. BMDT-TTF molecules are arranged along the a axis with their molecular planes almost parallel to each other. The overlap of the molecular planes, however, is small (Fig. 2). The inclined BMDT-TTF molecules with dihedral angles of 57-58° construct the two-dimensional S···S network parallel to the

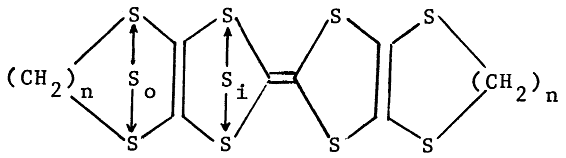
Table 1. Fractional atomic coordinates (× 10^4). The e.s.d.'s are given in parentheses [4)]

	x	y	z
S1	-206(3)	521(1)	3734(4)
S2	837(3)	416(1)	6281(4)
S3	460(3)	1403(1)	3660(4)
S4	1512(3)	1293(1)	6273(4)
S5	1731(3)	819(1)	1236(4)
S6	2806(3)	699(1)	-1329(3)
S7	1012(3)	-104(1)	1251(3)
S8	2140(3)	-239(1)	-1274(4)
S9	2309(4)	1713(1)	1146(4)
S10	3425(3)	1586(1)	-1377(4)
S11	291(3)	-977(1)	1287(4)
S12	1372(3)	-1111(1)	-1305(4)
C1	136(9)	205(3)	4997(13)
C2	400(11)	939(3)	4418(13)
C3	875(10)	887(4)	5598(13)
C4	1106(12)	1649(4)	5037(15)
C5	2081(10)	487(4)	-40(12)
C6	1785(9)	98(4)	-23(13)
C7	2290(10)	1236(3)	462(13)
C8	2772(10)	1183(4)	-666(13)
C9	980(11)	-584(4)	563(13)
C10	1461(10)	-631(3)	-567(12)
C11	2715(14)	1954(5)	-401(17)
C12	707(13)	-1354(4)	88(15)
CL1	5047(7)	2500	1641(9)
CL2	2845(9)	2500	3404(12)
CL3	234(6)	2500	-2338(6)
O1	1253(24)	2500	-2998(31)
O2	-401(25)	2500	-3360(27)
O3	220(14)	2152(4)	-1615(15)
CS1	4952(27)	2500	3350(31)
CS2	4012(37)	2310(11)	3771(36)

ac plane (Fig. 1), while in the crystal of (BMDT-TTF)$_3$PF$_6$(1,2-dichloroethane) the molecular planes of the BMDT-TTF molecules are nearly perpendicular to each other.$^{5)}$ Interaction of the BMDT-TTF molecules along the b axis is interrupted by ClO_4^- anions and 1,2-dichloroethane molecules. The comparison of the C=C and C-S bond distances between the molecules A and B indicates that the donor molecules are ionized as $A^+B^0B^0$.$^{5)}$ In the ground state, therefore, the holes are considered to be tend to be localized on the molecules A and (BMDT-TTF)$_3$ClO$_4$(1,2-dichloroethane) is not considered to be a simple metal.$^{6)}$

Let us consider (1) electronic and (2) steric factors of a series of BMDT-TTF, BEDT-TTF, and BPDT-TTF (Fig. 3).

(1) In a series of BMDT-TTF, BEDT-TTF, and BPDT-TTF, the π-like HOMO of BMDT-TTF spreads most widely over the molecule, because BMDT-TTF contains the minimum number of σ-bonding carbons.$^{7)}$ Such an extension of the π-system should increase the transverse overlap of the HOMO.



	n
BMDT-TTF	1
BEDT-TTF	2
BPDT-TTF	3

Fig. 3.

(2) The S_o/S_i ratio of BMDT-TTF is nearly 1.0 (for BEDT-TTF S_o/S_i=1.2, for BPDT-TTF S_o/S_i=1.2),$^{5)}$ where S_o and S_i are the spread of sulfur atoms to the transverse direction. 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. In addition, the change of the dihedral angle between adjacent molecular planes will not affect the number of close intermolecular S···S contacts.$^{5)}$ When the external heterorings cannot take a stable conformation, these molecules do not take an infinite face-to-face stacking. A typical example is BEDT-TTF.$^{3)}$ BPDT-TTF in which the chair conformation of the incorporated seven-membered heterorings is fixed can construct the infinite face-to-face stacking, in spite of the non-planarity of the molecule.$^{8)}$

These electronic and steric conditions suggest that BMDT-TTF will take a wide variety of the molecular arrangement which lead to the multi-dimensional molecular conductors.

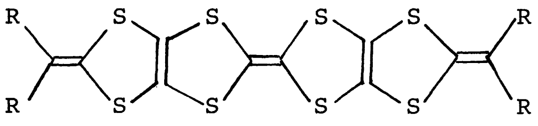
Finally, there are synthetic overtones associated with the above consideration. For the modification of the BEDT-TTF molecule, the following features should be preferable;

(1) π-like HOMO widely spreads over the molecule

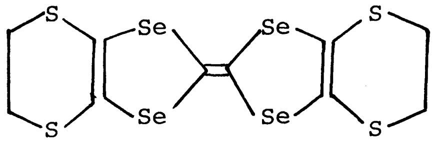
(2) S_o/S_i ratio is 1.0

(3) the terminal functional groups have rigid planarity.

1 and 2 are example molecules. The selenium analogue of the BEDT-TTF molecule should be of interest. In the BEDT-TSF (bis(ethylenedithio)tetraselenafulvalene(3) molecule, the S_o/S_i ratio is estimated to be about 1.09 (based on the structural data of $(TMTSF)_2PF_6$,[9] α- and β-$(BEDT\text{-}TTF)_2PF_6$). The van der Waals radius of selenium R(Se) is larger than that of sulfur R(S) (R(Se)/R(S)=1.08). Therefore, the extension of the selenium orbitals in the transverse direction is comparable to that of the sulfur orbitals. This will lead to the enhanced transverse intermolecular interaction.



1: R = H
2: R = CH_3-



3

References

1) S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, Phys. Rev. Lett., 50, 270 (1983).
2) E. B. Yagubskii, I. F. Shchegolev, V. N. Laukin, P. A. Kononovich, M. V. Kartosovnic, A. V. Zvarykina, and L. I. Buravov, Pis'ma Zh. Eksp. Teor. Fiz., 39, 12 (1984).
3) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 107, 33 (1984).
T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett., 1983, 1963; ibid., 1984, 957.
4) One of the carbon atoms in 1,2-dichloroethane (CS2) shows the positional disorder.
5) R. Kato, A. Kobayashi, Y. Sasaki, H. Kobayashi, Chem. Lett., 1984, 993.
6) Preliminary condictivity measurement showed that the electrical conductivity along the elongated axis was ca. 1 $(\Omega\ cm)^{-1}$ at room temperature and was thermally activated.
7) T. Mori, A. Kobayashi, Y. Sasaki, R. Kato, and H. Kobayashi, Chem. Lett., 1984, 1335.
8) R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 1984, 781.
9) N. Thorup, G. Rindorf, H. Soling, and K. Bechgaard, Acta. Crystallogr., Sect.B, 37, 1236 (1981).

(Received July 10, 1984)