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CRYSTAL STRUCTURE AND ELECTRICAL CONDUCTIVITY OF $(BPDT\text{-}TTF)_3(PF_6)_2$

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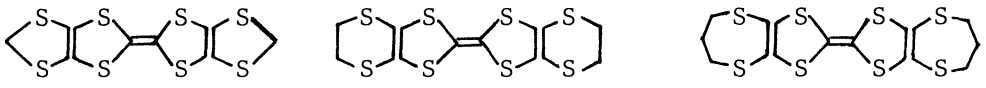
The crystal of $(BPDT\text{-}TTF)_3(PF_6)_2$ (BPDT-TTF=bis(propylenedithio)-tetrathiafulvalene) contains the one-dimensional columns of BPDT-TTF molecules along the a axis. These columns are interrelated to each other by close S···S contacts. The non-planarity of the molecule results in a relatively small number of intra- and inter-stack close S···S contacts. The conductivity is thermally activated, and the anisotropy of the conductivity is $\sigma_a : \sigma_b : \sigma_c = 1 : 10^{-1} : 10^{-3}$.

Recent studies on the cation radical salts of BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene) have renewed interest in designing organic donor molecules in view of the ground-state metal where metal-insulator transition is absent.[1] In the BEDT-TTF molecule, the tetrathiafulvalene π-framework has been extended by incorporating six-membered heterorings. This chemical modification has expanded the π-system in the molecule[2] and is responsible for the inter-molecular S···S contacts along the transverse direction in the crystal. The influence of the transverse S···S contacts manifests as a variety of physical properties; two-dimensional conducting properties and quasi-one-dimensional conduction along the transverse direction.[1]

In order to study the molecular features responsible for the multi-dimensional S···S interaction, we are investigating the TTF derivatives extended by incorporating heterorings with various ring sizes. (Fig. 1)[3] We report here the structure and the electrical conductivity of $(BPDT\text{-}TTF)_3(PF_6)_2$ (BPDT-TTF=bis(propylenedithio)-tetrathiafulvalene).



BMDT-TTF BEDT-TTF BPDT-TTF

Fig. 1.

The galvanostatic electrolysis of a 1,1,2-trichloroethane solution containing BPDT-TTF (10^{-3} mol dm^{-3}) and $(n\text{-}Bu)_4NPF_6$ (10^{-1} mol dm^{-3}) gave black hexagonal plates. Elemental anal. Found: C, 28.19; H, 2.58; S, 51.10%. Calcd for $C_{36}H_{36}S_{24}P_2F_{12}$: C, 28.30; H, 2.37; S, 50.35%. Crystal data: Monoclinic,

space group C2/m, a=13.156(5), b=12.802(2), c=16.865(4) Å, β=93.94(2)°, V=2833.7 Å^3, Z=2.[4]

The crystal structure is shown in Fig. 2. Two crystallographically independent BPDT-TTF molecules are named hereafter as molecules A and B. The center of the molecule A is on the two-fold axis and the long axes of both molecules A and B lie on the mirror plane. The seven-membered heterorings in the BPDT-TTF molecule take a chair conformation, and the plane containing the TTF framework bends obviously (especially, in the molecule B). Although the planarity of the molecule is broken, there exists face-to-face stacking of the BPDT-TTF molecules along the a axis (Figs. 3 and 4).

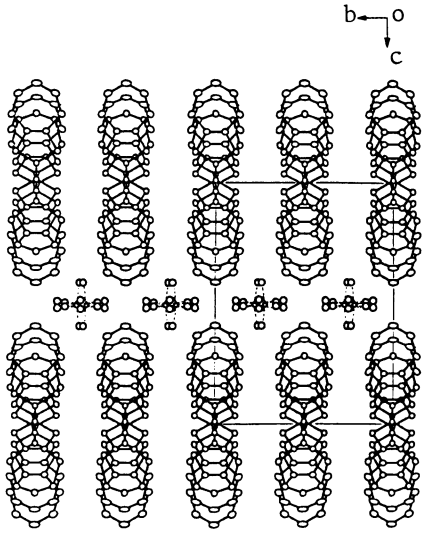


Fig. 2. Crystal structure viewed along the a* axis.[5]

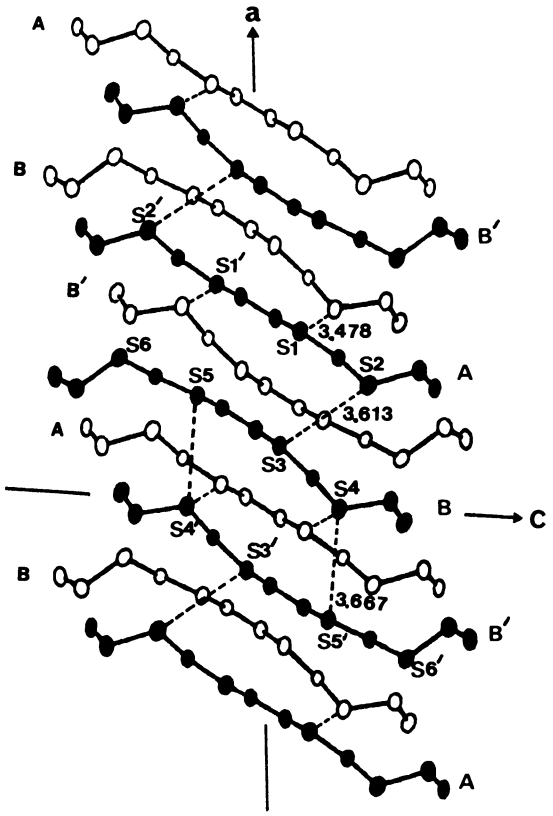


Fig. 3. Molecular stacking of BPDT-TTF molecules. The molecule B' is related to the molecule B by the two-fold axis. The front column (●) is related to the back column (○) by the symmetry operation (x+1/2,y+1/2,z).

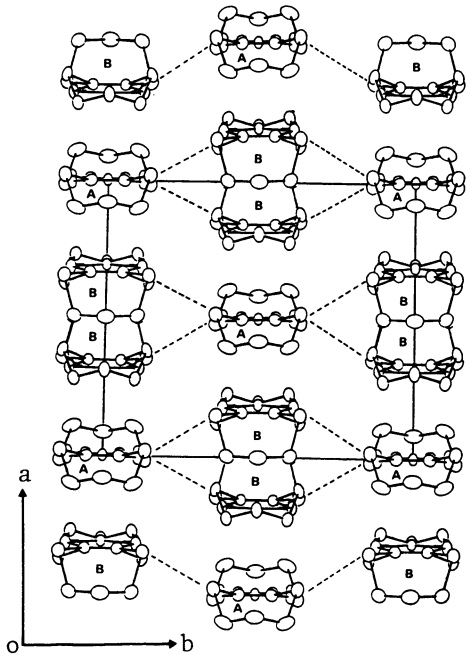


Fig. 4. Molecular stacking of BPDT-TTF molecules viewed along the c* axis.

There are a few short intra-stack S···S distances (slightly shorter than the van der Waals distance, 3.7 Å). The shortest S···S distance (3.478 Å) is observed between stacks (between molecules A and B), and is approximately parallel to the diagonal axis of the ab plane (Fig. 4). This is the only short inter-stack S···S distance (Fig. 5). As shown in Fig. 2, interaction of the BPDT-TTF molecules along the c axis is interrupted by PF_6^- anions.

The variations of the electrical conductivities measured along the a, b, and c axes (σ_a, σ_b, and σ_c) versus inverse temperature are shown in Fig. 6 for representative crystals. $(BPDT\text{-}TTF)_3(PF_6)_2$ is most conductive along the a axis, parallel to the BPDT-TTF columns. At room temperature, the anisotropy is $\sigma_a : \sigma_b : \sigma_c = 1 : 10^{-1} : 10^{-3}$. Around room temperature, the variations of the conductivities with temperature are small (the highest value of σ_a is ca. 0.3 $(\Omega\ cm)^{-1}$). Below ca. 250 K, the conductivities fall rapidly with lowering temperature, showing semiconductive character (the activation energies are in the range of 0.05 to 0.07 eV). Although the temperature dependence of the conductivities resembles that of the system exhibiting metal-semiconductor transition, obvious metallic behavior has not been observed.

The crystal structures of the organic conductors based on BEDT-TTF are characterized by the transverse inter-molecular S...S contacts. An infinite face-to-face stacking of the BEDT-TTF molecules has not been observed, since the terminal ethylene groups prevent the molecular stacking.[1] A large thermal motion of the ethylene groups indicates that the external six-membered heterorings cannot take a stable conformation.

The ring expansion (from six- to seven-members) affects mostly the planarity of the molecule and does not expand the sulfur atoms to the transverse direction, that is, the significant difference in the spread of the incorporated heterorings (S2-S2, S4-S4, and S6-S6 distances in Fig. 5) between BEDT-TTF

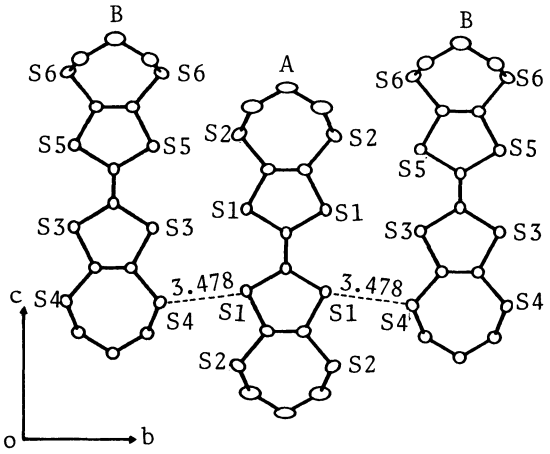


Fig. 5. Inter-stack S···S contacts, shorter than the van der Waals distance.

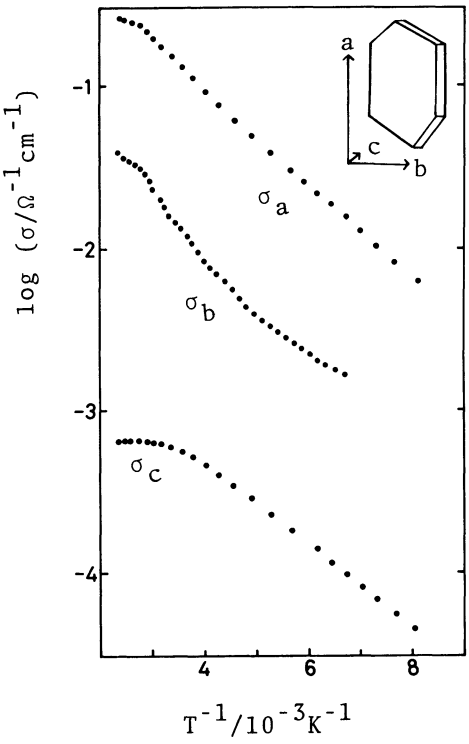


Fig. 6. Electrical conductivities of $(BPDT\text{-}TTF)_3(PF_6)_2$ along the a, b, and c axes.

and BPDT-TTF is not observed. This non-planarity of the molecule is largely responsible for the loose inter- and intra-stack S...S contacts in $(BPDT\text{-}TTF)_3(PF_6)_2$, compared with BEDT-TTF compounds.

On the other hand, the temperature factors of the terminal propylene groups in the BPDT-TTF molecule are not so large compared with those of other atoms, and the chair conformation of the incorporated seven-membered heterorings is considered to be fixed. Thus, in spite of the non-planarity of the molecule, the BPDT-TTF molecules clasp each other and construct the infinite face-to-face stacking.

In conclusion, the crystal of $(BPDT\text{-}TTF)_3(PF_6)_2$ contains the one-dimensional columns of the BPDT-TTF molecules, but the non-planarity of the molecule results in a relatively small number of intra-stack close S...S contacts. The shortest S...S distance is observed between stacks. These features of the crystal structure should be closely related to the relatively small anisotropy of the electrical conductivity in the ab plane.

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2) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett., 1982, 1963.

3) BEDT-TTF and BPDT-TTF can be prepared from the synthetic route given by M. Mizuno, A. G. Garito, and M. P. Cava, where 2-thioxo-1,3-dithiolates are important precursors; J. Chem. Soc., Chem. Commun., 1978, 18. BMDT-TTF (bis(methylenedithio)-tetrathiafulvalene) has been prepared by almost the same method, but the corresponding 2-thioxo-1,3-dithiole which was prepared from the reaction of the bis(isotrithionedithiolato)zincate with dibromomethane was converted to the 2-oxo-1,3-dithiole for coupling using triethylphosphite.

4) 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 2619. The structure was solved by the direct method and refined to the conventional R value of 0.084.

5) The PF_6^- anions show the positional disorder. The P-F bonds are indicated by dotted lines.

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