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Crystal Structure of α-(BEDT-TTF)$_2$PF$_6$

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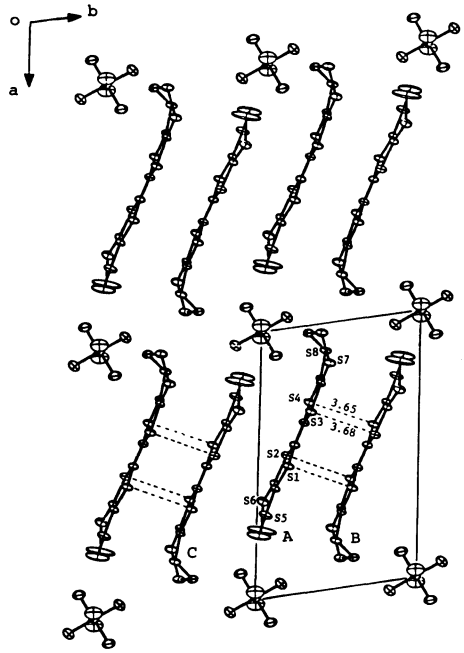
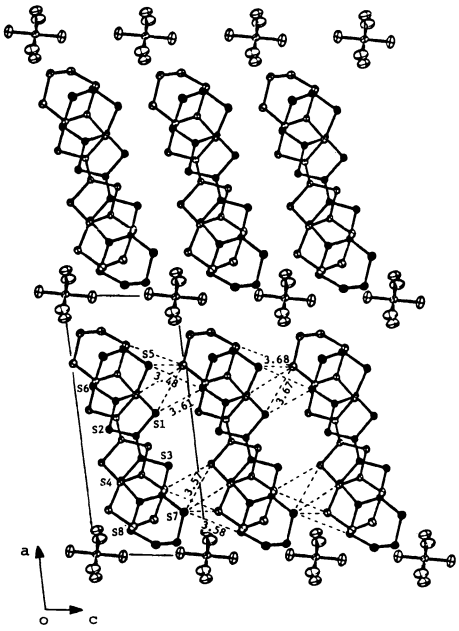
The crystal of α-(BEDT-TTF)$_2$PF$_6$ belongs to triclinic system (BEDT-TTF: bis(ethylenedithiolo)-tetrathiafulvalene). The close intermolecular contacts along the c axis suggests the strong tendency for the side-by-side arrangement of BEDT-TTF molecules. The electrical resistivity measurements show that α-(BEDT-TTF)$_2$PF$_6$ is a semiconductor with a small band gap of about 0.1 eV.

Recently the superconductivity of (BEDT-TTF)$_2$ReO$_4$ has been observed, which is the first observation of superconductivity in sulfur donor organic system.[1] The crystals of BEDT-TTF compounds have the characteristic side-by-side arrangement of BEDT-TTF molecules, which differs from the face-to-face stack of the planar molecules usually observed in the molecular metals. We have reported that β-(BEDT-TTF)$_2$PF$_6$ is the first organic conductor whose conductivity is the largest in the direction parallel to the molecular plane.[2] In this paper, the crystal structure of α-(BEDT-TTF)$_2$PF$_6$ will be presented.

The crystals of (BEDT-TTF)$_2$PF$_6$ were obtained electrochemically. X-Ray examination of the crystals revealed the polymorphism. The crystal of α-(BEDT-TTF)$_2$PF$_6$ is block-shaped and that of β-(BEDT-TTF)$_2$PF$_6$ is elongated plate.[2] The crystal date of α-(BEDT-TTF)$_2$PF$_6$ are: triclinic, space group $P\bar{1}$, a=14.711(2), b=8.597(1), c=6.462(1) Å, α=95.71(1), β=97.64(1), γ=98.87(1)°, V=794.3(2) Å^3, Z=1.

The crystal structure is shown in Fig. 1.[3] The PF_6^- anion is located on the centers of symmetry. As shown in Fig. 1, BEDT-TTF molecules are stacked face-to-face to form a column along the b axis. The mode of intermolecular overlapping are shown in Fig. 2. The intermolecular short contacts are given in Figs. 1 and 3. There is no short intermolecular contact between the molecules A and C (Fig. 1a) but there are two independent S..S contacts between the molecules A and B, slightly shorter than the van der Waals distance (3.7 Å). Thus, BEDT-TTF columns are considered to be composed of the weakly coupled BEDT-TTF dimers. The mode of the intradimer overlapping (A..B) is that of the direct overlapping and the mode of interdimer overlapping (A..C) is that of "ring-external bond type overlapping" usually found in 1-D organic metals. However, the intermolecular distance along the stack is not short enough to form 1-D system. Much shorter contacts are observed between the stacks. As shown in Fig. 3, the contacts shorter than 3.60 Å can be observed only along the c axis, which implies





(a) (b)

Fig. 1. (a) Crystal structure viewed along the c* axis. The molecules A and B are related by the symmetry operation (1-x,1-y, 1-z). (b) Crystal structure viewed along the b* axis.

the side-by-side arrangement of BEDT-TTF molecules. The shortest S..S distance is 3.48 Å which becomes 3.38 Å at 89 K.[3] The side-by-side array of BEDT-TTF is the most characteristic feature of the crystal structure of BEDT-TTF compounds.[2,4] The bond lengths and angles are given in Fig. 4. The anomalous thermal parameters of C(7) and C(8) indicate the positional disorder of one of the two ethylene groups. The structure analysis at 89 K revealed that the disorder disappears at low temperature.[4] The thermal expansion anomaly of the cell dimensions indicates that a positional order-disorder transition of the ethylene group takes place around 170 K.[3,5]

BEDT-TTF molecule is almost planar except for the ethylene groups, which is in contrast to the non-planar structure of neutral BEDT-TTF molecules.[6] The bond lengths given in Fig. 4 are in good agreement with those of other BEDT-TTF compounds

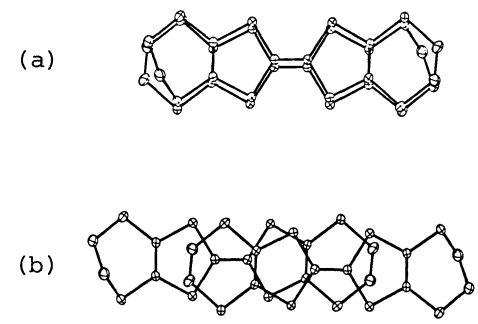


Fig. 2. Mode of intermolecular overlapping.
(a) molecules A and B (see Fig. 1a)
(b) molecules A and C

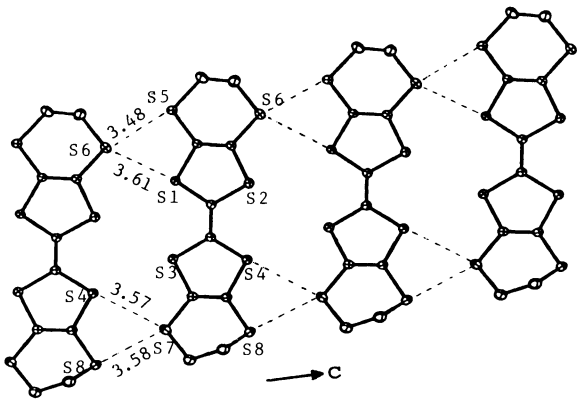


Fig. 3. The side-by-side arrangement of BEDT-TTF along the c axis.

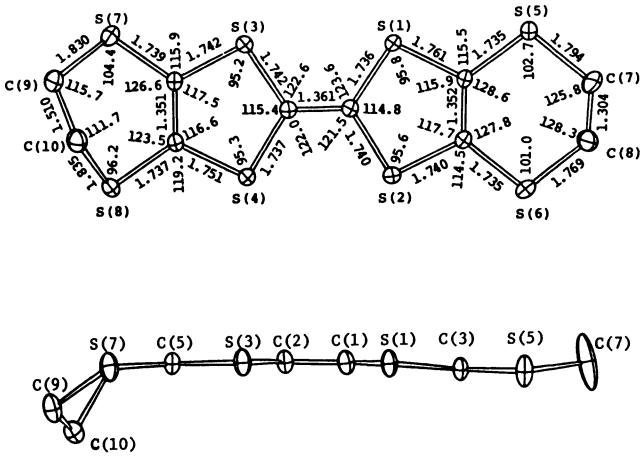


Fig. 4. Molecular structure of BEDT-TTF. The standard deviations of the bond lengths and angles are about 0.010 Å and 0.5°, respectively.

with the formal charge of 1/2 (BEDT-$TTF^{1/2}$: $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$[5]; β-$(BEDT\text{-}TTF)_2PF_6$[2]). But they significantly differ from those of the neutral molecules.[6] The large difference is observed in the central ethylenetetrathio group. The C=C bond length and the mean S-C bond length are 0.04 Å longer and 0.02 Å shorter than the corresponding bond lengths of neutral BEDT-TTF molecules, respectively. Since the highest occupied molecular orbital (HOMO) has the large amplitude at the atomic positions of the central ethylenetetrathio group but the amplitude is small for the outer ethylenetetrathio groups,[7] the difference in the bond lengths seems to be consistent with the variation of the bond orders accompanied by the change in the formal charge of BEDT-TTF.

As mensioned before, BEDT-TTF molecules in the $(BEDT\text{-}TTF)_2X$ compounds (X=ClO_4, PF_6) have a strong tendency for the side-by-side arrangement. The possible origin of this transverse array of BEDT-TTF molecules may be as follows:

(1) Since the atoms of the ethylene groups are not on the molecular plane, intermolecular steric repulsion makes the usual face-to-face overlapping unstable.

(2) In the π-donor molecules with chalcogen atoms, the face-to-face overlapping may not be necessary required for the intermolecular interaction because the mixing of the pπ and dπ atomic orbitals can be expected. The side-by-side arrangement is not suited for pπ-pπ interaction but it is not so unfavorable for dπ-dπ interaction.

(3) Since every sulfur atom in the six-membered rings has two short S..S contacts (Fig. 3), the sulfur atom seems to play an important role for the formation of the transverse arrangement. Since the energy levels of the occupied σ-orbitals are considered to be well below that of HOMO, the σ-orbitals may not contribute to the electrical conduction but it may contribute to the formation of the side-by-side arrangement. It might be possible that the σ(or *n*) orbitals interact with the unoccupied molecular orbital of the adjacent molecule through sulfur atoms. Similar intermolecular interaction can be expected in the well-known "2D-organic metal", HMTSF-TCNQ whose two-dimensionality is considered to come from the interstack interaction between Se atom of HMTSF and the terminal N atom of TCNQ.[8]

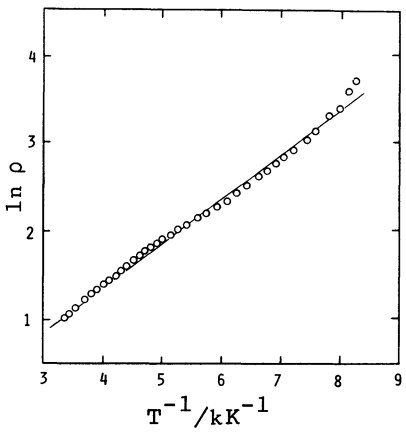


Fig. 5. Electrical resistivity of α-$(BEDT\text{-}TTF)_2PF_6$ along the direction approximately perpendicular to the a axis.

Most of the molecular metal known to date are

regarded as 1-D systems. Since the CDW (or SDW) instability inherent in 1-D metal tends to break the metallic state, the transverse interaction must be introduced in order to stabilize the metallic state. However if the transverse interaction is sufficiently strong, the system will be one-dimensional in the transverse direction. In fact, β-(BEDT-TTF)$_2$PF$_6$ is most conductive along the direction parallel to the side-by-side array. The metal-insulator transition has been observed at 297 K.[2] On the other hand, (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$ is a 2-D metal, which retains metallic conductivity down to 1.4 K.[9] The band structure calculation suggests that (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$ is a semimetal.[8] Reflection spectra also suggests the semimetallic properties of the compounds.[10] Preliminary measurement of the electrical resistivity indicate that α-(BEDT-TTF)$_2$PF$_6$ is a semiconductor with a small band gap of about 0.1 eV (Fig. 5). The variety of the electrical properties of BEDT-TTF compounds may be originated from the delicate balance of the intermolecular parallel and perpendicular interactions.

References

1) S.S.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) H.Kobayashi, T.Mori, R.Kato, A.Kobayashi, Y.Sasaki, G.Saito and H.Inokuchi, Chem. Lett., 1983, 581.
3) The structure was determined at room temperature using 3884 independent reflections measured with Mo Kα radiation for which $|Fo|>3\sigma(|Fo|)$ ($2\theta<60°$). The final R factor is 0.056. The low-temperature structure was also determined at 89 K using 9828 independent reflections ($2\theta<90°$) in order to obtain detailed structural information, which will be reported elsewhere by H. Kobayashi et al.
4) H.Kobayashi, A.Kobayashi, Y.Sasaki, G.Saito, T.Enoki and H.Inokuchi, J. Am. Chem. Soc., 105, 297 (1983).
5) H.Kobayashi, A.Kobayashi, Y.Sasaki, G.Saito, T.Enoki and H.Inokuchi (to be published)
6) H.Kobayashi, A.Kobayashi, Y.Sasaki, G.Saito and H.Inokuchi (to be published)
7) T.Mori, A.Kobayashi, Y.Sasaki, H.Kobayashi, G.Saito and H.Inokuchi, Chem. Lett., 1982, 1963.
8) A.N.Bloch, T.F.Carruthers, T.O.Poehler and D.O.Cowan, "Chemistry and Physics of One-Dimensional Metals", pp 47-85, ed. by H.J.Keller, Plenum Press, New York and London (1977).
9) G.Saito, T.Enoki, K.Toriumi and H.Inokuchi, Solid State Commun., 42, 557 (1982).
10) H.Tajima et al. (to be published)

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