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ONE-DIMENSIONAL NATURE OF THE BAND-STRUCTURE PARAMETERS OF $(BPDT\text{-}TTF)_3(PF_6)_2$ AND $(BPDT\text{-}TTF)_2I_3$

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Calculation of band-structure parameters of novel organic conductors, $(BPDT\text{-}TTF)_3(PF_6)_2$ and $(BPDT\text{-}TTF)_2I_3$ (BPDT-TTF: bis(propylenedithio)tetrathiafulvalene), elucidates their one-dimensional nature. The tendency of BPDT-TTF to form highly anisotropic compounds is explained by means of the small spread of the highest occupied molecular orbital (HOMO) to the outer heterorings.

A considerable number of organic conductors based on BEDT-TTF have been prepared and characterized (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene).$^{1)}$ It has already been reported that two of them show superconductivity.$^{2,3)}$ It is characteristic of the BEDT-TTF compounds that the side-by-side intermolecular interaction is comparable to the face-to-face interaction. Since one-dimensional metal is instable to the Peierls transition, high dimensionality is one of the important requirements for designing organic superconductors.

Recently, the crystal structures of $(BPDT\text{-}TTF)_3(PF_6)_2$, $(BPDT\text{-}TTF)_2I_3$ and $(BMDT\text{-}TTF)_3PF_6(C_2H_4Cl_2)$ have been reported (BMDT-TTF: bis(methylenedithio)tetrathiafulvalene);$^{4-6)}$ in BPDT-TTF and BMDT-TTF, the ethylene groups of BEDT-TTF are replaced by propylene and methylene respectively. We report the calculation of band-structure parameters of $(BPDT\text{-}TTF)_3(PF_6)_2$ and $(BPDT\text{-}TTF)_2I_3$, and discuss the difference in the HOMO among BMDT-TTF, BEDT-TTF, and BPDT-TTF.

Figure 1 shows the arrangement of BPDT-TTF in $(BPDT\text{-}TTF)_3(PF_6)_2$ (space group C2/m).$^{4)}$ The BPDT-TTF molecules form sheets parallel to [001]. These sheets are separated by PF_6 anions located between them. The molecular orbitals of crystallographically independent two molecules (A and B) are calculated by means of the extended Hückel method. The Slater exponents and the ionization potentials (including sulfur 3d orbitals) are the same as those used in a previous report.$^{7)}$ The intermolecular overlaps S of the HOMO are calculated as shown in Table 1. Table 1 also shows parameters, ϕ and D, describing the configuration of the neighbor molecules;$^{7)}$ they are defined in Fig. 2. The BPDT-TTF molecules are stacked face-to-face (ϕ=90°) along the a-axis. Three molecules form a repeating unit and there are two modes of intermolecular overlaps. But these two overlaps

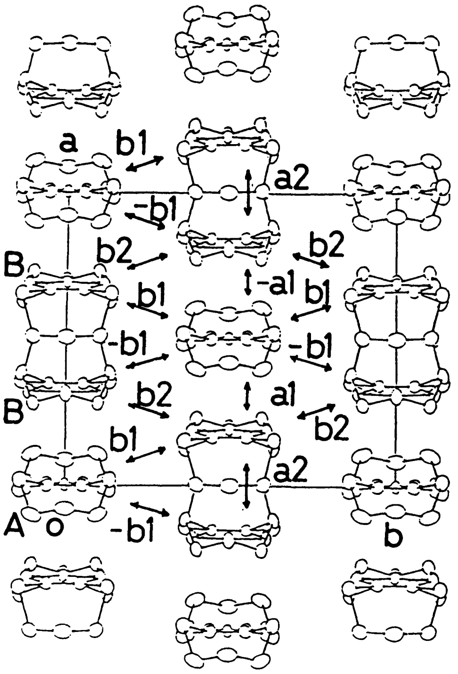
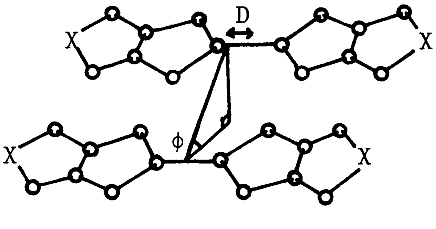


Fig. 1. Intermolecular overlaps in $(BPDT\text{-}TTF)_3(PF_6)_2$.

Table 1. Intermolecular overlaps of the HOMO in $(BPDT\text{-}TTF)_3(PF_6)_2$

Direction		$S /10^{-3}$	ϕ /°	D /Å
a1	[100]	19.6	90	1.4
a2	[100]	13.2	90	4.5
b1	[160]	0.66	15	2.3
b2	[160]	2.65	17	0.8



$X=-(CH_2)_3-$

Fig. 2. Relative orientation of two BPDT-TTF molecules.

a1 and a2 are not largely different each other (Fig. 1 and Table 1). The trasverse overlaps b1 and b2 are much smaller than a1 and a2; the anisotropy is considerably large. This is consistent with the anisotropy of the conductivity, $\sigma_a/\sigma_b \approx 10$.4) Since the periodicity along the a-axis is 3-fold, the band structure is semiconductive. The transfer integrals t evaluated by t=ES and E=-10 eV give a band gap of about E_g=0.11 eV. This agrees with the value obtained from the conductivity, E_g=0.10-0.14 eV.4)

The crystal structure of $(BPDT\text{-}TTF)_2I_3$ is shown in Fig. 3 (space group $P\bar{1}$).5) The intermolecular overlaps of the HOMO are, as before, calculated as shown in Table 2. It has been pointed out that the crystal structure of $(BPDT\text{-}TTF)_2I_3$ closely resembles that of superconducting β-$(BEDT\text{-}TTF)_2I_3$.5) However, the nature of the intermolecular overlaps is quite different.8) In β-$(BEDT\text{-}TTF)_2I_3$, the longitudinal interaction p2 is about 1/3 of p1; in $(BPDT\text{-}TTF)_2I_3$, p2 is about 1/2 of p1. It may be said that BPDT-TTF shows less tendency to make a dimer than BEDT-TTF. In β-$(BEDT\text{-}TTF)_2I_3$, a transverse interaction q1 is larger than the smaller longitudinal interaction p2, and the anisotropy of the interaction is very small. As a result, the Fermi surface of β-$(BEDT\text{-}TTF)_2I_3$, obtained by the simple tight-binding approximation, is closed in the bc-plane. On the contrary, in $(BPDT\text{-}TTF)_2I_3$, q1 is about 1/2 of p2. In general, the transverse interactions in the BPDT-TTF compounds are considerably smaller than those in the BEDT-TTF compounds. The band-structure parameters in Table 2 give open Fermi surface perpendicular to the p(=b+c) direction. This agrees with the anisotropy of the conductivity, $\sigma_p/\sigma_c \approx 10$.5) However, this compound shows semiconductive conduc-

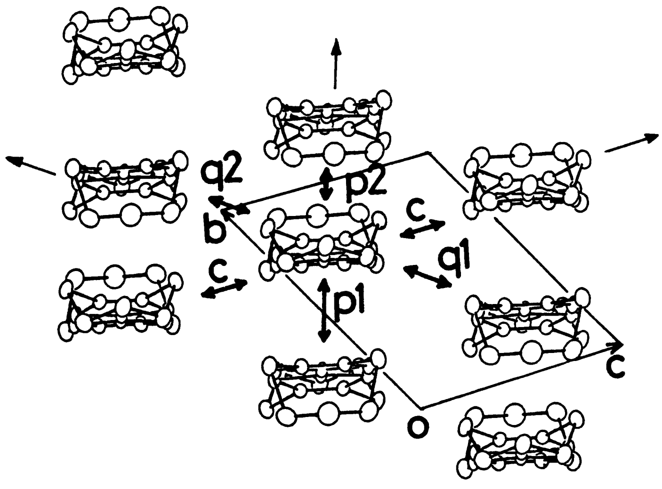


Fig. 3. Intermolecular overlaps in $(BPDT\text{-}TTF)_2I_3$.

Table 2. Intermolecular overlaps of the HOMO in $(BPDT\text{-}TTF)_2I_3$

Direction		$S\ /10^{-3}$	ϕ /°	D /Å
p1	[011]	-21.3	87	1.5
p2	[011]	-12.7	86	4.4
q1	[01$\bar{1}$]	-6.4	21	0.5
q2	[01$\bar{1}$]	-3.3	21	2.4
c	[001]	1.6	11	2.0

tivity even at room temperature. It is possible that the chain along [011] is distorted and the Fermi surface is nested even at room temperature. But superlattice has not been observed so far. Another possibility is localization caused by electronic correlation.

In BEDT-TTF compounds, it has been considered that the steric effect of the ethylene groups prevents the formation of face-to-face stacking and enhances the two-dimensional nature.[1,7)] Although, at first sight, the steric effect of BPDT-TTF seems to be larger than that of BEDT-TTF, the flexibility of the propylene groups makes it possible for BPDT-TTF to stack face-to-face.

Figure 4 shows atomic population of the HOMO of BMDT-TTF, BEDT-TTF, and BPDT-TTF. The population on the outer sulfur S_2 decreases as BMDT-TTF>BEDT-TTF>BPDT-TTF. In BMDT-TTF, the HOMO spreads most widely over the molecule. The population on S_2 is sensitive to the deviation of the group X from the molecular plane. If the group X deviates from the molecular plane, the π-like orbitals on the S_2 atoms contribute to the σ-bonding with the out-of-plane carbons. Therefore, their contribution to the π-like HOMO is reduced. Since transverse short S•••S contacts are found in $S_2 \cdots S_2$ and $S_1 \cdots S_2$ as well as $S_1 \cdots S_1$, the transverse overlap of the HOMO is expected to reach maximum when the populations of the HOMO on S_1 and S_2 are nearly equal. On the contrary, in the BPDT-TTF compounds, the population on S_2 is much smaller than that on S_1. Therefore, the transverse overlaps in the BPDT-TTF compounds are considerably smaller than those in the

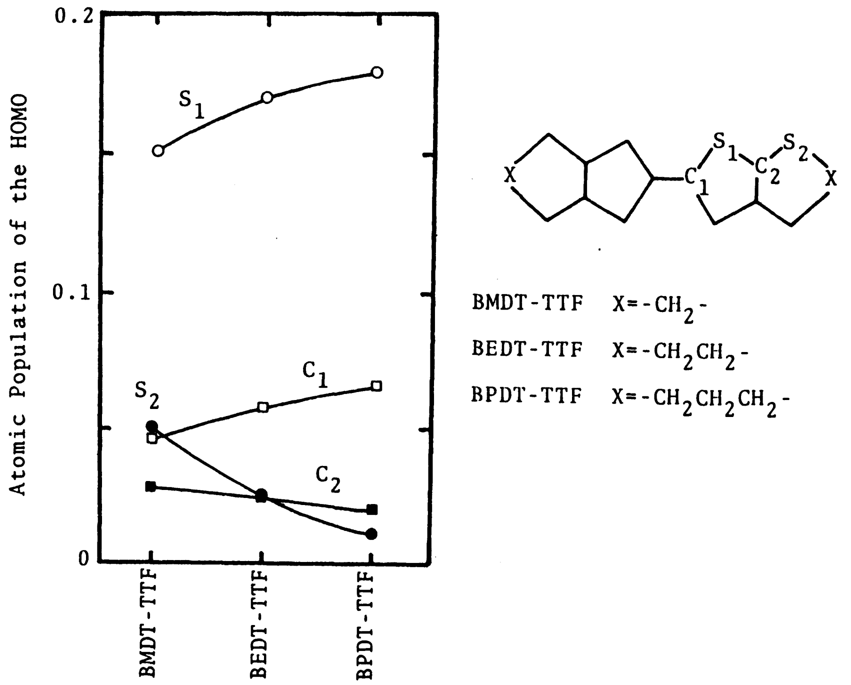


Fig. 4. Atomic population of the HOMO of BMDT-TTF, BEDT-TTF, and BPDT-TTF.

BEDT-TTF compounds.

It may be of interest that, in the molecules of the BEDT-TTF family, the degree of the spread of the HOMO and the dimensionality of the compounds are changed by the choice of the substituents X. This fact will be important in designing new organic conductors.

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