CHEMISTRY LETTERS, pp. 1963-1966, 1982.

TWO-DIMENSIONAL BAND STRUCTURE OF AN ORGANIC METAL, PERCHLORATE SALT OF BIS(ETHYLENEDITHIOLO)-TETRATHIAFULVALENE $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$

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The intermolecular overlap integrals and the band structure of the perchlorate salt of bis(ethylenedithiolo)-tetrathiafulvalene $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ were calculated using semiempirical molecular orbital calculation. The ratio of the transverse and the longitudinal overlap integrals is 3-10 and the complex is regarded as a new-type two-dimensional organic semimetal.

So far a linear stacking of planar molecules has been regarded as the indispensable requirement of organic metals. One of the central interests of this field has been concerned with the physical properties of typical conductors with one-dimensional electronic structure, such as charge and spin density waves and the Peierls instabilities. The discovery of the organic superconductor $(TMTSF)_2X$ (X= PF_6, AsF_6, SbF_6, and ClO_4) has refreshed the interests in organic conductors.[1)] It was pointed out that in $(TMTSF)_2X$ the interchain coupling plays an important role on the suppression of the Peierls instability.[2)] However our recent calculation indicated that $(TMTSF)_2X$ has a quasi-one-dimensional plane-like Fermi surface.[3)] Recently Saito et al. reported that the perchlorate salt of bis(ethylenedithiolo)-tetrathiafulvalene $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ retains metallic conductivity down to 16K, below which the resistivity increases slightly, but it shows high conductivity $670\Omega^{-1}cm^{-1}$ even at 1.4K.[4)] The X-ray structure analysis shows that $(BEDT\text{-}TTF)_2ClO_4$ does not have column structure characteristic to one-dimensional organic conductors.[5,6)] In this letter we report an attempt to calculate the intermolecular overlap integrals and to presume the band structure in $(BEDT\text{-}TTF)_2ClO_4$.

First we performed molecular orbital calculation by means of extended Hückel method.[7)] The highest occupied molecular orbital (HOMO) has similar symmetry, which corresponds with b_{1u} in ideal D_{2h} symmetry, as those of TTF and TMTSF (Fig. 1). Since the energy level of the HOMO is energetically far from the other levels, we considered only the HOMO in the following band calculation.[8] A unit cell contains four BEDT-TTF molecules (Fig. 2). Symbols A and B designate crystallographically independent molecules. The intermolecular overlap integrals of the HOMO are shown in Table 1. Sulfur 3d orbitals are not included in the calculation because they provide very little change of the ratio of the overlap integrals.[3] The interaction along the [102] direction resembles the stacking of the usual organic conductors. However, since the S-S distances are relatively large, the overlap integrals along [102] are the smallest. There is no face-to-face intermolecular overlapping along the $[\bar{1}02]$ direction, but some short S-S contacts and the appropriate molecular orientation cause the largest overlap integrals. In spite of the shortest S-S distances, the magnitudes of the overlap integrals along [100] are in the middle of the others. This is due to the p_π character of the HOMO. The interaction along the b axis is considered to be much smaller because of the large separation of the BEDT-TTF molecules.

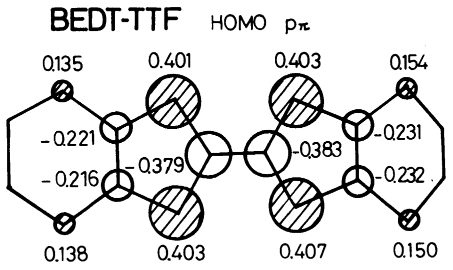

Fig. 1. Coefficients of the HOMO.

The transfer integrals are related to the overlap integrals by the equation

$$t_i = E\ S_i, \qquad (1)$$

where E is a constant of the order of the potential energy of the HOMO. The secular equation to be solved is

$$|H_{ij}(k) - \varepsilon(k) S_{ij}| = 0. \qquad (2)$$

The Fock matrix $H_{ij}(k)$ can be obtained from t_i [9]

$$H_{11}(k)=H_{22}(k)=H_{33}(k)=H_{44}(k)=0$$

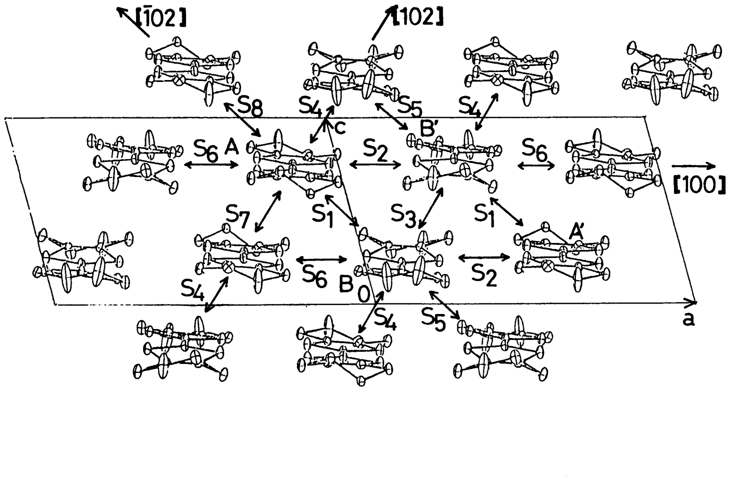

Fig. 2. Intermolecular interaction of BEDT-TTF.

Table 1. Overlap integrals of the HOMO illustrated in Fig. 2.

	Direction	$\times 10^{-3}$
S_1	$[\bar{1}02]$	-5.287
S_2	[100]	-1.570
S_3	[102]	-0.688
S_4	[102]	-0.621
S_5	$[\bar{1}02]$	8.138
S_6	[100]	-1.919
S_7	[102]	0.551
S_8	$[\bar{1}02]$	5.525

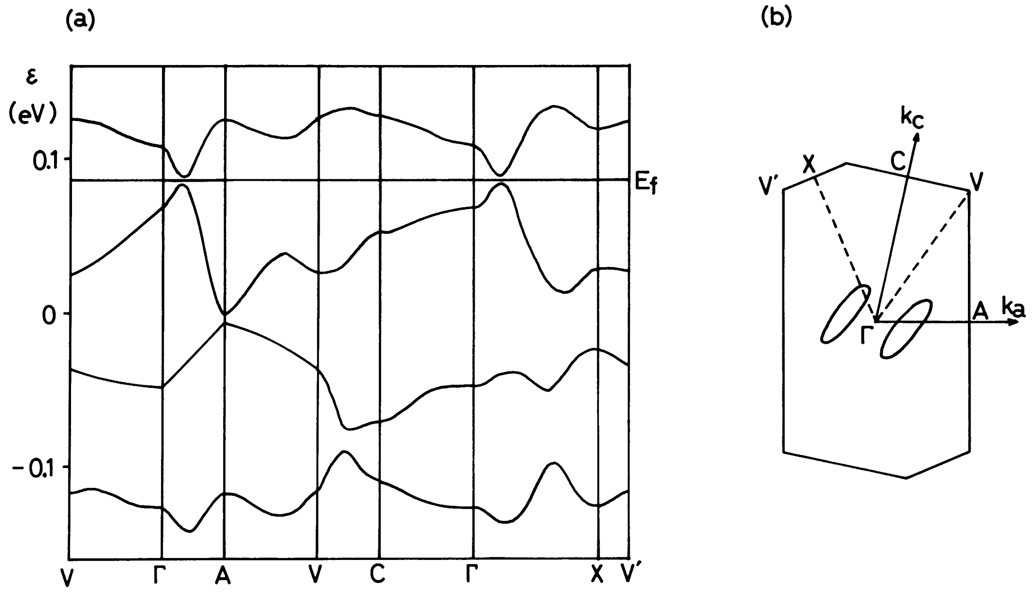

Fig. 3. Energy band structure of $(BEDT\text{-}TTF)_2ClO_4$.

$$\begin{aligned}
&H_{12}(k)=H_{43}(k)=H_{21}(k)^*=H_{34}(k)^*=t_1+t_5e^{ikc}\\
&H_{13}(k)=H_{31}(k)^*=t_4+t_8e^{-ika}+t_9e^{i(kc-ka)}\\
&H_{14}(k)=H_{23}(k)=H_{41}(k)^*=H_{32}(k)^*=t_2+t_7e^{-ika}\\
&H_{24}(k)=H_{42}(k)^*=t_3+t_6e^{-ikc}.
\end{aligned} \tag{3}$$

Solving the real quadruple equation resulted from Eqs. 2 and 3, we obtained the band structure in Fig. 3(a). The constant E in Eq. 1 was taken as -10eV. Since a unit cell contains four molecules, there are four energy levels. From the stoichiometry of the complex it is resulted that three quarters of the four energy levels are filled. Thus we find the Fermi level between the third and the fourth levels. These levels approach each other in the area designated in Fig. 3(b), but the detail around this point could not be determined satisfactorily on account of the enhanced error of the degenerated solutions. Two possibilities remain to be determined; a narrow gap semiconductor or a semimetal. Because of the metallic conductivity down to low temperatures, the latter interpretation is preferred. If one considers as a small interaction along the [010] direction as the order of a tenth of the smallest interaction in the

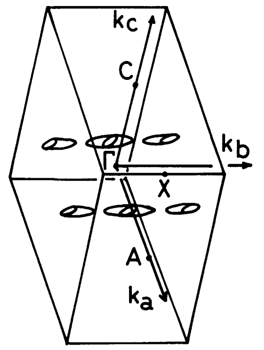

Fig. 4. Proposed Fermi surface.

Table 2. Overlap integrals and the experimental transfer integrals.

		Smax	$S_{/\!/}/S_{\perp}$	$t_{/\!/}$/eV
TTF-TCNQ[9-10]	TCNQ	20×10^{-3}	~100	0.1
	TTF	9×10^{-3}		
$(TMTSF)_2X$[3]		36×10^{-3}	~10	0.3
$(BEDT\text{-}TTF)_2ClO_4$		6×10^{-3}	0.1~0.3	?

a-c plane, both the third and the fourth levels can cross the Fermi level in the different region of k_b. Therefore we propose that the Fermi surface consists of two closed hole and electron parts which lie alternately along the b axis (Fig. 4).

The overlap integrals calculated by extended Hückel method and the transfer integrals obtained from the plasma frequency in TTF-TCNQ, $(TMTSF)_2X$, and $(BEDT\text{-}TTF)_2ClO_4$ are listed in Table 2. The overlap in $(BEDT\text{-}TTF)_2ClO_4$ is considerably smaller than the others. If one boldly neglects the difference of the band structure, the $t_{\parallel}$ in $(BEDT\text{-}TTF)_2ClO_4$ is expected to be the order of 0.05eV. The ratio of the longitudinal and the transverse overlap integrals decreases in the order; TTF-TCNQ>$(TMTSF)_2X$>$(BEDT\text{-}TTF)_2ClO_4$, which demonstrates the reducing anisotropy. In most of the organic metals with face-to-face stacking, the Fermi surface is expected to be a plane. In fact the band calculation in TTF-TCNQ was reported to produce a one-dimensional plane Fermi surface.9) On the contrary, in $(BEDT\text{-}TTF)_2ClO_4$ the similar calculation leads to the multidimensional band structure. The absense of the Peierls transition is explained from the result that this complex has no one-dimensional Fermi surface to nest. Note that this is caused by the characteristic crystal structure; the distortion of the molecules from a planar structure, the absence of a face-to-face stacking, and the short transverse contacts.

In summary we confirmed that the band structure of $(BEDT\text{-}TTF)_2ClO_4$ is completely different from those of other one-dimensional organic metals. Our band calculation strongly indicates that $(BEDT\text{-}TTF)_2ClO_4$ is a new-type multi-dimensional organic semimetal. The discovery of the metallic nature of $(BEDT\text{-}TTF)_2ClO_4$ brings us to expect the possibility of another two- and three-dimensional organic metals.

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6) From now on let us omit the solvent molecule $(C_2H_3Cl_3)_{0.5}$ from the formulas.
7) The semiempirical parameters were chosen after Ref. 11. AO's are Slater-type.
8) This approximation was tested in the band calculation of $(TMTSF)_2X$. The band structure obtained only from the HOMO fairly coincided with the result of the calculation including all valence orbitals.
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(Received October 1, 1982)