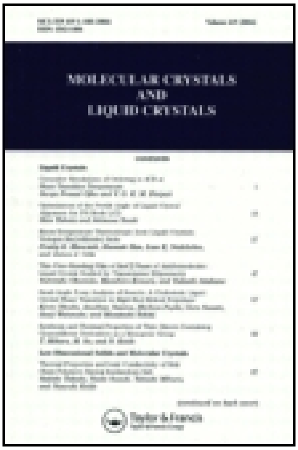

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Organic Conductors Based on Multi-Sulfur π-Donor And/Or π-Acceptor Molecules-Bedt-Ttf, Bmdt-Ttf, Bpdt-Ttf, And m(dmit)$_2$-

Hayao Kobayashi [a] , Reizo Kato [a] , Takehiko Mori [b a] , Akiko Kobayashi [b a] , Akiko Kobayashi [b a] , Yukiyoshi Sasaki [b a] , Gunzi Satto [c a] & Hiroo Inokuchi [c a]

[a] Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba, 274, Japan

[b] Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan

[c] Institute for Molecular Science, Okazaki, 444, Japan

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ORGANIC CONDUCTORS BASED ON MULTI-SULFUR π-DONOR AND/OR π-ACCEPTOR MOLECULES—BEDT-TTF, BMDT-TTF, BPDT-TTF, AND $M(dmit)_2$—

HAYAO KOBAYASHI, REIZO KATO
Department of Chemistry, Faculty of Science,
Toho University, Funabashi, Chiba 274, Japan

TAKEHIKO MORI,[†] AKIKO KOBAYASHI, and
YUKIYOSHI SASAKI
Department of Chemistry, Faculty of Science, The
University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

GUNZI SAITO[††] and HIROO INOKUCHI
Institute for Molecular Science, Okazaki 444, Japan

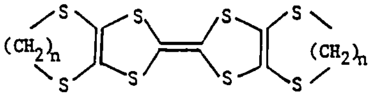
Abstract Crystal and electronic structures of various types of molecular metals based on multi-sulfur π-donor and π-acceptor molecules are presented. Band structures of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ and $(BEDT\text{-}TTF)_3(ClO_4)_2$ indicate their semimetallic (or narrow-gap semiconductive) properties. In $\beta\text{-}(BEDT\text{-}TTF)_2PF_6$, BEDT-TTF dimers are arranged along the transverse direction and the Fermi surface is open perpendicular to this direction. The superconducting $\beta\text{-}(BEDT\text{-}TTF)_2I_3$ has nearly isotropic 2-D Fermi surface. The positive charges in $(BMDT\text{-}TTF)_3ClO_4(DCE)$ tend to localize and form a Wigner lattice. Similar charge separation makes $(BMDT\text{-}TTF)_3PF_6(DCE)$ a 1-D conductor. (BMDT-TTF)(TCNQ), $(DBTTF)[Ni(dmit)_2]$, and $(TMTSF)[Ni(dmit)_2]$ are two-chain compounds with high conductivities ($\sigma_{R.T.}=200$ -300 Scm^{-1}). (BMDT-TTF)(TCNQ) has crossing bands, whereas the others have parallel bands. $(TMTSF)\text{-}[Ni(dmit)_2]$ has a periodically modulated superlattice (a,9b,c).

[†] Present address: Institute for Molecular Science, Okazaki 444, Japan

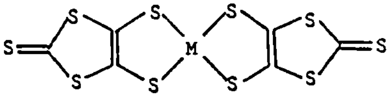
[††] Present address: Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

INTRODUCTION

Because of the one-dimensionality of the most of the organic metals, the uniform stacking of the planar π-donor and/or π-acceptor molecules has been considered to be most fundamental requirement for the design of the molecular metals. It is well-known that the system with plane-like Fermi surface is unstable against the periodical modulations of the lattice and spin structures. A simple way to avoid these instabilities is the introduction of the multi-dimensional intermolecular interactions. Recent discoveries of the organic superconductors based on the sulfur donor molecule BEDT-TTF have aroused considerable interest.[1-3] In this paper, various types of the molecular conductors based on the multi-sulfur π-donor and/or π-acceptor molecules, BEDT-TTF(ET), BMDT-TTF(MT), BPDT-TTF(PT) and $M(dmit)_2$ (M=Ni, Pt) will be presented.



BMDT-TTF(n=1); BEDT-TTF(n=2)
BPDT-TTF(n=3)



$M(dmit)_2$:(M=Ni, Pd, Pt)

BEDT-TTF COMPOUNDS

The ET compounds is characterized by the variety of their structural properties, which are in a striking contrast to the isomorphism of the $(TMTSF)_2X$ systems.[4] Main origin of the polymorphism of the ET compounds is considered to be the steric repulsion of the ethylene groups, which prevents the infinite face-to-face stacking of the molecules.

$(ET)_2ClO_4(TCE)_{0.5}$ (TCE=1,1,2-trichloroethane) is a 2-D conductor.[5] The molecular arrangement of ET and the anisotropy of the intermolecular overlap integrals indicate the 2-D nature of the system.[6,7] The extended Huckel band calculation gave a semimetallic (or narrow-gap semiconductive) band, which shows no trace of one-dimensionality.[7]

Similar to $(ET)_2ClO_4(TCE)_{0.5}$, the intermolecular overlap integral(S) of $(ET)_3(ClO_4)_2$ is largest along the oblique direction and smallest along the most stacking direction. The relatively large anisotropy of S, the charge density, and the 3-fold molecular arrangement along the direction of the largest interaction suggest the incomplete nesting of the Fermi surface, where the areas of electrons and holes are arranged alternately along the direction perpendicular to that of the largest interaction. The Fermi surface will be vanished by the small modification of the molecular arrangement in the unit cell, which is consistent with the (semi)metal-insulator transition observed around 170 K.[8]

The crystal structure and electrical conductivity of β-$(ET)_2PF_6$ shows that this system is the first 1-D molecular metal along the transverse direction.[9] Although the side-by-side interaction is not so large, the band picture will be valid even along the transverse direction because the extension of TTF framework by incorporating six-membered heterorings will reduce the on-site Coulomb repulsion. Strong alternation of S along the a axis $(q>a_1>c>>a_2,p)$(Fig. 1) suggests that ET molecules are dimerized and the metallic band is formed along the transverse array of the dimers. Thus, the metal-insulator transition around 297 K(Tc) and the doubling of the lattice constant along the c axis (the side-by-side direction) indicate the development of the Peierls gap below Tc. This system shows that the molecular

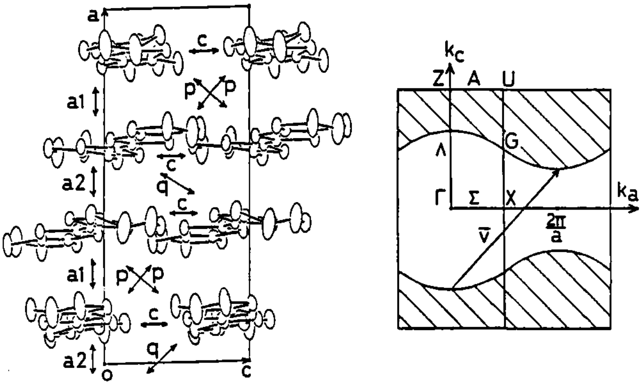


Fig. 1. Molecular arrangement and band structure of β-$(ET)_2PF_6$

conductor can be metallic along the transverse direction.

In this connection, it should be recalled that the superconducting β-$(ET)_2I_3$ has 2-D band structure with nearly isotropic closed 2-D Fermi surface(Fig. 2).[10]

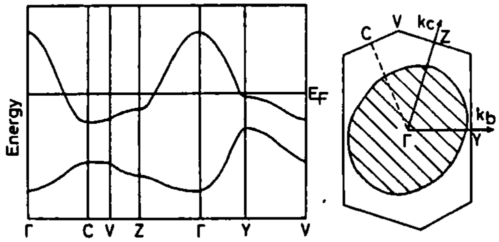
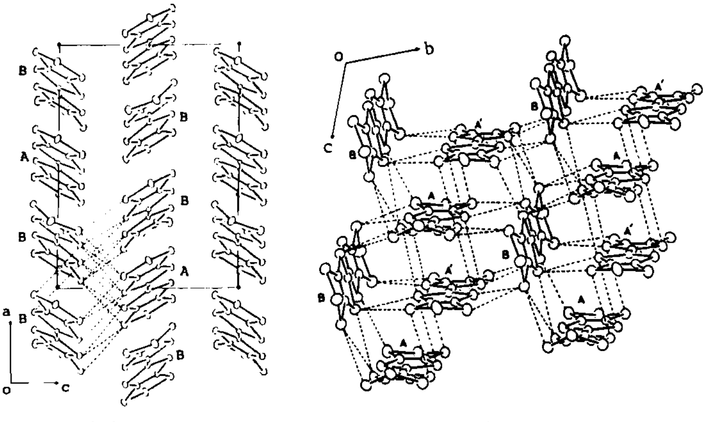


Fig. 2. Band structure of β-$(ET)_2I_3$.

BMDT-TTF AND BPDT-TTF COMPOUNDS

Based on the examination of the molecular geometries and the charge distributions on sulfur atoms of MT, ET, and PT, we have presumed that the transverse interaction will be enhanced in the MT compounds.[11] The dimensionality of the system is reduced as, MT>ET>PT. This indicates that the bulkiness of the alkyldithio substituent is not a good measure for the steric hindrance against the molecular stacking.

Unlike the ET salts with the small donor/anion ratio ($2\sim1$), the PF_6 and ClO_4 salts of MT have the donor/anion ratio of 3. That is, the positive charges are diluted in these system. The comparison of the bond lengths of the two crystallographically independent molecules A and B in $(MT)_3ClO_4(DCE)$(DCE=1,2-dichloroethane) (Fig. 3a) shows that the positive charges are localized in the site of molecule A (site A). The charge distribution of this system can be expressed as $(A^+B^0B^0)(ClO_4^-)(DCE^0)$. Despite of the isotropic overlap integrals in the (010) plane, there is no electron conduction path connecting the neighbouring sites A, because the HOMO of B is fully occupied. Therefore, the positive charge is considered to be localized on the site A. The charge localization implies that the positive charges tend to separate as far as possible and form a Wigner lattice. The neutral molecules B, solvent molecules (DCE), and ClO_4^- anions intercepting the conduction path reduce

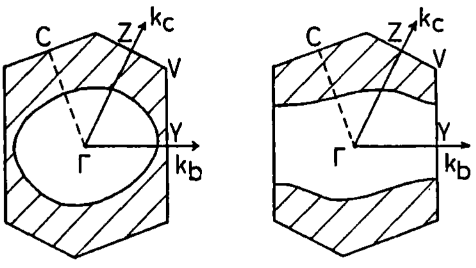


(a) (b)

Fig. 3. Molecular arrangement. (a) $(MT)_3(ClO_4)(DCE)$
(b) $(MT)_3(PF_6)(DCE)$

the Coulomb repulsion between the positive charges. Since the anion...B distance is shorter than the anion...A distance, the charge localization can not be attributable to the difference of the site potentials between A and B.

Similar charge separation is also observed in $(MT)_3(PF_6)(DCE)$.[11] The positive charges are distributed on the site of molecule A, which form 1-D column along the c axis (Fig. 3b). The charge distribution in this complex can be expressed as $(A^{+1/2}A^{+1/2}B^0)(PF_6^-)(DCE^0)$. Owing to the interception of the electron conduction path by the neutral molecules B, the electronic structure becomes one-dimensional. If the site potential of B is equal to that of A, the band structure is completely two-dimensional because of the 2-D network of sulfur atoms (Fig. 3b, 4a). However, the charge localization implys that the potential of the site B is lower than that of the site A, which is consistent with the close contact between molecule A and PF_6^-. The band structure obtained on the assumption of the difference of the site potential (ΔE) of 0.5 eV clearly shows the 1-D nature of the electronic structure(Fig. 4b), which gives a good interpretation to the large anisotropy of the resistivity ($\rho_c : \rho_b : \rho_a = 1 : 300 : 10^4$). This complex shows that not only molecular arrangement but also charge separation strongly influence on the dimensionality of the system.



(a) (b)

Fig. 4. Fermi surface of $(MT)_3PF_6(DCE)$
(a) $\Delta E = 0$
(b) $\Delta E = 0.5$ eV

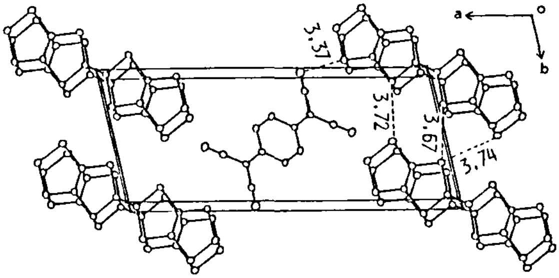


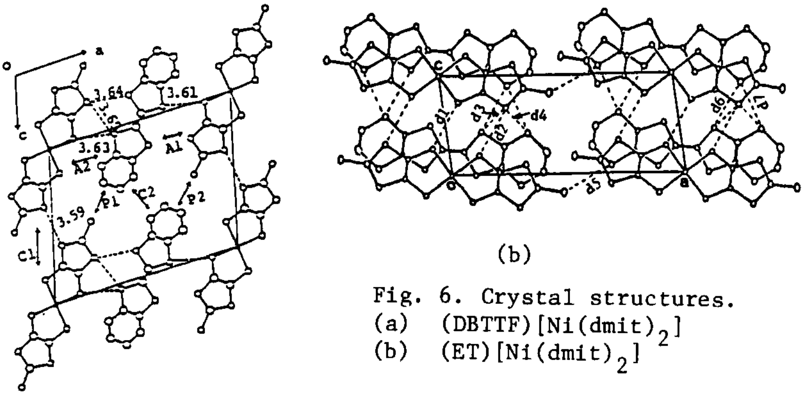
Fig. 5. Crystal structure of (MT)(TCNQ).

Figure 5 shows crystal structure of (MT)(TCNQ) ($\sigma_{R.T.} \sim 200\ \mathrm{Scm}^{-1}$). The donor and acceptor molecules are stacked separately to form uniform segregated stacks along the c axis.[12] The overlap integrals show that the band width of this system is comparable to that of TTF TCNQ. The interchain interaction between the MT columns is considerably large ($S_{/\!/}/S_{\perp} \sim 4.5$). Thus the one- and two-dimensionalities coexist in the crystal. Even if TCNQ columns tend to distort periodically, the Fermi surface will not be disappeared because of the large transverse intermolecular interaction between the MT molecules. This system shows an example of the way to introduce the 2-D interaction in the organic conductors.

Unlike MT complexes, PT complexes ($(PT)_2I_3$, $(PT)_3(PF_6)_2$) show the stacking structure.[4,11]

[M(dmit)$_2$] COMPLEXES

More intensive method to introduce 2- or 3-dimensionality can be obtained by examination of the crystal structure of M(dmit)$_2$ complexes (M=Ni, Pd, Pt). We have pointed out that $(Et_4N)_{0.5}$[Ni(dmit)$_2$] is a precursor of 3-D metal.[13] Very recently Cassoux et al. reported the "true 3-D" molecular metal, (TTF)-[Ni(dmit)$_2$].[14]



(a)

(b)

Fig. 6. Crystal structures.
(a) (DBTTF)[Ni(dmit)$_2$]
(b) (ET)[Ni(dmit)$_2$]

Figure 6a shows the structure of (DBTTF)[Ni(dmit)$_2$] ($\sigma_{R.T.}\sim 300\ \mathrm{Scm}^{-1}$).[15] The donor and acceptor molecules are stacked to form segregated uniform columns along the b axis. The magnitude of S along the stacks is comparable to that of (MT)(TCNQ). However, the sign of the intracolumn overlap integral in the DBTTF column is the same as that in the Ni(dmit)$_2$ column. That is, (DBTTF)[Ni(dmit)$_2$] is the 2-chain system with "parallel band". Therefore the Fermi surface of this system is stable against the intercolumn interaction. This is a new aspect of the 2-chain compound. Unlike (DBTTF)[Ni(dmit)$_2$], (ET)[Ni(dmit)$_2$] has mixed stacking of the donors and acceptors, indicating a new route to design of organic metals (Fig. 6b).[16]

(TMTSF)[Ni(dmit)$_2$] has a superlattice (a,9b,c).[17] The fundamental structure contains the segregated uniform stacks of the donor and acceptor molecules(Fig. 7). Despite of the large conductivity ($\sigma_{R.T.}\sim 300\ \mathrm{Scm}^{-1}$), the system is a narrow gap semiconductor (Ea(R.T.)/k$\sim$340 K). The overlap integrals show the large dispersion of TMTSF column, while the band width of Ni(dmit)$_2$ column is very small. Simple band picture

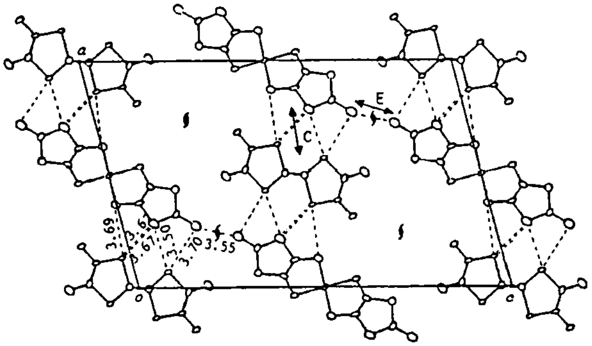


Fig. 7. Crystal structure of (TMTSF)[Ni(dmit)$_2$].

indicates that the system will be metallic if the periodical distortion wave does not exist. There may be two types of the lattice distortion which make the metallic state unstable: (1) the Peierls distortion ($2k_F$) (2) the lattice deformation with the wave number $2k_o$ (k_o is the reciprocal vector where upper and lower bands contact). Preliminaly estimation of the degree of the charge transfer (ρ) by IR spectra appears to prefer the second possibility because ρ appears to be larger than that estimated from the wave number of the periodical lattice distortion wave.

In this paper we present various aspects of a new family of the molecular conductors based on the multi-sulfur donor and/or acceptor molecules. It should be stressed that the one-dimensionality imposed on the molecular metals has been removed. Examination of the intermolecular overlap integrals gives a good perspective for the design of new type of the molecular metals.

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