Band Electronic Structure Study of Two-Dimensional Organic Metal (BEDT-TTF)$_2$Cu$_5$I$_6$ with a Polymer Anion Layer

Dae Bok Kang

Department of Chemistry, Kyungsung University, Pusan 608-736. Received May 16, 1991

The electronic behavior of a organic metal (BEDT-TTF)$_2$Cu$_5$I$_6$ observed to be stable at low temperatures was examined by performing tight-binding band electronic structure calculations. The suppression of a metal-insulator tansition is likely to originate from its quasi-two-dimensional Fermi surface with no nesting, in agreement with experiment.

Introduction

Charge transfer salts of the sulfur-containing organic donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or simply ET, **1**) with monovalent anions have led to a number of low-dimensional organic metals and superconductors.[1] The discovery of ambient-pressure superconductor β-(BEDT-TTF)$_2$I$_3$ (superconducting transition temperature, $T_c = 1.4$ K at ambient pressure[2]; $T_c = 8.0$ K in 0.5 kbar pressure[3]) has stimulated a search, among the BEDT-TTF salts, for new organic metals which are stable to metal-insulator transitions.


1
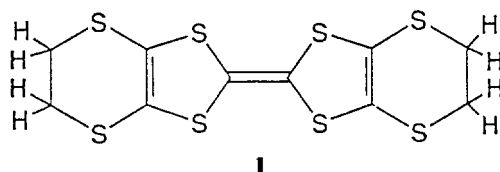
For a metal to be superconducting upon lowering the temperature, it should avoid the electronic instability toward metal-insulator transition associated with a good Fermi surface nesting.[4] In general, the Fermi surface of a one-dimensional (1D) metal is well-nested, so that such a 1D metal is found to undergo a metal-insulator transition. Therefore, the suppression of a metal-insulator transition in organic conductors is expected to originate from the pressence of a quasi-two-dimensional electronic system with no Fermi surface nesting that is formed by the specific packing arrangement of the BEDT-TTF donor molecules in the crystals. At the same time, the role of an anion structure is also essential, since it can influence the character of the packing and the electronic characteristics of the conducting donor molecule system in these salts. Metal complex polymeric anions are of great interest in this connection. If such an anion forms a two-dimensional network in the crystal, it should facilitate the formation of a two-dimensional layer of the organic donor molecule system.

In the present work, we discuss the crystal and electronic structures of the charge transfer salt (BEDT-TTF)$_2$Cu$_5$I$_6$ found to be a typical two-dimensional organic metal on the basis of the associated Fermi surface of the valence bands derived from the HOMO's of four BEDT-TTF donor molecules in each unit cell.

Crystal Structure and Physical Properties

The BEDT-TTF salt with the Cu$_5$I$_6$- complex anion,
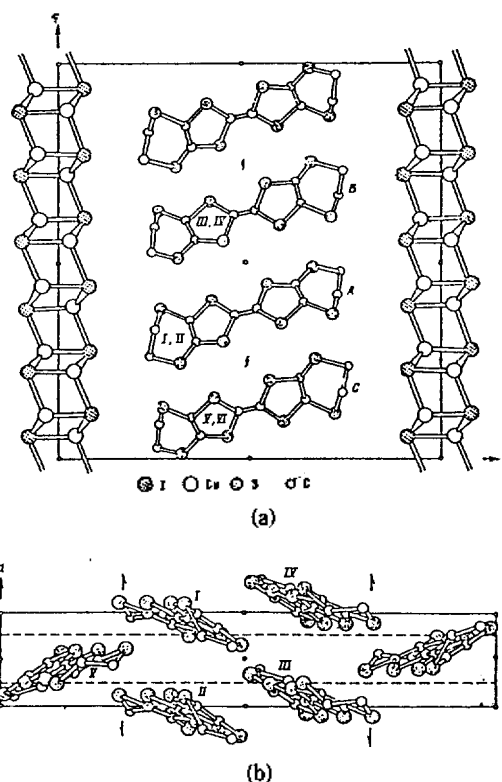
Figure 1. (a) Projection view of (BEDT-TTF)$_2$Cu$_5$I$_6$ crystal structure along the a direction (from Figure 1 of Reference 5). (b) Projection view of BEDT-TTF donor molecule layer along the b direction (from Figure 2 of Reference 5).

(BEDT-TTF)$_2$Cu$_5$I$_6$, has been synthesized and characterized.[5] As shown in Figure 1, its structure consists of BEDT-TTF donor molecule layers alternating with honeycomb-like polymeric networks of Cu$_5$I$_6$ anions along the b direction. The donor molecule layer is made up of regular BEDT-TTF stacks along the a direction. The (BEDT-TTF)-(BEDT-TTF) interplanar distance is 3.80 Å, and the adjacent donor molecules within the stack are laid with the transverse shift relative to one another.

All $S \cdots S$ intrastack contacts are no shorter than the van der Waals radii sum of the S atoms (3.6 Å), but there are a number of shortened interstack $S \cdots S$ contacts (3.36-3.63 Å), which suggest the presence of strong interstack interactions in the donor layer. The room temperature conductivity of single crystals in the ac plane is almost isotropic (15-45

516 *Bull. Korean Chem. Soc., Vol. 12, No. 5, 1991*

Dae Bok Kong

Table 1. The Exponents ζ and Valence Shell Ionization Potentials H_{ii}(eV) of the Slater Type Atomic Orbitals $\chi_i^{a,b}$

	χ_i	ζ_i	ζ_i'	H_{ii}
S	$3s$	2.662 (0.5564)	1.688 (0.4874)	−20.0
	$3p$	2.338 (0.5212)	1.333 (0.5443)	−13.3
C	$2s$	1.831 (0.7616)	1.153 (0.2630)	−21.4
	$2p$	2.730 (0.2595)	1.257 (0.8025)	−11.4
H	$1s$	1.30		−13.6

[a] The s and p orbitals of S and C are given as a linear combination of two Slater type orbitals with exponents ζ and ζ', each is followed by a weighting factor in parentheses. [b] A modified Wolfsberg-Helmholz formula was used to calculate the off-diagonal elements H_{ij}.
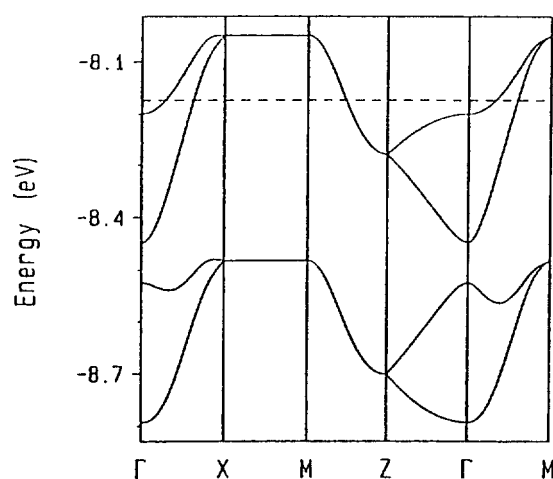

Figure 2. Dispersion relations of the four highest occupied bands calculated for (BEDT-TTF)$_2$Cu$_5$I$_6$. The dashed line refers to the Fermi level, and Γ, X, Z, and M represent wave vector points (0,0), $(a^*/2,0)$, $(0,c^*/2)$, and $(a^*/2,c^*/2)$, respectively, of the first Brillouin zone within the a^*c^* plane.

$\Omega^{-1}\cdot\text{cm}^{-1}$). The conductivity anisotropy in the ab plane, to the contrary, is high ($\sigma_a/\sigma_b \cong 10^4$). On decreasing the temperature the resistance along the a direction decreases and reaches a minimum in the range 2-15 K for the crystals of different pressures. At lower temperature a slight increase in the resistance is observed.[6] Thus, the character of the crystal structure and the physical properties of (BEDT-TTF)$_2$Cu$_5$I$_6$ indicates that this compound is a quasi-two-dimensional (2D) organic metal, in which the metallic state remains stable down to very low temperatures.

Band Dispersions and Fermi Surface

We examine the band electronic structure of (BEDT-TTF)$_2$ Cu$_5$I$_6$ by performing tight-binding band calculations[7] based upon the extended Hückel method.[8] The atomic parameters employed in our calculations are summarized in Table 1. In order to better describe the interstack S$\cdots$S contact interactions, the s and p orbitals of carbon and sulfur were represented by double-ζ Slater type orbitals.

Figure 2 displays the dispersion relations of the four hi-
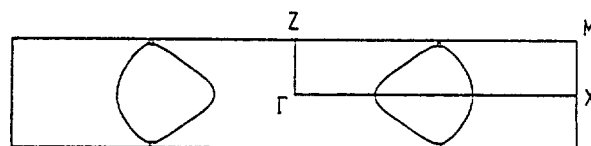
Figure 3. Fermi surface associated with the half-filled band of Figure 2.

ghest occupied bands calculated for the 2D donor molecule network present in (BEDT-TTF)$_2$Cu$_5$I$_6$. These four bands are largely derived from the HOMO's of four donor molecules in each unit cell. Because of symmetry present in the crystal structure, the upper two bands merge into one along $X\rightarrow M$ and $M\rightarrow Z$, so do the bottom two. With the formal oxidation of (BEDT-TTF)$_4^{2+}$ per unit cell, there are six electrons to fill the four bands, so that the upper two bands become half filled. Figure 3 shows the Fermi surface associated with these bands. In agreement with various structural characteristics and electrical conductivities, our band electronic structure calculations reveal that the (BEDT-TTF)$_2$Cu$_5$I$_6$ salt is a 2D metal resulting from the closed 2D Fermi surface with no nesting. In general, the electrical conductivity of a metal is good in the direction orthogonal to its Fermi surface. Consequently, the occurrence of the closed Fermi surface in the a^*c^* plane of the first Brillouin zone in Figure 3 implies that the salt would have nearly isotropic electrical coductivity in the plane of the donor molecule layer (crystallographic ac plane). This result is consistent with the reported 2D metallic observation of the salt.[5,6]

Discussion

While the intermolecular S$\cdots$S distances are important, they are not the only measure of the extent of interaction between the adjacent donor molecular i and j, which can be described in terms of their HOMO-HOMO interaction energy[10] $\beta_{ij}=\langle\psi_i|H^{eff}|\psi_j\rangle$, where ψ_i and ψ_j are the HOMO's of donor molecules i and j, respectively. Since the HOMO is a π-type orbital, the σ- and π-type interactions occur with the face-to face and the side-by-side intermolecular configurations, respectively. In general, the former arrangement provides better overlap (i.e., larger β_{ij} value) between the HOMO's than does the latter. Accordingly, it is not surprising that the extent of interaction between the adjacent donor molecules with the S$\cdots$S contact distances greater than 3.6 Å along the intrastack direction is comparable to that with the numerous shortened S$\cdots$S contact distances along the interstack direction in (BEDT-TTF)$_2$Cu$_5$I$_6$. Both the intrastack and the interstack interactions contribute to the band structure leading to the closed Fermi surface, which is responsible for the 2D electrical properties of this salt. Also, the presence of the polymeric metal-complex anion nets is likely to be one of the factors impeding the electronic instability toward a metal-insulator transition at low temperatures on the basis of geometric considerations of the donor molecule layers in the (BEDT-TTF)$_2$Cu$_5$I$_6$ crystals.

References

1. J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, and M. -H. Whangbo, *Prog. Inorg. Chem.* **35**, 51 (1987).

2. E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. W. Karatsovnik, A. V. Zvarykina, and L. I. Buravov, *JETP Lett.*, **39**, 12 (1984).

3. (a) V. N. Laukhin, E. E. Kostyuchenko, Yu. V. Sushko, I. F. Shchegolev, and E. B. Yagubskii, *JETP Lett.*, **41**, 81 (1985); (b) K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura, and T. Ishiguro, *J. Phys. Soc. Jpn.*, **54**, 1236 (1985).

4. M. -H. Whangbo, *Inorganic Compounds with Unusual Properties*, R. B. King, ed., American Chemical Society, in press.

5. R. P. Shibaeva and R. M. Lobkovskaya, *Sov. Phys. Crystallogr.*, **33**(2), 408 (1988).

6. L. I. Buravov, A. V. Zvarykina, M. V. Kartzovnik, N. D. Kushch, V. N. Laukhin, R. M. Lobkovskaya, V. A. Merzhanov, D. N. Fedutin, R. P. Shibaeva, and E. B, Yagubskii, *Zh. Exsp. Teor. Fiz.*, **92**, 594 (1987).

7. (a) M. -H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, H. H. Wang, K. D. Carlson, and G. W. Crabtree, *J. Am. Chem. Soc.*, **107**, 5815 (1985); (b) M. -H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 6093 (1978).

8. R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

9. J. H. Ammeter, H. B. Burgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 3686 (1978).

10. M. -H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, and H. H. Wang, *Inorg. Chem.*, **24**, 3500 (1985).

Stereochemical Induction in the Generation of 1-Chloro-1-phenyl-2-neopentylsilene

Bok Ryul Yoo and Il Nam Jung*

Organometallic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791

Myong Euy Lee and Chang Hwan Kim

Department of Chemistry, Yonsei University, Seoul 120-749. Received May 17, 1991

The reaction of dichlorophenylvinylsilane with *tert*-butyllithium in hydrocarbon solvents at room temperature or below generated the Z and E-isomers of 1-chloro-1-phenyl-2-neopentylsilene. The intermediates were trapped by cyclopentadiene, anthracene and methoxytrimethylsilane to give a consistent 90/10 ratio for the Z-silene to E-silene adduct. This result was interpreted as an evidence for stereochemical induction in the silene generation reaction.

Introduction

The reaction of *tert*-butyllithium with chlorodimethylvinylsilane in hydrocarbon solvent at low temperatures gave rise to 1,1-dimethyl-2-neopentylsilene which dimerized to the typical 1,3-disilacyclobutane[1] and trapped to [4+2] adducts in the presence of dienes.[2] In extention of this work, the E- and Z-isomers of 1-methyl-1-phenyl-2-neopentylsilene were generated from the reaction of *tert*-butyllithium with chloromethylphenylvinylsilane.[3,4] A consistent 70 to 30 ratio for the E- to Z-silene adducts trapped by dienes was interpreted as an evidence for stereochemical induction in the silene generation reaction.[4]
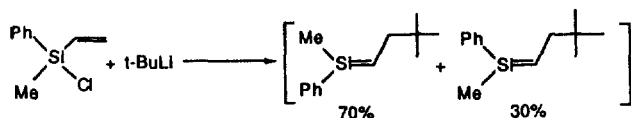
In this paper we report the generation of the E- and Z-isomers of 1-chloro-1-phenyl-2-neopentylsilene and the sub-

stituent effects on the stereochemical induction favoring the formation of the Z-isomer.

Results and Discussion

When Z- and E-1-chloro-1-phenyl-2-neopentylsilene, **1**, were generated by the reaction of *tert*-butyllithium with dichlorophenylvinylsilane in hexane at low temperature in the presence of cyclopentadiene, GLC analysis of the reaction mixture indicated four volatile components comprising 74% of the products. The fragmentation patterns of GC/MS spectra for the four components were identical to each other, which strongly suggested that the four components were considered to be the anticipated four isomeric 2-silanorbornenes, **2a-d**. The isotopic molecular ion $[M^+]$ and other major peaks of the isomers in mass spectra were observed at m/e, 292 (20%), 290 (58%), 169 (33%) and 167 (100%) respectively. These isomers were purified by a preparative gas chromatography and subsequent spectral analyses in comparison with the spectral data of the similar structures[3] led to the assignments