Comparisons can be made to the structure of α-Bi$_2$O$_3$,[11,12] which possesses two symmetrically distinct bismuth atoms, Bi(1) and Bi(2). Bi(1) has five nearest-neighbor oxides in a distorted square-pyramidal arrangement with a lone pair directed toward the remaining 6-fold vertex.[11] Bi(2) is octahedrally coordinated.[11] The Bi–O separations about Bi(1) in α-Bi$_2$O$_3$ closely resemble the Bi–O separations in **2**.[12] The shortest Bi–O distance in α-Bi$_2$O$_3$ is to the apical oxide, 2.13 Å. In the basal set there are two shorter, 2.21 and 2.22 Å, and two longer Bi–O distances, 2.55 and 2.63 Å, parallelling the pattern shown by **2**. In many Bi(III) oxy compounds the Bi centers are surrounded by five or six nearest neighbors at distances of 2.1–2.7 Å.[13]

Solutions of **2** in methoxyethanol (0.2 M) remained homogeneous after addition of up to 12 molar equiv of H$_2$O. When such solutions were brought to reflux, metastable β-Bi$_2$O$_3$ formed as a crystalline yellow precipitate.[14] In contrast, the room-temperature hydrolysis of **2** in THF (0.2 M) with stoichiometric quantities of water rapidly gave a gelatinous precipitate, which collapsed to an amorphous powder with continued stirring. Finally, the *tert*-pentoxide **5** was selected for thermolysis studies; its superior volatility makes it the best candidate for a vapor-deposition source compound. Thermal decomposition under a N$_2$ stream at 200 °C followed by a 600 °C anneal gave a mixture of α-Bi$_2$O$_3$ (major) and γ-Bi$_2$O$_{3+x}$ (minor).[15]

In summary, bismuth trialkoxides are stable, isolable compounds and have good solubility and volatility in examples with appropriate bulky or chelating alkoxide ligands. The compounds are hydrolytic and thermolytic precursors to bismuth oxides. Efforts to use them in the preparation of bismuth-containing superconductors are in progress.[16]

Note Added in Proof. Professor L. G. Hubert-Pfalzgraf, Université de Nice, has informed us that our groups independently solved the structure of **2** at approximately the same time.

Acknowledgment. W.E.B. and M.A.M. warmly thank Dr. Subhash C. Goel for ideas, advice, and encouragement. Support was provided by the National Science Foundation under Grant No. DMR-8914196. The Washington University X-Ray Crystallography Facility was funded by the NSF Chemical Instrumentation Program (Grant CHE-8811456). The Washington University High-Resolution NMR Service Facility was funded in part by NIH Biomedical-Research-Support Shared-Instrument Grant 1 S10 RR02004 and a gift from the Monsanto Co.

Supplementary Material Available: Listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (7 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

---

(11) Malmros, G. *Acta Chem. Scand.* **1970**, *24*, 384.

(12) Harwig, H. A. *Z. Anorg. Allg. Chem.* **1978**, *444*, 151.

(13) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, U.K., 1984; p 891.

(14) (a) Medernach, J. W.; Snyder, R. L. *J. Am. Ceram. Soc.* **1978**, *61*, 494. (b) Note that data in JCPDS File 18-244 are incorret.[14a]

(15) α-Bi$_2$O$_3$: JCPDS File 14-699. γ-Bi$_2$O$_{3+x}$: JCPDS File 6-312.

(16) A reviewer has suggested an alternate description of the structure of **2**: The one short and two medium Bi–O separations identify a pyramidal Bi(OR)$_3$ repeat unit, made polymeric by the two additional, long (weak) Bi–O bridges. These weak bridges possess the attributes of "secondary bonding" as defined by Alcock.[17]

(17) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 2.

Department of Chemistry
Washington University
St. Louis, Missouri 63130

Michael A. Matchett
Michael Y. Chiang
William E. Buhro*

Received September 11, 1989

Molecular Identities in First-Principles Self-Consistent-Field Band Electronic Structures of the Organic Superconducting Salts β-(BEDT-TTF)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, IBr$_2^-$)

Organic donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or simply ET) gives rise to a number of ambient-pressure 2:1 superconducting salts, which include the β-phase salts β-(ET)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, and IBr$_2^-$, for which the superconducting transition temperature T_c = 1.4,[1] 5.0,[2] and 2.8 K,[3] respectively), the κ-phase salts κ-(ET)$_2$X (X$^-$ = I$_3^-$ and Cu(NCS)$_2^-$, for which T_c = 3.6[4] and 10.4 K,[5] respectively), and θ-(ET)$_2$I$_3$ (T_c = 3.6 K[6]). A structural pattern common to all these salts is that they have layers of donor molecules ET alternating with layers of anions in one crystallographic direction (i.e., the *c* direction).[7] With the formal oxidation states (ET)$_2^+$ and X$^-$ for the 2:1 salts (ET)$_2$X, it is expected that the ET layers are primarily responsible for the partially filled band, and hence for the metallic properties, of (ET)$_2$X. In agreement with this prediction, the electrical conductivities of the superconducting (ET)$_2$X salts are much greater in the plane of the ET layers.[1] Thus the electronic structures relevant for their normal metallic states are well described by extended Hückel tight-binding (EHTB) band calculations[8] on a single ET layer. In calculations of Mori et al.,[9] this EHTB band calculation is simplified by calculating only those bands resulting from the HOMO's of ET molecules on the basis of the overlap integrals between the HOMO's of nearest-neighbor ET molecules. Concerning the nature of the partially filled bands of the superconducting 2:1 salts, the regular EHTB[8] and its simplified[9] approaches provide similar results since these bands are essentially made up of the HOMO's of ET molecules. Thus the highest occupied (HO) bands are half-filled, as expected from the formal oxidation state (ET)$_2^+$, and their Fermi surfaces have a simple shape of a distorted circle[8,9] or overlapping distorted circles.[6b,10]

---

(1) (a) Yagubskii, E. G.; Shchegolev, I. F.; Laukhin, V. N.; Kononvich, P. A.; Kartsovnik, M. V.; Zvarykina, A. V.; Buravov, L. I. *JETP Lett.* **1984**, *39*, 12. (b) Williams, J. M.; Emge, T. J.; Wang, H. H.; Beno, M. A.; Copps, P. T.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 2558.

(2) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nuñez, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2465.

(3) Williams, J. M.; Wang, H. H.; Beno, M. A.; Emge, T. J.; Sowa, L. M.; Copps, P. T.; Behroozi, F.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 3839.

(4) Kobayashi, A.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 459.

(5) (a) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55. (b) Urayama, H.; Yamochi, H.; Saito, G.; Sato, S.; Kawamoto, A.; Tanaka, A.; Mori, T.; Maruyama, Y.; Inokuchi, H. *Chem. Lett.* **1988**, 463. (c) Gärtner, S.; Gogu, E.; Heinen, I.; Keller, H. J.; Klutz, T.; Schweitzer, D. *Solid State Commun.* **1988**, *65*, 1531. (d) Carlson, K. D.; Geiser, U.; Kini, A. M.; Wang, H. H.; Montgomery, L. K.; Kwok, W. K.; Beno, M. A.; Williams, J. M.; Cariss, C. S.; Crabtree, G. W.; Whangbo, M.-H.; Evain, M. *Inorg. Chem.* **1988**, *27*, 965, 2904.

(6) (a) Kobayashi, H.; Kato, R.; Kobayashi, A.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1986**, 789. (b) Kobayashi, A.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1986**, 2017. (c) Kobayashi, H.; Kato, R.; Kobayashi, A.; Mori, T.; Inokuchi, H.; Nishio, Y.; Kajita, K.; Sasaki, W. *Synth. Met.* **1988**, *27*, A289.

(7) For a review, see: Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M.-H. *Prog. Inorg. Chem.* **1987**, *35*, 51.

(8) Whangbo, M.-H.; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H.; Carlson, K. D.; Crabtree, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 5815.

(9) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Chem. Lett.* **1984**, 957.

(10) (a) Kini, A. M.; Beno, M. A.; Son, D.; Wang, H. H.; Carlson, K. D.; Porter, L. C.; Welp, U.; Vogt, B. A.; Williams, J. M.; Jung, D.; Evain, M.; Whangbo, M.-H.; Overmyer, D. L.; Schirber, J. E. *Solid State Commun.* **1989**, *69*, 501. (b) Oshima, K.; Mori, T.; Inokuchi, H.; Urayama, H.; Yamochi, H.; Saito, G. *Phys. Rev. B* **1988**, *38*, 938.

0020-1669/90/1329-0360$02.50/0

However, a first-principles self-consistent-field (SCF) band electronic structure of β-(ET)$_2$I$_3$, recently calculated by Kübler et al.[11] using the augmented spherical wave (ASW) method, presents a picture quite different from the one described above. This ASW–SCF band study shows an open Fermi surface, thereby suggesting that β-(ET)$_2$I$_3$ is a pseudo-one-dimensional metal. In addition, it shows a small electron pocket at Γ resulting from a band whose dispersion crosses the Fermi level even along the c^* direction as though β-(ET)$_2$I$_3$ is a three-dimensional metal. To resolve this striking discrepancy of the AWS–SCF band calculations from the EHTB results, we carry out first-principles SCF band electronic structure calculations on β-(ET)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, IBr$_2^-$) by employing the pseudofunction (PSF) method.[12] In the PSF–SCF band calculations, the potential has a dual representation:[12] First, the muffin-tin spheres about all atoms of the unit cell are represented by spherically symmetric potentials with two sets of sp^3 pseudofunctions per atom. Second, the entire unit cell is represented by nonspherical potentials constructed from 86 797 (i.e., 29 × 41 × 73) plane waves. Such a large expansion of plane waves is necessary to correctly describe covalently bonded systems.[12]

Figure 1 shows the band dispersions calculated for β-(ET)$_2$IBr$_2$ in the vicinity of the Fermi level. β-(ET)$_2$I$_3$ and β-(ET)$_2$AuI$_2$ have the band electronic structures similar to that of Figure 1. Important features of the band electronic structures of β-(ET)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, IBr$_2^-$) can be summarized as follows: (a) All the bands of β-(ET)$_2$X maintain the molecular identities as to whether they represent the ET molecules or the anions, as expected for any material made up of distinctive molecular species. Thus, for X$^-$ = IBr$_2^-$ and I$_3^-$, the HO bands a$_1$ and a$_2$ are derived from the ET molecules (i.e., from the HOMO of ET), the lowest unoccupied (LU) band c is derived from the anions (i.e., from the LUMO of X$^-$), and the two unoccupied bands b$_1$ and b$_2$ lying above the LU band are derived from the ET molecules (i.e., from the LUMO of ET). For X$^-$ = AuI$_2^-$, the bands derived from the HOMO and LUMO of the anion are slightly raised in energy with respect to the bands of the ET molecules, so that the two bands derived from the HOMO of AuI$_2^-$ lie between the two bands a$_1$ and a$_2$ derived from the HOMO of ET, while the one band derived from the LUMO of AuI$_2^-$ lies between the two bands b$_1$ and b$_2$ derived from the LUMO of ET. (b) For all X$^-$ = I$_3^-$, AuI$_2^-$, and IBr$_2^-$, the Fermi level of β-(ET)$_2$X cuts only the HO a$_1$ band representing the ET molecules, which is half-filled. Like all other bands, the HO band is practically dispersionless along the c^* direction (e.g., Γ → Z), and its dispersion relations along other directions are essentially the same as those obtained from the EHTB band calculations. Therefore, the Fermi surface of the HO band should have a cylinder-like shape with its axis along the c^* direction.

The above observations (a) and (b) support the main conclusions of the EHTB calculations concerning the electronic structures of β-(ET)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, IBr$_2^-$).[8,9] The ASW–SCF band calculations of Kübler et al.[11] approximate the potential by overlapping muffin-tin spheres of atoms, with empty spheres introduced for the open space outside the muffin-tin areas. Therefore, unlike the PSF–SCF and the EHTB band calculations, the ASW–SCF band calculations do not provide adequate nonspherical potentials for describing low-symmetry, covalently bonded systems. This explains why the results of the ASF–SCF calculations do not agree with those of the EHTB and the PSF–SCF band calculations and also why the ASF–SCF band calculations give unphysical bands that are associated with electrons localized in the empty spheres.[11]

Experimentally, the shape and the cross-sectional area of a Fermi surface are estimated by Shubnikov–de Haas (SdH) measurements.[13] Both the EHTB and the PSF–SCF band calculations suggest that the Fermi surface of β-(ET)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, IBr$_2^-$) should have a cross-sectional area that is 50% of the first Brillouin zone (FBZ) at the basal plane. The SdH measurements on β-(ET)$_2$IBr$_2$ by Kartsovnik et al.[13a] indicated an extremely small area (i.e., 1% of the FBZ), while those on β-(ET)$_2$IBr$_2$ and β-(ET)$_2$I$_3$ by Toyota et al.[13b] suggested a substantially large area (i.e., about 30% of the FBZ). However, the SdH measurements on β^*-(ET)$_2$I$_3$ (i.e., β-(ET)$_2$I$_3$ under an applied pressure greater than 0.5 kbar, which exhibits superconductivity at $T_c \simeq 8$K[14]) by Kang et al.[13c] show that its Fermi surface cross-sectional area is close to 50% of the FBZ, as expected from the EHTB and the PSF–SCF band calculations.

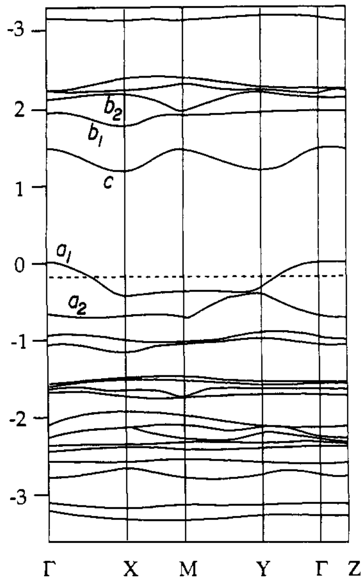

Figure 1. Dispersion relations of the energy bands calculated for β-(ET)$_2$IBr$_2$, where the dashed line refers to the Fermi level. In units of the reciprocal vectors a^*, b^*, and c^*, the wave vector points Γ, X, Y, M, and Z are given as follows: Γ = (0, 0, 0), X = (a^*/2, 0, 0), Y = (0, b^*/2, 0), M = (a^*/2, b^*/2, 0), and Z = (0, 0, c^*/2).

The unoccupied band derived from the LUMO of X$^-$ lies below (for X$^-$ = I$_3^-$ and IBr$_2^-$) or between (for X$^-$ = AuI$_2^-$) the two unoccupied bands derived from the LUMO of ET. The fact that the unoccupied band of the insulting anion layer lies not far from the Fermi level might facilitate electron tunneling, and hence electrical conductivity, along the c^* direction of β-(ET)$_2$X. It is of interest to note that the high-temperature CuO$_2$-layer superconductors have similar structural and electronic features: The metallic CuO$_2$ layers are separated by the insulating layers of cations, and the unoccupied bands of the latter lie close to the Fermi level of the CuO$_2$-layer $x^2 - y^2$ bands.[15]

---

(11) Kübler, J.; Weger, M.; Sommers, C. B. *Solid State Commun.* **1987**, *62*, 801.

(12) Kasowski, R. V.; Tsai, M.-H.; Rhodin, T. N.; Chambliss, D. D. *Phys. Rev. B* **1986**, *34*, 2656.

(13) (a) Kartsovnik, M. V.; Laukhin, V. N.; Nizhankovskii, V. I.; Ignatev, A. A. *JETP Lett.* **1988**, *47*, 363. (b) Toyota, N.; Sasaki, T.; Murata, K.; Honda, Y.; Tokumoto, M.; Bando, H.; Kinoshita, N.; Anzai, H.; Ishiguro, T.; Muto, Y. *J. Phys. Soc. Jpn.* **1988**, *57*, 2616. (c) Kang, W.; Montambaux, G.; Cooper, J. R.; Jérome, D.; Batail, P.; Lenoir, C. *Phys. Rev. Lett.* **1989**, *62*, 2559. (d) Oshima, K.; Mori, T.; Inokuchi, H.; Urayama, H.; Yamochi, H.; Saito, G. *Phys. Rev. B* **1988**, *38*, 938. (e) Murata, K.; Toyota, N.; Honda, Y.; Sasaki, T.; Tokumoto, M.; Bando, H.; Anzai, H.; Muto, Y.; Ishiguro, T. *J. Phys. Soc. Jpn.* **1988**, *57*, 1540.

(14) (a) Schultz, A. J.; Wang, H. H.; Williams, J. M.; Filhol, A. *J. Am. Chem. Soc.* **1986**, *108*, 7853. (b) Schultz, A. J.; Beno, M. A.; Wang, H. H.; Williams, J. M. *Phys. Rev. B* **1986**, *33*, 7823. (c) Schirber, J. E.; Azevedo, L. J.; Kwak, J. F.; Venturini, E. L.; Beno, M. A.; Wang, H. H.; Williams, J. M. *Solid State Commun.* **1986**, *59*, 525. (d) Laukhin, V. N.; Kostyuchenko, E. E.; Sushko, Yu. V.; Shchegolev, I. F.; Yagubskii, E. B. *JETP Lett.* **1985**, *41*, 81. (e) Murata, K.; Tokumoto, M.; Anzai, H.; Bando, H.; Saito, G.; Kajimura, K.; Ishiguro, T. *J. Phys. Soc. Jpn.* **1985**, *54*, 1236.

(15) For a review see: Hass, K. A. *Solid State Phys.* **1989**, *42*, 213.

To summarize, our first-principles PSF–SCF band calculations on β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-) support the essential results of the EHTB band calculations,[8,9] but not those of the ASW–SCF band calculations by Kübler et al.[11] The unphysical nature of the results of Kübler et al. may have originated from the fact that their calculations, though based upon first principles, do not provide adequate nonspherical potentials needed for describing molecular solids.

Acknowledgment. Work at North Carolina State University was supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Sciences, under Grant DE-FG05-8ER45259.

Central Research and Development
Experimental Station
E. I. du Pont de Nemours & Company
Wilmington, Delaware 19880-0356
Robert V. Kasowski*

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204
Myung-Hwan Whangbo*

Received October 19, 1989