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$(\mathrm{BEDO})_{2.4}\mathrm{I}_3$: The First Robust Organic Metal of BEDO-TTF

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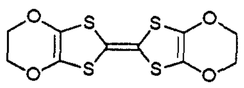
The design of electron donors for metallic and superconducting organic solids requires the incorporation of a large number of increasingly polarizable elements such as S, Se, and Te.[1] Contrary to this dictum, we designed the new donor BEDO-TTF (1, aka BEDO), which has oxygen substituents.[2]



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One would expect that a decrease in size and polarizability associated with a change from sulfur to oxygen would adversely affect the intrastack and particularly the interstack chalcogen interactions, deemed crucial for stabilizing the superconducting state.[3] However, if organic superconductors were BCS superconductors,[4] then a change to the lower atomic mass chalcogen would be beneficial because (1) it would decrease the overall molecular mass of the constituent molecules and consequently raise T_c[5] and (2) oxygen being smaller and less polarizable would decrease the metallic bandwidth, the density of states near the Fermi level would go up, and T_c would be raised.

Here we present results on a BEDO salt that indicate that, contrary to the above, oxygen substitution can *increase the metallic bandwidth*, thus stabilizing the metallic state down to low temperature and producing an organic solid that is akin to a typical inorganic metal in its transport and magnetic properties.

Figure 1 shows a plot of the conductivity as a function of temperature for $(\mathrm{BEDO})_{2.4}\mathrm{I}_3$.[6] The results of these transport measurements are typical of a wide-band metal; corroborating facts are (1) a large resistance ratio between room temperature and 1.2 K ($R_{RT}/R_{1.2} \approx 275$); (2) a small, isotropic (at least in 2 D) value of the thermopower, which tends toward 0 at zero temperature;[7] (3) Pauli, temperature-independent paramagnetism and a monotonically decreasing EPR line width with decreasing temperature.[7]

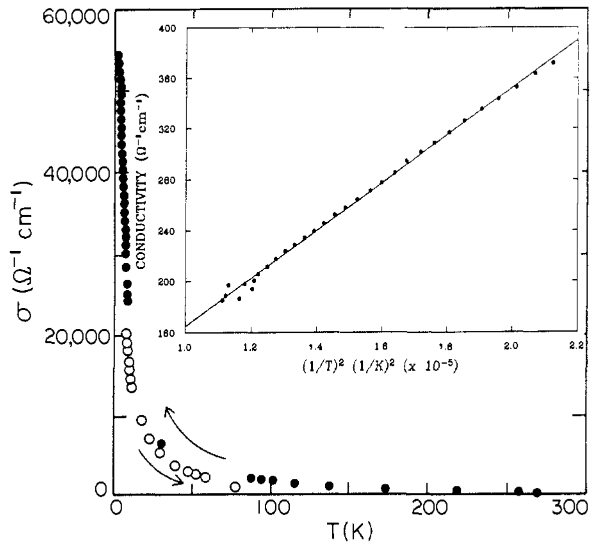

Figure 1. Temperature dependence of the conductivity of $(\mathrm{BEDO})_{2.4}\mathrm{I}_3$ between 300 and 1.2 K: ●, decreasing temperature; ○, increasing temperature. The decreasing and increasing temperature data points overlap in the temperature range 50–1.2 K. Inset: inverse square temperature dependence of the resistivity in the range 300–210 K.

From the value of the magnetic susceptibility, we can deduce a transfer integral value of $t = 0.25$. If the bandwidth is $W \approx 4t$, then the resulting conduction bandwidth of 1 eV is on the order of that of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ ($W = 0.92$ eV),[8] the highest recorded for an organic metal based on charge-transfer complexes and 2–20 times that of $(\mathrm{BEDT\text{-}TTF})_2\mathrm{I}_3$ salts.[9] The T^{-2} dependence of the resistivity (or conductivity inset in Figure 1) has been related to two dimensionality in metals.[10]

Crystallographic analysis indicates that $(\mathrm{BEDO})_{2.4}\mathrm{I}_3$ forms a composite structure, with two interpenetrating lattices.[11] The *b*-axis cell dimension (9.620 Å) for the iodine component is indicative of I_3^-. In a composite structure, the ratio of component cell volumes determines the stoichiometry; in this case it is 2.39, in good agreement with analytical data ($\mathrm{BEDO}/\mathrm{I}_3 = 2.4$). Interaction between the two lattices in the crystal leads to a displacive modulation of the BEDO structure with the *b*-axis periodicity of I, and modulation of the I lattice with the periodicity of BEDO,[12] giving rise to satellite reflections in the diffraction pattern. We note that $(\mathrm{TTF})_7\mathrm{I}_5$ also has a composite structure[13] but with a

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(1) Proceedings of recent international conferences contain detailed accounts. (a) Aldissi, M., Ed. *Synth. Met.* **1988**, *27*(1–4); **1989**, *28–29*. (b) Shirakawa, H., Yamabe, T., Yoshino, K., Eds. *Synth. Met.* **1987**, *17–19*. (c) Pecile, C., Zerbi, G., Bozio, R., Girlando, A., Eds. *Mol. Cryst. Liq. Cryst.* **1985**, *117–121*. (d) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227. (e) Comes, R., Bernier, P., Andre, J. J., Rouxel, J., Eds. *J. Phys., Colloq.* **1983**, *44*, C3.

(2) Suzuki, T.; Yamochi, H.; Srdanov, G.; Hinkelmann, K.; Wudl, F. *J. Am. Chem. Soc.* **1989**, *111*, 3108.

(3) Wudl, F. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 67. Wudl, F. *J. Am. Chem. Soc.* **1981**, *103*, 5885.

(4) The typical experiments such as Se isotope effect determination have not yet been carried out on organic superconductors. The deuterium isotope effect goes "the wrong way" in the case of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$; an explanation is given by Schwenk et al.: Schwenk, H.; Andres, K.; Wudl, F.; Aharon-Shalom, E. *J. Phys., Colloq. C3* **1983**, *44*, 1041.

(5) The BCS isotope effect formula predicts that the lower the atomic mass, the higher T_c by the relationship $M^\alpha T_c$ = constant.

(6) The crystals were grown electrochemically by the same literature procedures employed for the preparation of BEDT iodides (e.g.: 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). Elemental analysis was in perfect accord with the proposed stoichiometry, also confirmed by X-ray crystallography (vide infra). The material is formed in only *one* phase under these conditions in the form of black needles.

(7) See figure in supplementary material.

(8) Kikuchi, K.; Ikemoto, I.; Yakushi, K.; Kuroda, H.; Kobayashi, K. *Solid State Commun.* **1982**, *42*, 433.

(9) Tajima et al. (Tajima, H.; Yakushi, K.; Kuroda, H.; Saito, G. *Solid State Commun.* **1985**, *56*, 159) derived a value of 0.05 eV for the bandwidth of β-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{I}_3$, but Koch et al. (Koch, B.; Geserich, H. P.; Rupple, W.; Schweitzer, D.; Dietz, K. H.; Keller, H. *Mol. Cryst. Liq. Cryst.* **1984**, *119*, 343) found values of $4t$ = 0.9 and 0.6 eV for the β form and $4t$ = 1 and 0.4 eV for the α form.

(10) If umklap processes are taken into account, this behavior is expected from 2D metals. If there is electron–phonon scattering, this behavior is also expected for 1D metals but over the whole temperature range; in the Figure 1 inset, the temperature range is only 300–210 K. Bulaevskii, I. N. *Adv. Phys.* **1988**, *37*, 443.

(11) Composite structure where the two components, BEDO and I, have a different periodicity in the *b*-axis direction. Cell dimensions for BEDO are as follows: a = 5.3269 (1) Å, b = 4.029 (1) Å, c = 16.885 (2) Å; α = 88.29 (2)°, β = 83.45°, γ = 81.21 (2)°. Cell dimensions for I are as follows: a = 5.840 (1) Å, b = 9.620 (2) Å, c = 17.115 (1) Å; α = 99.55°, β = 80.19°, γ = 115.67°. The b axes of the two component structures are parallel, while a_I is in the plane of b_BEDO and a_BEDO and c_I is in the plane of b_BEDO and c_BEDO. The structure was solved by recently developed methods (Petricek, V.; Coppens, P. *Acta Crystallogr.* **1988**, *A44*, 235. Maly, K.; Petricek, V.; Coppens, P., to be published).

(12) Janner, A.; Janssen, T. *Acta Crystallogr.* **1980**, *36*, 399, 408.

(13) Johnson, C. K.; Watson, C. R. *J. Chem. Phys.* **1976**, *64*, 2271. We thank a referee for this information.

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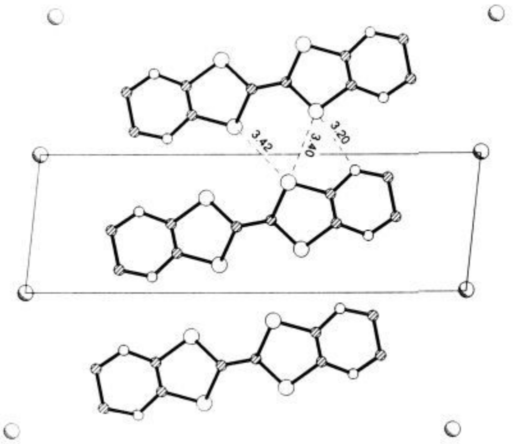
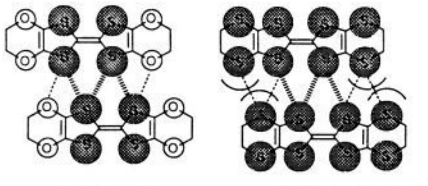


Figure 2. Projection of a unit cell of $(BEDO)_{2.4}I_3$ down the *b* axis. The triiodide counterions are at the corners of the unit cell. Two additional molecules in adjacent stacks are also shown to indicate the short interchalcogen contacts. Refer to footnote 11 for details.

different cation arrangement and I^-, rather than I_3^-.

The *b*-axis projection which coincides for the two lattices is shown in Figure 2. The shortest average[14] S–S contact (which is only of fulvenoid sulfurs) is 3.402 Å, *0.29 Å shorter than the corresponding distance* in α-(BEDT-TTF)$_2$I$_3$. The shortest interstack S–O contact is 3.206 Å, 0.12 Å shorter than the sum of O and S van der Waals radii.[15] In the refinement of the displacive modulations, the BEDO molecules were treated as rigid bodies. The displacements of the BEDO molecules have an amplitude of 0.033 Å, in the direction approximately along the long molecular axis. These displacements are smaller than those observed in β-(ET)$_2$I$_3$,[16] a difference that correlates with the strength of the S–S interactions.

Assuming, in analogy to the (TMTSF)$_2$X salts,[3] that the important intermolecular interactions responsible for the electronic properties of these solids are due to the fulvene chalcogens, we conclude that the stabilization of the metallic state in $(BEDO)_{2.4}I_3$, relative to BEDT-TTF salts, is due to the enhanced overlap between fulvene sulfur atoms facilitated by the decreased steric bulk of the ethylenedioxo relative to the ethylenedithio substituents, as shown schematically below, where the heavier dashed lines represent the fulvene sulfur interactions.



$BEDO_{2.4}I_3$ α (BEDT-TTF)$_2$I$_3$

The effect of oxygen in $(BEDO)_{2.4}I_3$ is therefore not only electronic but also, and perhaps more importantly, one of *steric enhancement of intermolecular interaction.*

Acknowledgment. We thank the National Science Foundation for support through Grant DMR-88-20933.

Supplementary Material Available: Results of magnetic measurements and thermopower and positional and thermal parameters of $(BEDO)_{2.4}I_3$ (4 pages). Ordering information is given on any current masthead page.

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[14] The average value does not take into account the displacive modulation which introduces a shortening in some and a lengthening in other unit cells.

[15] Bondi, J. *Chem. Phys.* **1964**, *68*, 441.

[16] Leung, P. C. W.; Emge, T. J.; Beno, M. A.; Wang, H. H.; Williams, J. M.; Petricek, V.; Coppens, P. *J. Am. Chem. Soc.* **1985**, *107*, 6184.

Nucleophilic Cleavage of One-Electron σ Bonds: Stereochemistry and Cleavage Rates

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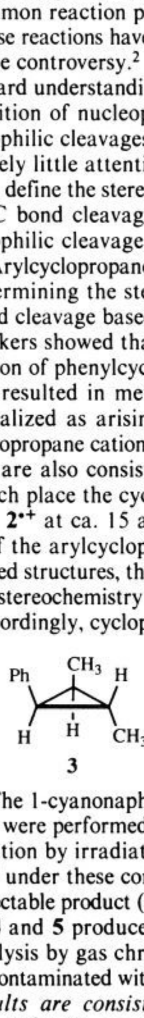
Nucleophilic addition reactions represent one of the most common reaction pathways available to organic cation radicals. These reactions have been the subject of current interest[1] and even some controversy.[2] It is interesting to note that, to date, efforts toward understanding these reactions have largely focused on the addition of nucleophiles to π cation radicals. In contrast, nucleophilic cleavages of cation radical σ bonds have received relatively little attention.[3] In this paper we describe experiments that define the stereochemistry of several nucleophilic one-electron C–C bond cleavages as well as provide rate constants for nucleophilic cleavage.

Arylcyclopropane cation radicals were chosen as substrates for determining the stereochemistry of nucleophilic one-electron σ bond cleavage based upon the work of Rao and Hixson.[4] These workers showed that the *p*-dicyanobenzene-photosensitized oxidation of phenylcyclopropane (**1**) and 1,1-diphenylcyclopropane (**2**) resulted in methanol addition products that were best rationalized as arising from nucleophilic capture of *ring-closed* cyclopropane cation radicals.[5] Ring-closed structures for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are also consistent with thermodynamic cycle calculations which place the cyclopropane one-electron bond energies of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ at ca. 15 and 7 kcal mol^{-1}, respectively.[6]

If the arylcyclopropane cation radicals do indeed have ring-closed structures, they provide potential substrates for determining the stereochemistry of nucleophilic one-electron σ bond cleavages. Accordingly, cyclopropanes **3–5** were prepared for this purpose.[7]



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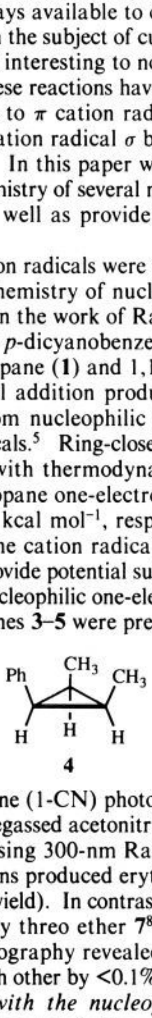

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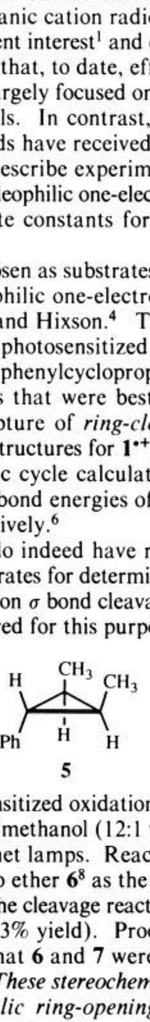

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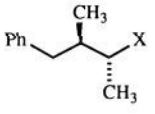
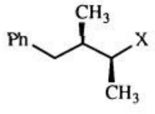
The 1-cyanonaphthalene (1-CN) photosensitized oxidations of **3–5** were performed in degassed acetonitrile/methanol (12:1 v/v) solution by irradiation using 300-nm Rayonet lamps. Reaction of **3** under these conditions produced erythro ether **6**[8] as the sole detectable product (96% yield). In contrast, the cleavage reactions of **4** and **5** produced only threo ether **7**[8] (83% yield). Product analysis by gas chromatography revealed that **6** and **7** were intercontaminated with each other by <0.1%. *These stereochemical results are consistent with the nucleophilic ring-opening of* $\mathbf{3}^{\bullet+}$*–*$\mathbf{5}^{\bullet+}$ *with essentially complete inversion of configuration at carbon.* Ring-opening of the cation radicals, during or after electron transfer, followed by rapid nucleophilic capture is excluded by the fact that the photolyses of **3–5** and 1-CN in the absence of methanol resulted in no detectable interconversion of the cyclopropanes.





6: X = OCH$_3$ **7**: X = OCH$_3$
8: X = OH **9**: X = OH
10: X = CN **11**: X = CN

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