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Bis(ethylenedioxy)tetrathiafulvalene: The First Oxygen-Substituted Tetrathiafulvalene

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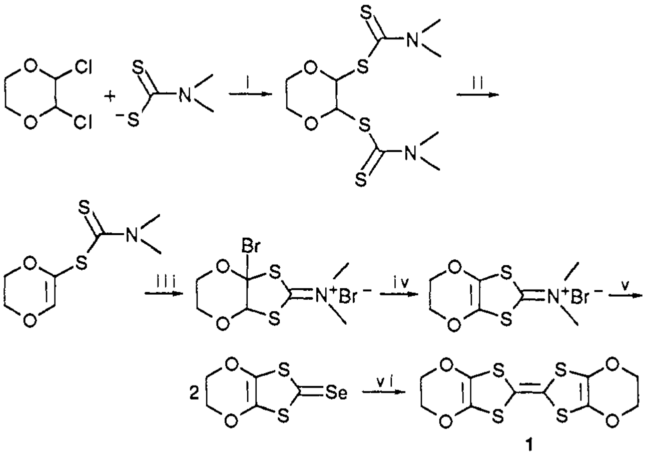
Since the discovery of the high conductivity of its chloride salt,[1] tetrathiafulvalene (TTF) and all its derivatives have become the most investigated donors for the generation of organic metals and superconductors. In the TTF family, the organic metallic state can be achieved with the unsubstituted and variously substituted sulfur, selenium, and tellurium heterocycles but the superconducting state can, so far, be achieved only with derivatives akin to tetramethyltetraselenafulvalene and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, a.k.a. "ET").[2] The highest recorded superconducting transition temperature for an organic superconductor is $T_c = 11.2$ K[3] for (BEDT-TTF-d_8)$_2$Cu(NCS)$_2$, previously reported by Saito's group[4] as $T_c = 10.4$ K for the protio sample. While these temperatures are considerably lower than those of the inorganic ceramic, copper oxide based, superconductors (125 K),[5] the rate at which the organic superconductor transition temperatures have been rising with time is still quite impressive [(TMTSF)$_2$PF$_6$, 0.9 K/25 kbar in 1980[6] (BEDT-TTF-d_8)$_2$Cu(SCN)$_2$, 11.2 K/1 bar in 1988[3,4]].

Scheme I[a]



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[a] (i) CH$_3$CN/reflux, 48%; (ii) 110 °C/DMSO, 58%; (iii) Br$_2$/CH$_2$Cl$_2$, 0 °C, 84%; (iv) 110 °C/25 Torr, 92%; (v) H$_2$Se/MeOH, room temperature, 89%; (vi) (MeO)$_3$P/C$_6$H$_6$, reflux, 63%.

Table I[a]

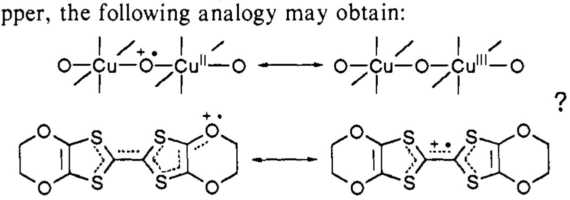
compd	$^1E^{rev}_{1/2}$, mV	$^2E^{rev}_{1/2}$, mV	ΔE, mV	i^1_{pa}, μA	c, mM
TTF	367	748	381	50.1	1.58
BEDT-TTF	567	829	262	0.205[b]	0.03[b]
BEDO-TTF	435	699	264	18.4	0.53

[a] Conditions: acetonitrile/0.1 M TBAPF$_6$, $T = 22 \pm 1$ °C, glassy carbon working electrode, scan rate 0.1 V/s, Ag/AgCl reference electrode. [b] Saturated solution, Pt electrode.

Table II. Interatomic Distances (Å)

bond	dist	bond	dist	bond	dist
S(1)-C(3)	1.754 (4)	S(3)-C(1)	1.758 (5)	O(3)-C(9)	1.444 (6)
S(1)-C(2)	1.757 (5)	C(1)-C(2)	1.357 (6)	C(3)-C(4)	1.336 (6)
S(2)-C(4)	1.752 (5)	C(7)-C(8)	1.329 (6)	C(3)-O(1)	1.365 (6)
S(2)-C(2)	1.771 (4)	C(7)-O(3)	1.366 (5)	O(2)-C(4)	1.368 (5)
S(4)-C(8)	1.759 (5)	O(4)-C(8)	1.372 (6)	O(2)-C(6)	1.441 (7)
S(4)-C(1)	1.761 (5)	O(4)-C(10)	1.448 (6)	O(1)-C(5)	1.452 (5)
S(3)-C(7)	1.752 (5)				

The eruption in solid state science publications caused by the discovery of the copper oxide superconductors[7] has inspired a number of theorists to suggest that the chemical species responsible for the mixed valence in these solids is not the copper couple (Cu^{II}/Cu^{III}) but essentially oxygen radical cations ("holes on oxygen").[8] Some have gone as far as suggesting that results of their calculations can be extrapolated to the design of organic polymeric superconductors.[8a] Inspired by these results, we have been thinking about the possibility of observing metallic and perhaps superconducting behavior with charge-transfer salts based on oxygen-containing donors. Indeed, if the organic superconductors were BCS superconductors,[2] the lighter the component atoms within a series of identical donors, the higher the T_c is expected to be (BCS isotope effect applied to organic superconductors). Also, assuming that the TTF core could be equated to copper, the following analogy may obtain:



However, TTF derivatives with *resonance* electron-donating substituents, such as sp^3-hybridized oxygen or nitrogen *directly* attached[9] to TTF do not exist; the same can be said for tetra-

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[9] Chen et al. (Chen, W.; Cava, M. P.; Takassi, M. A.; Metzger, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 7903) prepared a pyrrole-annulated TTF where the nitrogen *is not* directly attached to the TTF. Hsu and Chiang (Hsu, S.-Y.; Chiang, Y.-L. *Synth. Met.*, in press) prepared tetrahydrofuran-annulated TTF where the oxygen *is not* directly attached to the TTF.

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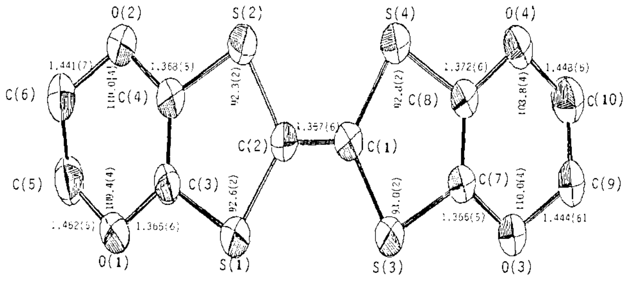

Figure 1. ORTEP drawing of a molecular unit of **1** with selected bond lengths and angles; for additional interatomic distances see Table II.

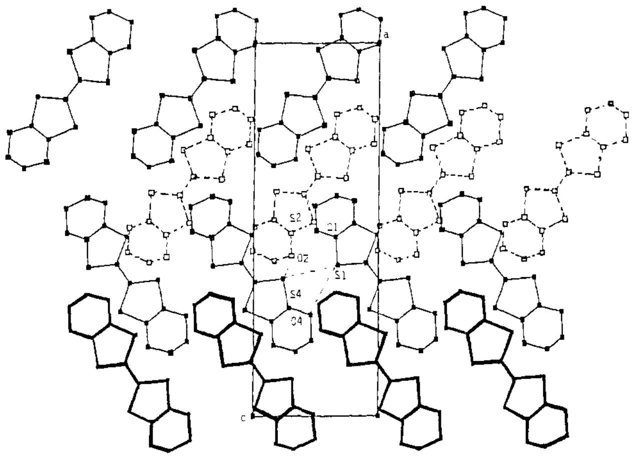

Figure 2. Parts of three sheets in the *a*–*c* plane of the structure of **1** showing close intermolecular contacts with dashed lines. The *b* direction is into the plane of the figure.

oxafulvalenes themselves.[10] Besides the remote connection with ceramic superconductors depicted above, ether-oxygen substitution as a probe of the electronic character of TTF in relation to delocalization of charge in the radical cation and dication was another reason for the preparation of the title compound.

In this publication we describe the preparation and some properties of the first oxygen-substituted TTF (BEDO-TTF, a.k.a. "BO"), an elementologue of ET.

The donor was prepared as shown in Scheme I by adaptation of literature procedures.[11]

The new donor is an air-stable, orange, crystalline solid[12] that is soluble in most organic solvents. Surprisingly, its first ionization potential ($^1E_{1/2}$) in acetonitrile solution is slightly *higher* (by ca. 0.07 eV) and $^2E_{1/2}$ is *lower* (by 0.05 eV) than that of TTF (Table I). A full discussion of this observation is deferred to the full paper. It reacts with the usual acceptors and produces organic metals[13] with, for example, I_3^-, IBr_2^-, and $Cu(SCN)_2^-$. For the I_3^- salt, the resistance ratio between 300 and 30 K is ca. 200, its magnetic susceptibility is temperature independent (Pauli) (300–20 K), and its EPR signal (g = 2.0073; cf. TTF, g = 2.0083) in solution has a concentration-dependent line width of only 0.1–1.0 G.

The results of the X-ray structure determination[14] are shown in Figures 1 and 2. The conformation of BO is tub-shaped with a rather long inter-ring bond of 1.357 (6) Å, particularly when compared to ET (1.319 Å);[15] all other bond lengths and angles appear normal. As far as the sp^2 C–O bond is concerned, the dithiole ring behaves as if it were aromatic, imparting a degree of multiple-bond character to the C(3)–O(1) and C(4)–O(2) bonds [1.365 (6) and 1.368 (5) Å, respectively]; these bond lengths are similar to those found in aromatic methoxy compounds.[16] It will be interesting to learn how much these interatomic distances will decrease when the molecule is charged.[17,18] The solid consists of sheets of BO along the *a*–*c* plane (Figure 2) with short contacts between chalcogen atoms within the sheets (S(1)–O(4) = 3.32 Å, sum of van der Waals radii = 3.32; S(1)–S(4) = 3.50 Å, sum of van der Waals radii = 3.60 Å) and longer chalcogen contacts between sheets (S(4)–O(2) = 3.41 Å; S(2)–O(1) = 3.78 Å).

Acknowledgment. We thank the National Science Foundation for support through Grant DMR-8514944. We also thank Nancy Keder for assistance with the X-ray structure analysis.

Supplementary Material Available: Tables of interatomic distances, bond angles, and equivalent isotropic temperature factors for BEDO-TTF (3 pages); tables of observed and calculated structure factors for BEDO-TTF (7 pages). Ordering information is given on any current masthead page.

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(12) Mp 178 °C dec. Anal. Calcd for $C_{10}H_8O_4S_4$: C, 37.49; H, 2.52; S, 40.02. Found: C, 37.62; H, 2.52; S, 39.96. LRMS (EI) 320 (0.47, M^+), 292 (0.22, $M^+ - C_2H_4$), 204 (0.511, $M^+ - C_4H_4O_2S$), 176 (0.285, $C_4S_4^+$), 160 (0.313, M^{+2} or $M^+/2$), 102 (0.092), 88 (1.00, $C_2S_2^+$), 76 (0.373, CS_2^+). Ir (KBr) 2940 w, 1650 m, 1450 w, 1275 w, 1245 w, 1205 m, 1180 sh, 1165 s, 1095 m, 1015 w, 965 m, 870 m, 590 w, 565 w; UV–vis [λ_{max} (ϵ), CH_3CN] 200 (1.33×10^4), 315 (1.14×10^4), 337 (9.69×10^3), 517 (1.48×10^2) [cf. ET 197 (3.6×10^4), 320 (1.7×10^4), 345 sh (1×10^4), 480 (2.9×10^2)]; NMR ($CDCl_3$, ppm relative to TMS) 4.25 s. IP (UV photoelectron spectroscopy) 6.45 eV (D. Lichtenberger et al. (unpublished); we thank Professor Lichtenberger and Dr. Roy L. Johnston for private communication).

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(14) $C_{10}H_8O_4S_4$, orthorhombic; space group $P2_12_12_1$; $Z = 4$; $a = 7.515$ (2), $b = 7.627$ (2), $c = 21.794$ (5) Å; $V = 1249.16$ Å^3, $D_c = 1.69$ g cm^{-1}, $D_{exp} =$ 1.65 g cm^{-1}, $\mu = 7.1$ cm^{-1}; $2\theta \geq 60°$; 1599 reflections used for refinement; R = 0.048, $R_w = 0.063$; $S = 2.02$. Details to be published (Srdanov, G., paper in preparation).

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(17) The crystal structure of an iodide salt is currently being determined (Srdanov, G., unpublished).

(18) In the crystal structure of *p*-methoxybenzoic acid, the bond in question has decreased to 1.356 Å (Colapietro, M.; Domenicano, A. *Acta Crystallogr.* **1978**, *B34*, 3277). In 5-methoxy-2-nitrosophenol, where the methoxy group is in conjugation with what is proposed to be an *o*-quinone monooxime tautomer, the $CH_3O—C=C$ bond length is further reduced to 1.34 Å (Bartindale, G. W. R.; Crowder, M. M.; Morley, K. A. *Acta Crystallogr.* **1958**, *12*, 111).