

S0040-4039(96)00450-9

## 2-(1,3-Benzodithiol-2-ylidene)-1,3-benzoxathiole (Dibenzo-oxatrithiafulvalene, DBOTTF): The First Tetraheterofulvalene containing Oxygen

Samuel T. D'Arcangelis\* and Dwaine O. Cowan\*

Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218

Abstract: The synthesis and characterization of 2-(1,3-benzodithiol-2-ylidene)-1,3-benzoxathiole (dibenzo-oxatrithiafulvalene, DBOTTF), the first example of a tetraheterofulvalene containing oxygen within the fulvalene moiety, are described. Redox potentials of DBOTTF are compared with the other known dibenzotetraheterofulvalene derivatives. Copyright © 1996 Elsevier Science Ltd

The first organic metal, tetrathiafulvalene tetracyano-*p*-quinodimethane (TTF-TCNQ), was discovered in 1973.<sup>1</sup> Over the last twenty years a variety of new organic charge-transfer (C-T) complexes and complex salts has been synthesized.<sup>2</sup> Ambient pressure superconductivity in this class of compounds was first discovered in 1980.<sup>3</sup> Since then, superconducting critical temperatures (T<sub>c</sub>) as high as 12.4 K have been achieved at ambient pressure in the complex salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) series of C-T complexes.<sup>4</sup> Many research groups continue to seek structure-property correlations in organic conductors, and elevation of T<sub>c</sub> in organic superconductors.

Inorganic and organic metals that exhibit the poorest room temperature metallic conductivities often exhibit the highest superconducting  $T_c$ .<sup>5</sup> In the domain of C-T complexes containing tetraheterofulvalenes, tetratellurafulvalenes, tetraselenafulvalenes, and finally tetrathiafulvalenes in that order have produced poorer metals, and at the same time have produced more superconductors, with increasingly higher  $T_c$ 's.<sup>6</sup> These two trends are supported by some formulations from the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity.<sup>7</sup> These observations imply a trend toward tetraheterofulvalenes containing oxygen for increasing the  $T_c$  of the fulvalene class of C-T complexes. We therefore sought a general synthetic route for tetraheterofulvalenes containing oxygen. In this communication we report the synthesis of dibenzo-oxatrithiafulvalene, (DBOTTF, 5), an oxatrithiafulvalene, the first reproducible example<sup>8</sup> which contains an oxygen incorporated within<sup>9</sup> the fulvalene moiety.

DBOTTF was targeted as a simple model for a more general synthesis of oxatrithiafulvalene derivatives. As illustrated in Scheme 1, [(2-hydroxyphenyl)thio]acetic acid, methyl ester (2) was efficiently synthesized upon nucleophilic attack of chloroacetic acid methyl ester by hydroxythiophenol (1) in the presence of triethylamine. Thioether 2 was chlorinated to chloro[(2-hydroxyphenyl)thio]acetic acid, methyl ester (3) with Nchlorosuccinimide (NCS), in a manner described by Bordwell and coworkers.<sup>10</sup> Chlorothioether 3 was quickly converted into 1,3-benzoxathiole-2-carboxylic acid, methyl ester (4) with Li<sup>+</sup>[dimethylsulfoxide, (DMSO)]<sup>-</sup> in DMSO,<sup>11</sup> in an intramolecular Williamson ether synthesis. Coupling of benzoxathiole 4 with bis(dimethylaluminum)-1,2-benzenedithiol, in the manner similar<sup>12</sup> to that described by Mori and Inokuchi for the synthesis of unsymmetrical tetrathiafulvalenes,<sup>13</sup> produced 2-(1,3-benzodithiol-2-ylidene)-1,3benzoxathiole (dibenzo-oxatrithiafulvalene, DBOTTF, 5), a bright, lemon yellow solid.<sup>14</sup>

Scheme 1. Synthetic pathway to DBOTTF.



Reagents and conditions: i) toluene, 5.0 eq ClCH<sub>2</sub>COOCH<sub>3</sub>, 1.2 eq NEt<sub>3</sub>, rt, 16 h., chrom. silica/CH<sub>2</sub>Cl<sub>2</sub> ii) 50% CHCl<sub>3</sub>/50% CCl<sub>4</sub>, 1 eq NCS, rt, 2 h. iii) DMSO, 1 eq n-BuLi, rt, 30 min. iv) CH<sub>2</sub>Cl<sub>2</sub>, 0.5 eq o-((H<sub>3</sub>C)<sub>2</sub>AlS)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 40°C, 5 min, chrom. silica/CCl<sub>4</sub>, in the dark.

Cyclic voltammetry (CV) reveals that DBOTTF (5) exhibits two reversible one-electron oxidations. As shown below in Table 1, values of the first oxidation potentials of all the known dibenzo- derivatives compare closely with those of DBOTTF.<sup>15</sup>

Compound-Common name	acronym	E10x	E20x	ΔΕ
Dibenzo-oxatrithiafulvalene	DBOTTF	+0.72	+1.22	+0.50
Dibenzotetrathiafulvalene	DBTTF <sup>15</sup>	+0.71	+1.14	+0.43
Dibenzotetraselenafulvalene	DBTSF <sup>15</sup>	+0.78	+1.17	+0.39
Dibenzotetratellurafulvalene	DBTTeF <sup>15</sup>	+0.71	+1.05	+0.36

Table 1. Cyclic Voltammetry of the Known Dibenzotetraheterofulvalenes <sup>a</sup>

<sup>a</sup> All CV data were obtained in 0.2 M Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> in dry CH<sub>2</sub>Cl<sub>2</sub> versus SCE, under argon. Ferrocene/ferrocenium redox wave was used as a reversible one-electron standard.  $\Delta E = E_2^{OX} - E_1^{OX}$ .

The first oxidation/reduction of DBOTTF,  $E_1^{0x}$ , remains reversible even in the presence of small amounts of water in the electrolyte solution. Reversibility of the second oxidation becomes apparent when the electrolyte solution is thoroughly dried with a small amount of added activated basic alumina. The value of  $E_2^{0x}$  for electron donors or acceptors is of particular interest. Relative differences in oxidation/reduction potentials of donors and acceptors have been correlated to the degree of solid state charge transfer.<sup>16</sup> Partial charge transfer is one essential factor in the inducement of a conduction band in organic C-T and complex salts.

We have synthesized the first oxatrithiafulvalene, DBOTTF, an electron donor that exhibits properties worthy of study for use in assembling organic conductors. Substitution of an oxygen for a sulfur in a tetrathiafulvalene has a minimal effect on the oxidation/reduction potentials on these electron donors, particularly on the value of  $E_1^{ox}$ . A general synthesis for other analogs of oxatrithiafulvalene is currently being developed by one of us (SD) for the purpose of creating a series of oxatrithiafulvalenes.

Support by the National Science Foundation Grants DMR-8921071 and DMR-9223481 is gratefully acknowledged.

CAS Registry Numbers: 2, [160901-56-4]; 3, [160901-58-6]; 4, [160901-57-5]; 5, [160901-59-7].

## **References and Notes:**

1. Ferraris, J.; Cowan, D. O.; Walatka, V.; Perstein, J. H. J. Am. Chem. Soc. 1973, 95, 948 and Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J.; Solid State Commun. 1973, 12, 1125.

2. For reviews on the history and theory of organic conductors and superconductors, see: Cowan, D. O.; Wiygul, F. M. Chem. Eng. News 7/21 1986, 64, 28-45, Adrian, F. J; Cowan, D. O. Chem. Eng. News 12/21 1992, 70, 24-41, and Bryce, M. R.; Murphy, L. C. Nature 1984, 309, 119-126.

3. Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G. T.; Jacobsen, C. S.; LaPlaca, S. J.; Pedersen, H. J.; Scott, H. J. J. Am. Chem. Soc. 1981, 103, 2440.

4. Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort,

K. G.; Thompson, J. E.; Stupta, D. L.; Jung, D.; Whangbo, M. H. Inorg. Chem. 1990, 29, 2555-2557.

5. Cowan, D. O., In New Aspects of Organic Chemistry I. Proceedings of the 4th International Kyoto Conference on New Aspects of Organic Chemistry, Yoshida, Z.; Shiba, T.; Ohshiro, Y., Eds., VCH Publishers, New York, 1989, 191.

6. Many reported tetratellurafulvalene complexes are good metals with respect to other C-T complexes and remain metals throughout large temperature domains. No superconducting complexes of tetratellurafulvalene currently exist. Only one complex of a tetraselenafulvalene derivative has produced an ambient pressure superconductor. Many ambient pressure superconductors incorporating one of a few derivatives of tetrathiafulvalene (most notably, BEDT-TTF) have been discovered.

7. Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. Phys. Rev. 1957, 108, 1175.

8. According to Ishida, T.; Ishihara, Y.; Yamaga, T.; Nogami, T. Synth. Met. 1993, 56, 1968-1971 and Suzuki, T.; Yamochi, H.; Srdanov, K.; Hinkelmann, K.; Wudl. F. J. Am. Chem. Soc. 1989, 111, 3108-3109, reactions conditions described in Safiev, O. G.; Nazarov, D. V.; Zorin, V. L.; Rakhmankulov, D. L. Khim. Geterotsikl. Soedin. 1988, 6, 852. for the synthesis of Bis-(1,3-benzodioxole)-2-2'-ylidene, (Dibenzo-tetraoxafulvalene, DBTOF) are not reproducible.

9. Synthesis for a tetrathiafulvalene with oxygens exocyclic with respect to the fulvalene moiety is described in: Suzuki, T.; Yamochi, H.; Srdanov, K.; Hinkelmann, K.; Wudl. F. J. Am. Chem. Soc. 1989, 111, 3108-3109.

10. Bordwell, F. G.; Wolfinger, M. D.; O'Dwyer, J. B. J. Org. Chem. 1974, 39, 2516-2519.

11. Corey, E. J.; Chaykovsky, M. J. Am. Chem. Soc. 1965, 87, 1345-1353.

12. Bis(dimethylaluminum)-1,2-benzenedithiol was employed in sub-equivalent amounts, because equivalent amounts allowed overreaction, producing some dibenzotetrathiafulvalene (DBTTF), which was very difficult to separate chromatographically from DBOTTF.

13. Mori, T.; Inokuchi, H. Chem. Lett. 1992, 1873-1876.

Spectroscopic data, for DBOTTF, 5: mp 154.7-156.9 °C. 300 MHz <sup>1</sup>H NMR & 7.237-7.025 irregular 14. multiplet; <sup>13</sup>C NMR eight tertiary <sup>13</sup>C signals at δ 126.56, 125.66, 125.61, 123.51, 121.91, 121.66, 121.54, 110.85 plus four quaternary  $^{13}$ C signals at  $\delta$  153.89, 137.13, 135.78, 124.53; IR (CCl4) 3065 (w), 1639 (s), 1592 (w), 1572 (w), 1564 (w), 1463 (vs), 1448, (s), 1273 (w), 1231, (vs), 1131 (s), 1118 (m), 1058 (w), 1047 (w), 1018 (w), 970 (m), 870 (m) cm<sup>-1</sup>; MS (electron impact, EI) m/z 227 (6.8%), 228 (1.7%), 259 (45.4%), 260 (7.5%), 261 (5.9%), 288 (100.0%), 289 (18.1%), 290 (16.2%), 291 (2.0%), 292 (1.0%); (chemical ionization, CI) m/z 289 (100.0%)(M+1), 290 (20.0%), 291 (15.8%), 292 (2.5%); (accurate mass) m/z calc: 287.9737, found: 287.9741 (fast atom bombardment, FAB) no peaks > m/z 289. for 4: <sup>1</sup>H NMR  $\delta$ 7.100 ddd (doublet of doublet of doublets) (1H), 7.029 ddd (1H), 6.915 ddd (1H), 6.890 dt (doublet of triplets) (1H), 6.260 s (1H), 3.766 s (3H);  $^{13}$ C NMR  $\delta$  168.66, 155.52, 126.29, 123.29, 121.80, 121.59, 110.48, 81.46, 52.79; MS (EI) m/z 137 (100.0%), 138 (7.6%), 139 (4.1%), 196 (20.4%), 197 (2.0%). for 3: <sup>1</sup>H NMR δ 7.527 ddd (1H), 7.378 ddd (1H), 7.033 dd (1H), 6.934 ddd (1H), 6.599 (v) s (1H), 5.410 s (1H), 3.789, s (3H); <sup>13</sup>C NMR δ 166.33, 157.48, 137.17, 132.94, 120.83, 115.71, 113.53, 62.77, 53.59; MS (EI) m/z 125 (40.4%), 137 (100.0%), 138 (9.8%), 139 (4.8%), 173 (25.0%), 174 (1.3%), 175 (9.7%), 200 (7.4%), 202 (2.8%), 232 (24.0%), 233 (3.5%), 234 (12.6%). for 2:  $^{1}$ H NMR  $\delta$  7.513 (v) s (1H), 7.321 dd (1H), 7.296 dddd (1H), 6.999 dd (1H), 6.865 dt (1H), 3.724 s (3H), 3.494, s (1H);  $^{13}$ C NMR  $\delta$  171.11, 157.40, 136.10, 131.48, 120.50, 117.86, 115.58, 52.52, 38.36; MS (EI) m/z 137 (55.5%), 138 (65.2%), 139 (59.1%), 166 (52.1%), 198 (100.0%), 199 (10.8%), 200 (4.9%). All <sup>13</sup>C NMR data (decoupled) and <sup>1</sup>H NMR data were obtained in deuterated chloroform (CDCl<sub>3</sub>).

15. Data obtained from: Lerstrup, K.; Talham, D.; Bloch, A.; Poehler, T.; Cowan, D. O. Chem. Commun. 1982, 336-337.

16. Saito, G.; Ferraris, J. P. Bull. Chem. Soc. Jpn. 1980, 53, 2141-2145.

(Received in USA 18 January 1996; revised 29 February 1996; accepted 1 March 1996)