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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

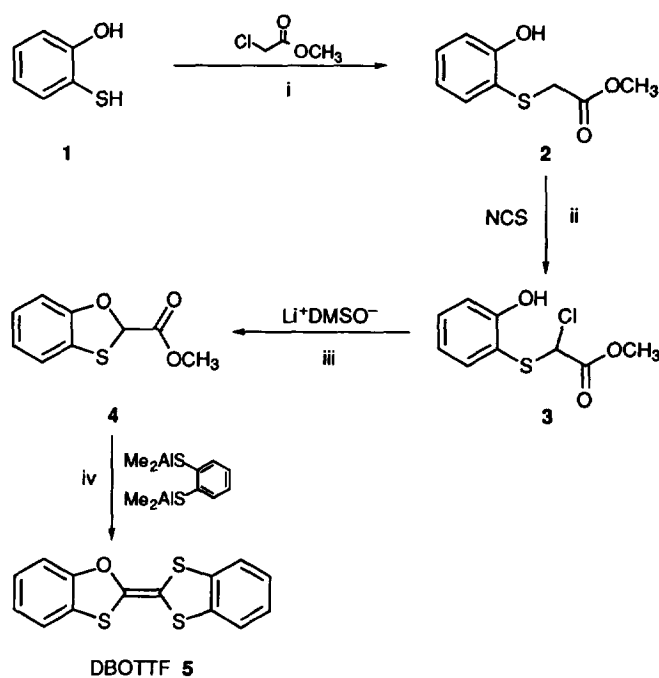
The first organic metal, tetrathiafulvalene tetracyano-*p*-quinodimethane (TTF-TCNQ), was discovered in 1973.¹ Over the last twenty years a variety of new organic charge-transfer (C-T) complexes and complex salts has been synthesized.² Ambient pressure superconductivity in this class of compounds was first discovered in 1980.³ Since then, superconducting critical temperatures (T_c) 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.⁴ Many research groups continue to seek structure-property correlations in organic conductors, and elevation of T_c in organic superconductors.

Inorganic and organic metals that exhibit the poorest room temperature metallic conductivities often exhibit the highest superconducting T_c .⁵ 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.⁶ These two trends are supported by some formulations from the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity.⁷ 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 example⁸ which contains an oxygen incorporated within⁹ 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 N-chlorosuccinimide (NCS), in a manner described by Bordwell and coworkers.¹⁰ Chlorothioether 3 was quickly converted into 1,3-benzoxathiole-2-carboxylic acid, methyl ester (4) with $\text{Li}^+[\text{dimethylsulfoxide, (DMSO)}]^-$ in DMSO,¹¹ in an intramolecular Williamson ether synthesis. Coupling of benzoxathiole 4 with bis(dimethylaluminum)-1,2-benzenedithiol, in the manner similar¹² to that described by Mori and Inokuchi for the synthesis of unsymmetrical tetrathiafulvalenes,¹³ produced 2-(1,3-benzodithiol-2-ylidene)-1,3-benzoxathiole (dibenzo-oxatrithiafulvalene, DBOTTF, 5), a bright, lemon yellow solid.¹⁴

Scheme 1. Synthetic pathway to DBOTTF.



Reagents and conditions: i) toluene, 5.0 eq $\text{ClCH}_2\text{COOCH}_3$, 1.2 eq NEt_3 , rt, 16 h., chrom. silica/ CH_2Cl_2
 ii) 50% CHCl_3 /50% CCl_4 , 1 eq NCS, rt, 2 h. iii) DMSO, 1 eq $n\text{-BuLi}$, rt, 30 min. iv) CH_2Cl_2 , 0.5 eq $o\text{-(H}_3\text{C)}_2\text{AIS)}_2\text{C}_6\text{H}_4$, 40°C, 5 min, chrom. silica/ CCl_4 , 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.¹⁵

Table 1. Cyclic Voltammetry of the Known Dibenzotetraheterofulvalenes ^a

Compound-Common name	acronym	E ₁ ^{ox}	E ₂ ^{ox}	ΔE
Dibenzo-oxatrithiafulvalene	DBOTTF	+0.72	+1.22	+0.50
Dibenzotetrathiafulvalene	DBTTF ¹⁵	+0.71	+1.14	+0.43
Dibenzotetraselenafulvalene	DBTSF ¹⁵	+0.78	+1.17	+0.39
Dibenzotetratellurafulvalene	DBTTeF ¹⁵	+0.71	+1.05	+0.36

^a All CV data were obtained in 0.2 M Bu₄N⁺BF₄⁻ in dry CH₂Cl₂ versus SCE, under argon. Ferrocene/ferrocenium redox wave was used as a reversible one-electron standard. ΔE = E₂^{ox} - E₁^{ox}.

The first oxidation/reduction of DBOTTF, E₁^{ox}, 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 E₂^{ox} 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.¹⁶ 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 E₁^{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.

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 14. *Spectroscopic data, for DBOTTF, 5*: mp 154.7-156.9 °C. 300 MHz ^1H NMR δ 7.237-7.025 irregular multiplet; ^{13}C NMR eight tertiary ^{13}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 δ 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⁻¹; 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*: ^1H NMR δ 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 δ 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*: ^1H 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); ^{13}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*: ^1H NMR δ 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 δ 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 ^{13}C NMR data (decoupled) and ^1H NMR data were obtained in deuterated chloroform (CDCl₃).
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