Synthesis, Structure, and Oxidation of Novel 4,7-Disubstituted Benzotrithioles. Formation and Characterization of Radical Cations with 11π Electron Framework

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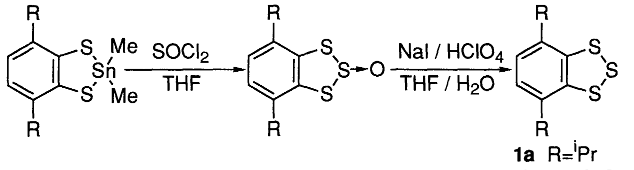
Novel benzene fused cyclic polysulfides, 4,7-disubstituted benzotrithioles, are synthesized and characterized by X-ray crystallographic analysis, and their one-electron oxidation resulted in the formation of stable 4,7-disubstituted benzotrithiolium radical cations with an 11π electron framework.

Although a number of cyclic polysulfides containing linked four,[1] five,[2] seven,[3] eight,[4] and nine[5] sulfur atoms have been reported, only a few examples of trithioles, which are known to be converted to unusual 7π radical cations[6] by one-electron oxidation, have been reported due to their inherent instability.[7] We recently reported that the construction of reversible one-electron redox systems using 4,7-diisopropylbenzotriselenole and found by ESR spectroscopy that its radical cation salt obtained on treatment with one-electron oxidant has a 7π framework.[8] However, delocalization of the spin between the trichalcogenide and benzene rings has not been clear. We report here the synthesis of stable 4,7-disubstituted benzotrithioles **1a**,**b** by taking advantage of a new synthetic strategy and the characterization of the crystal structure of **1b** by X-ray crystallographic analysis. Furthermore, we show that trithioles **1a**,**b** provide 4,7-disubstituted benzotrithiolium hexafluorophosphates **2a**,**b**, which are new type of isolable benzene fused trithiolium radical cation salts, by one-electron oxidation.

We employed 4,7-disubstituted 2,2-dimethyl-1,3,2-benzodithiastannoles in preparing the trithioles **1a**,**b** as synthetic equivalents of unstable 1,4-disubstituted 2,3-benzenedithiols. The stannoles were readily obtained by ortho lithiation and thiolation of commercially available 1,4-disubstituted benzene derivatives followed by stannylation in good yields.[9] Introduction of a sulfur atom at the 2-position was performed by the following method (Scheme 1). Stannole in THF was treated with 1.2 equiv. of thionyl chloride at -78 °C under an N_2 atmosphere. The mixture was stirred at -78 °C for 30 min and after usual work-up the crude product was purified by column chromatography (silica gel; eluent, $CCl_4/CHCl_3 = 1/1$) to give the corresponding 2-oxides in 97 (isopropyl) and 96% (methoxy) yields, respectively. Subsequently, a mixture of the 2-oxide and 5.0 equiv. of sodium iodide in THF/H_2O at 0 °C was treated with 60% $HClO_4$ (ca 50 equiv.) and was stirred at room temperature for 3 h.[10] After usual work-up, the crude product was purified by column chromatography (silica gel; eluent, CCl_4) to give **1a** and **1b** in 88 and 85% yields, respectively.



1a R=^{i}Pr
1b R=MeO

Scheme 1.

The crystal structure of **1b** was confirmed by X-ray crystallographic analysis (Figure 1).[11] Two sulfur atoms (S(1) and S(3)) are almost coplanar with the benzene ring, while the sulfur at 2-position lies out of this plane (S-S-S-C torsion angles are 39.1 and 40.3°). A unique distorted geometry of the 5-membered trithiole ring implies the presence of lone pair-lone pair repulsion of three divalent sulfur atoms. The sulfur-sulfur bond lengths are similar to those in S_8, and the sulfur-carbon(sp^2) bond lengths (1.770, 1.768 Å) are comparable with those determined for benzopentathiepin (1.774, 1.777 Å)[2b] and marginally longer than those of the general sulfur-carbon(sp^2) single bond lengths (1.75 Å). The bond lengths, bond angles, and torsion angles are similar to those for 4-nitro-6-trifluoromethylbenzotrithiole,[7d,e] the only benzene fused trithiole for which the crystal structure is reported.

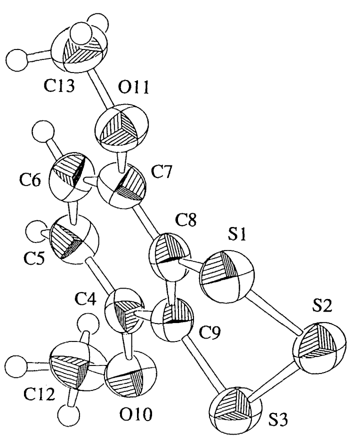
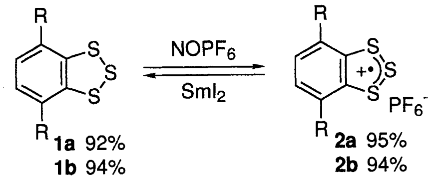


Figure 1.

ORTEP view of **1b**. Selected bond lengths (Å), bond angles (°), and torsion angles (°) are as follows: S(1)-S(2) 2.064(3), S(2)-S(3) 2.062(3), S(1)-C(8) 1.770(6), S(3)-C(9) 1.768(6), C(8)-C(9) 1.390(9); S(1)-S(2)-S(3) 95.5(1), S(2)-S(1)-C(8) 93.4(2), S(2)-S(3)-C(9) 93.7(2), S(1)-C(8)-C(9) 117.7(5), S(3)-C(9)-C(8) 118.4(5); S(1)-S(2)-S(3)-C(9) 39.1(3), S(3)-S(2)-S(1)-C(8) -40.3(2), S(1)-C(8)-C(9)-S(3) -2.9(8), S(1)-C(8)-C(7)-C(6) -173.2(6), S(1)-C(8)-C(9)-C(4) 175.6(5), S(3)-C(9)-C(8)-C(7) -179.6(6), S(3)-C(9)-C(4)-C(5) 178.0(6).

The cyclic voltammetry for trithioles **1a**,**b** was measured in MeCN at 20 °C containing 0.1 mol dm^{-3} $nBu_4N^+ClO_4^-$ as supporting electrolyte using glassy carbon working electrode and platinum counter electrode and Ag/0.01 mol dm^{-3} $AgNO_3$ in MeCN reference electrode under an Ar atmosphere. The voltammograms showed a well-defined reversible one-electron oxidation wave each at $E_{1/2}$=0.73 V (**1a**), 0.70 V (**1b**). This result clearly indicates that trithiole **1** provides a stable radical cation even at room temperature. New trithiolium radical cation salts **2a**,**b** were readily isolated in the one-electron oxidation of **1a**,**b** with 1 equiv. of $NOPF_6$ in ether-acetonitrile (Scheme 2). The dark purple salts **2a**,**b** were stable and the structures in solution were analyzed by ^{31}P NMR and ESR spectroscopy.[12] The salts **2a**,**b** dissolved readily in THF to give red-purple solutions. The ESR spectra of each solution at -50 °C showed the presence of triplet peaks (**2a**, g = 2.012, aH = 0.106 mT;



Scheme 2.

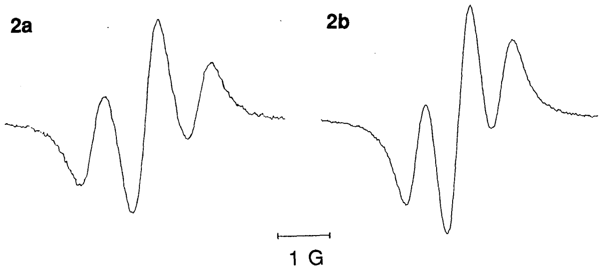


Figure 2. ESR spectra of **2a**,**b** in THF at -50 °C.

2b, g = 2.012, aH = 0.081 mT) attributable to a trithiolium radical cation, and the aH splitting (triplet) indicates a partially spin delocalized system over both benzene and trithiole rings with an 11π electron framework (Figure 2).[13] Unfortunately, it has not yet been successful to grow single crystals suitable for X-ray diffraction. Interestingly, the salts **2a**,**b** underwent one-electron reduction by treatment with 1 equiv. of samarium(II) iodide to give **1a**,**b** quantitatively.

Trithiole **1b** was treated with concentrated H_2SO_4 as an oxidant,[14] because the chemical reactivities of trithioles have received little attention due to their less stability. Hydrolysis of the H_2SO_4 solution of **1b** led to 1-oxide (29%), 2-oxide (19%), and **1b** (48%). Treatment of trithiolium salt **2b** with water resulted in a similar product distribution as follows; 1-oxide (33%), 2-oxide (17%), and **1b** (50%). These product studies, combined with direct evidence for the radical cations from ESR data, allowed mechanistic conclusions to be drawn about the one electron transfer step and formation of the intermediary radical cation in the oxidation with concentrated H_2SO_4. In contrast, the oxidation of trithiole **1b** with m-chloroperbenzoic acid (mCPBA) gave 1-oxide and 2-oxide in 71 and 24% yields, respectively.

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11 Crystal data for **1b**: M=232.33, $C_8H_8O_2S_3$, orthorhombic, space group $P2_12_12_1$, a=16.628(1), b=16.958(1), c=6.965(3) Å, V=1963.9(5) $Å^3$, Z=8, D_c=1.571 g cm^{-3}. The final cycle of full-matrix least-squares refinement was based on 1410 observed reflections (I>3.00σ(I)) and 300 variable parameters with R (R_w)=0.050 (0.060). The bond lengths and angles of the other molecule illustrated in Figure 1 are very similar to those listed in the figure.

12 Compound **2a**: Dark purple powder; mp 89.0-90.5 °C (decomp.); Anal. Calcd for $C_{12}H_{16}S_3PF_6$: C, 35.91; H, 4.02. Found: C, 36.02; H, 3.74. $\{^1H\}^{31}P$ NMR (162 MHz, THF-d_8, relative to H_3PO_4) δ -145.3 (sept, $J_{^{31}P^{19}F}$ =711 Hz). Compound **2b**: Dark purple powder; mp 161.0-162.5 °C (decomp.); Anal. Calcd for $C_8H_8O_2S_3PF_6$: C, 25.47; H, 2.14. Found: C, 25.82; H, 2.07. $\{^1H\}^{31}P$ NMR (162 MHz, THF-d_8, relative to H_3PO_4) δ -145.1 (sept, $J_{^{31}P^{19}F}$=711 Hz).

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