

THE FIRST SYNTHESIS AND CHARACTERIZATION OF BISBENZOTRITHIOLE CONTAINING TWO BENZOTRITHIOLES LINKED BY AN ALKANEDIOXY SPACER

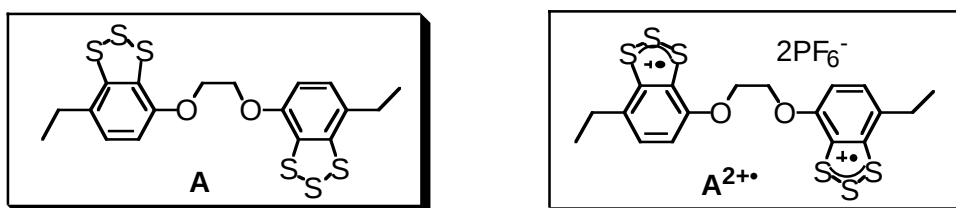
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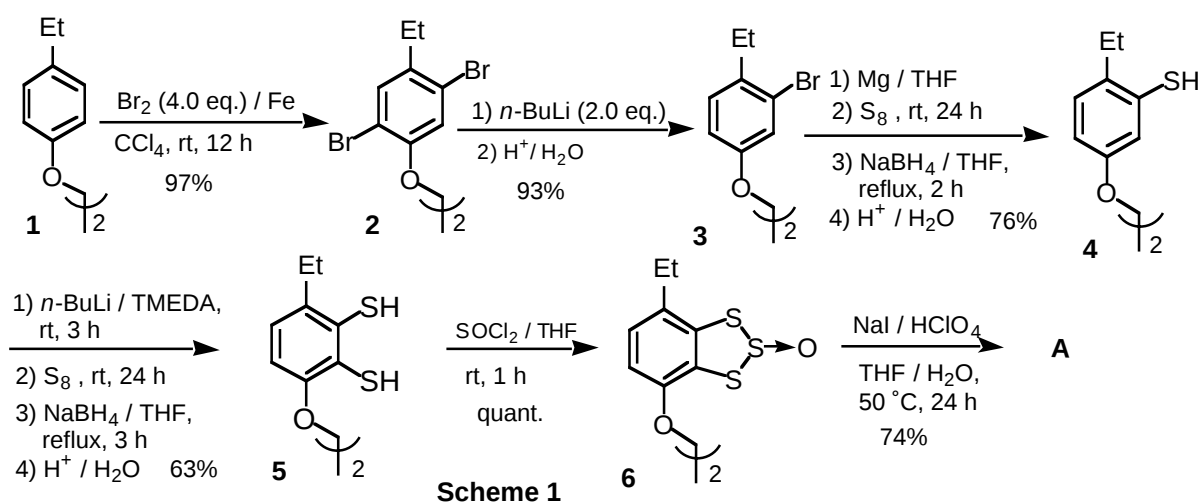
Abstract—The first synthesis and electrochemical characterization of 7,7'-diethyl-4,4'-ethylenedioxybis(benzo[1,2-*d*][1,2,3]trithiole) (**A**) containing two benzotrithiole rings linked by an ethylenedioxy group are described.

Cyclic benzopolychalcogenides such as benzopentathiepins,¹ benzotetrathiins,² and benzotrithioles³ have been studied by many heteroatom chemists in fields of synthetic, structural, and biological chemistry.⁴ We also established a synthetic methodology for obtaining benzopentathiepins⁵ and benzotrithioles⁶ by the sulfurization-cyclization of the corresponding benzenedithiols or their synthetic equivalents. These successes in the synthesis of cyclic benzopolychalcogenides and related compounds have allowed us to study the interaction between the polysulfide ring and a functional group, such as amino and sulfide groups. We found out that the benzopentathiepin was stable toward cyclic amines such as pyridine and pyrimidine and sulfide moiety contained in the thiophene ring.⁷ Now our interests focused on the intramolecular interaction of two polysulfide rings linked with a spacer such as alkanediyl and alkanedioxy groups. Here, we wish to report our preliminary findings on the first synthesis and electrochemical characterization of 7,7'-diethyl-4,4'-ethylenedioxybis(benzo[1,2-*d*][1,2,3]trithiole) (**A**), containing two benzotrithiole rings linked by an ethylenedioxy group.



A route for the synthesis of bisbenzotrithiole (**A**) was examined as follows (Scheme 1). Thus, tetrabromination of bis[1,2-(4-ethylphenoxy)]ethane (**1**) with bromine in CCl₄ and then debromination of resulting **2** using *n*-BuLi afforded bis[1,2-(3-bromo-4-ethylphenoxy)]ethane (**3**) in high yield. A Grignard reagent obtained from **3** by reaction with magnesium in THF was treated with elemental sulfur and then reduced with NaBH₄ under reflux of THF to give 1,2-bis(4-ethyl-3-mercaptophenoxy)-ethane

(4). The dithiol (4) obtained was converted to 1,2-bis(4-ethyl-2,3-dimercaptophenoxy)ethane (5) by ortholithiation, sulfurization, and then reduction with NaBH₄. The treatment of 5 with thionyl chloride afforded trithiole-2-oxide (6) and reduction of 6 with sodium iodide in the presence of HClO₄ gave the desired bisbenzotrithiole, 7,7'-diethyl-4,4'-ethylenedioxybis(benzo[1,2-*d*][1,2,3]trithiole) (**A**)⁸ in 32% overall yield.



The structure of bisbenzotrithiole (**A**) was confirmed spectroscopically and finally determined by X-Ray crystallography.⁹ The ORTEP drawing of compound (**A**) was shown in Figure 1. According to the result of X-Ray crystallography (Table 1), most bond lengths and angles and torsion angles of each trithiole ring were similar to the previous data for the benzotrithiole ring¹⁰. It is very interesting that the structure of **A** is linear and the two benzotrithiole rings are independent of each other. We were not able to observe any interaction between the two benzotrithiole rings in the crystal packing (Figure 1).

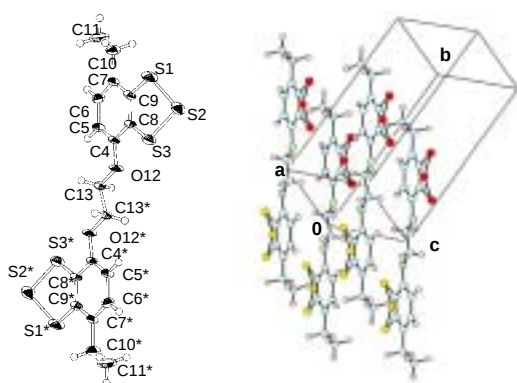


Figure 1. ORTEP drawing and crystal packing of **A**

Table 1. Selected distances and angles of **A**

Bond lengths (Å)	S(1)-C(9)	1.791(6)
	S(3)-C(8)	1.765(6)
	S(1)-S(2)	2.057(3)
	S(2)-S(3)	2.062(2)
	S(3)-C(8)-C(9)	120.8(4)
Bond angles (°)	S(1)-C(9)-C(8)	114.3(5)
	S(2)-S(1)-C(9)	95.2(2)
	S(2)-S(3)-C(8)	93.1(2)
	S(1)-S(2)-S(3)	95.1(1)
	S(3)-S(2)-S(1)-C(9)	40.3(2)
Torsion angles (°)	S(1)-S(2)-S(3)-C(8)	39.7(2)

Next, we investigated the electrochemical property for **A** by cyclic voltammetry, which gave a clear reversible redox voltammogram based on one step oxidation-reduction as shown in Figure 2.¹¹ The $E_{1/2}$ (V) value of 0.62 V obtained for **A** is close to the one for 1-ethyl-4-methoxybenzotrithiole¹² (Table 2). This result suggests that a radical cation species could be formed electrochemically by the oxidation of **A** and could return to a neutral molecule by reduction. Moreover, it was found that each ring of the two

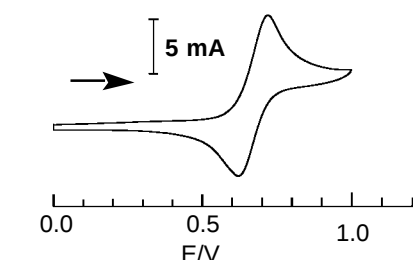
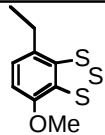
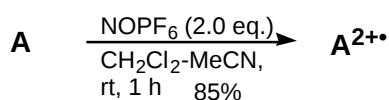


Figure 2. Cyclic voltammogram of **A**

Table 2. Redox potential

	A	
Epa (V)	0.67	0.66
Epc (V)	0.57	0.57
E1/2 (V)	0.62	0.62

trithioles was oxidized independently. Based on the results of electrochemistry, the oxidation of bisbenzotrithiole (**A**) was investigated using two equivalents of one electron oxidant. Thus, the oxidation of **A** with NOPF₆ in a mixed solvent of CH₂Cl₂/MeCN gave a dark blue powder product, bis-radical cation (**A**^{2+•}),¹³ which decomposed at 109.2 °C (Scheme 2).



Scheme 2

A typical septet peak at -143.7 ppm (¹J_{P-F} = 707 Hz) of the ³¹P NMR spectrum based on the formation of a bis-radical cation (**A**^{2+•}) appeared as shown in Figure 3 and the structure was finally established by elemental analysis. Using ESR spectroscopy, we were able to measure the bis-radical cation (**A**^{2+•}) to show a broad signal at g = 2.017 G as shown in Figure 4¹⁴, but the super fine structure could not be detected. These results suggest that both benzotrithiole rings were oxidized simultaneously by one electron oxidant, NOPF₆, to form two radical cations in the molecule.

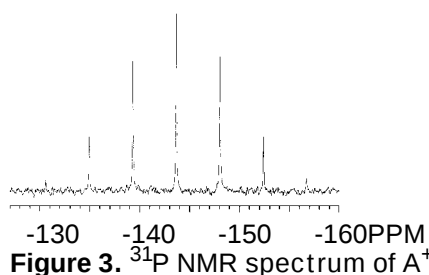


Figure 3. ³¹P NMR spectrum of **A**^{2+•}

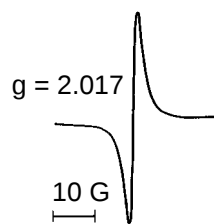


Figure 4. ESR spectrum of **A**^{2+•}

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8. Compound **A**: Orange needles, mp 157 °C (CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 1.19 (6H, t, *J* = 7.6 Hz, CH₃), 2.62 (4H, q, *J* = 7.6 Hz, CH₂), 4.34 (4H, s, OCH₂), 6.69 (2H, d, *J* = 8.3 Hz, ArH), 6.88 (2H, d, *J* = 8.3 Hz, ArH). ¹³C NMR (101 MHz, CDCl₃) δ: 14.6, 29.6, 68.0, 112.5, 128.1, 130.0, 133.7, 142.2, 153.1. IR (KBr) ν_{max}(cm⁻¹): 2969, 2890, 1579, 1548, 1462, 1386, 1264, 1224, 1104, 1049, 807, 775. MS (EI, 70 eV) *m/z*: 458 (M⁺). *Anal.* Calcd for C₁₈H₁₈O₂S₆: C, 47.13; H, 3.96. Found: C, 47.00; H, 4.03.
9. Selected crystal data for **A**: C₁₈H₁₈O₂S₆, *M* = 458.70, triclinic, space group P1(#2), *a* = 7.595 (3) Å, *b* = 12.555(8) Å, *c* = 5.314 Å, α = 100.54 (5)°, β = 93.42(4)°, γ = 98.38(4)°, *V* = 490.9(5) Å³, *Z* = 1, *D_c* = 1.551 g/cm³, *F*(000) = 238.00, μ = 65.27 cm⁻¹, radiation CuKα(λ = 1.54178 Å), 2θ_{max} = 136.3°, *R* = 0.068, *R_w* = 0.093.
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11. Conditions of Cyclic voltammetry: Concentration, 2 mM sample/PhCN/0.1M *n*-Bu₄N⁺ClO₄⁻; Working electrode, Glassy-carbon; Reference electrode, Ag/0.01 M AgNO₃; Counter electrode, Pt; Scan rate, 200 mVsec⁻¹.
12. Compound 1-ethyl-4-methoxybenzotrithiole was synthesized from 4-methoxyethylbenzene by our previous method (refs. 6 and 10). 1-Ethyl-4-methoxybenzotrithiole: Pale orange crystals, mp 100°C (CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 1.19 (3H, t, *J* = 7.5 Hz, CH₃), 2.62 (2H, q, *J* = 7.5 Hz, CH₂), 3.84 (3H, s, OCH₃), 6.62 (1H, d, *J* = 8.3 Hz, ArH), 6.90 (1H, d, *J* = 8.3 Hz, ArH). ¹³C NMR (101 MHz, CDCl₃) δ: 14.8, 29.5, 56.1, 110.3, 128.1, 128.5, 132.8, 141.9, 154.0. IR (KBr) ν_{max}(cm⁻¹): 2960, 2934, 2921, 2883, 2863, 2838, 1580, 1549, 1447, 1369, 1268, 1188, 1107, 1058. MS(EI) *m/z* 230 (M⁺). *Anal.* Calcd for C₉H₁₀OS₃: C, 46.92; H, 4.38. Found: C, 46.95; H, 4.37.
13. Bis-radical cation (A²⁺): Dark blue powder, mp 109.2-110.0 °C (decomp). ³¹P NMR (162 MHz, CD₃CN, relative to H₃PO₄) δ: -143.7 (sept, ¹*J*_{P-F} = 707 Hz). *Anal.* Calcd for C₁₈H₁₈O₂ F₁₂P₂S₆: C, 28.88; H, 2.42. Found: C, 29.00; H, 2.52.
14. A measurement of ESR spectrum for A²⁺ in MeCN as a solvent at 16 °C gave a value of *g* = 2.017 G.