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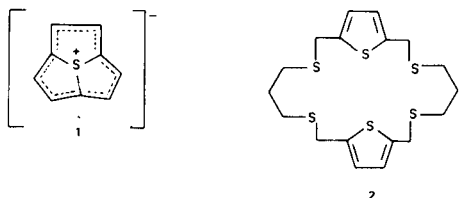
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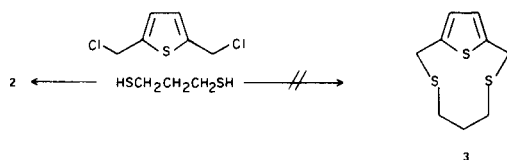
The macrocyclic polythia ether [7.7](2,6)dithia(2,5)thiophenophane **2** has been prepared by condensation of the dilithio salt of propane-1,3-dithiol with 2,5-bis(chloromethyl)thiophene.

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Macrocyclic polythia ether complexes of transition metals are of interest due to the apparent similarities they exhibit with systems of biological interest (1). In the course of efforts directed toward the synthesis of the novel sulfonium ylide **1** (the perimetric anionic moiety of which constitutes a closed cyclic 10 π -electron system) we encountered the macrocyclic polythia ether **2**. Since **2** represents a structural variation on known polythia ether structures (2,3) and as such may be of potential interest as a ligand in studies of macrocyclic metal complexes, we report here on its preparation.



One of our originally planned routes to **1** involved preparation of [7](2,6)dithia(2,5)thiophenophane **3** as an intermediate. Following a published procedure for the preparation of the corresponding benzenoid analog of **3** (3), a solution of the dilithio salt of propane-1,3-dithiol was added to a solution of 2,5-bis(chloromethyl)thiophene under high-dilution conditions. The only isolable product obtained was the crystalline dimer of **3**, i.e. [7.7](2,6)dithia(2,5)thiophenophane **2**, the structure of which was established by nmr and mass spectrometric data and an osmometric molecular weight determination. No product having spectroscopic characteristics attributable to **3** could be detected in the remaining crude product.



EXPERIMENTAL

Proton magnetic resonance spectra (pmr) were recorded using a Varian A-60A instrument. Mass spectra were obtained using a Varian M-66 cycloidal spectrometer. Microanalytical determinations and osmometry were performed by Galbraith Laboratories,

Knoxville, Tenn.

[7.7](2,6)Dithia(2,5)thiophenophane (**2**).

A solution of 1.90 g. (0.0105 mole) of 2,5-bis(chloromethyl)thiophene (**4**) in 500 ml. of tetrahydrofuran was added from a Hershberg funnel to 1200 ml. of aqueous tetrahydrofuran (THF-H₂O, 9:1) with vigorous stirring and during a 10 hour period while adding simultaneously, from another Hershberg funnel, a solution of 1.13 g. (0.0105 mole) of propane-1,3-thiol and 0.66 g. (0.0275 mole) of lithium hydroxide in 500 ml. of aqueous THF (THF-H₂O, 1:1). The final solution was stirred for an additional 60 hours, followed by removal of the solvent *in vacuo* and extraction of the remaining residue with methylene chloride. The organic extract was washed with sodium hydroxide solution, dried over anhydrous magnesium sulfate, concentrated, and diluted with 1 l. of *n*-hexane to yield a turbid mixture which was stored at -10° overnight. Concentration to 300 ml. afforded 0.46 g. of a filterable solid which was chromatographed on silica-gel and recrystallized to yield 0.13 g. (2.5%) of **2** as colorless crystals, m.p. 119.5-120.5°; pmr (deuteriochloroform): δ 1.65 (m [appearance of a quartet, J = 7 Hz], 4H), 2.47 (triplet, 8H, J = 7 Hz), 3.80 (singlet, 8H) and 6.7 (singlet, 4H); ms: M⁺ at *m/e* 432; Mol. Wt. 430 (osmometric, chloroform).

Anal. Calcd. for C₁₈H₂₄S₆: C, 49.95; H, 5.59. Found: C, 50.04; H, 5.47.

Acknowledgments.

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REFERENCES AND NOTES

(1) *E.g.* Cu(I) and Cu(II) complexes of macrocyclic polythia ethers have been examined in investigations of the possible role of the coordination geometry of copper as a source of the unusual spectral and redox properties associated with the "blue copper" proteins: E. R. Dockal, L. L. Diaddario, M. D. Glick and D. B. Rorabacher, *J. Am. Chem. Soc.*, **99**, 4530 (1977); E. R. Dockal, T. E. Jones, W. F. Sokol, R. J. Engerer, D. B. Rorabacher and L. A. Ochrymowycz, *ibid.*, **98**, 4322 (1976); **97**, 7485 (1975), and references cited.

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