

# Preparation and Characterization of 5,6-Dimethyl-5,6-dihydro-[1,4]diselenino[2,3-*d*][1,3]dithiole-2-thione and Similar Compounds

George C. Papavassiliou, George A. Mousdis, George C. Anyfantis, Nikos Assimomytis, and Barry R. Steele

National Hellenic Research Foundation, 48, Vassileos Constantinou Ave., Athens, 116-35, Greece

Reprint requests to Prof. G. C. Papavassiliou.  
Fax: 30210-7273794

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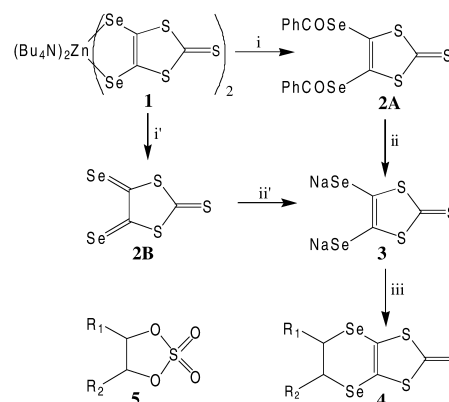
The compounds 5,6-dimethyl-5,6-dihydro-[1,4]diselenino[2,3-*d*][1,3]dithiole-2-thione, 5-methyl-5,6-dihydro-[1,4]diselenino[2,3-*d*][1,3]dithiole-2-thione and 5,6-dihydro-[1,4]diselenino[2,3-*d*][1,3]dithiole-2-thione were prepared and characterized analytically and spectroscopically.

**Key words:** Dithioles,  $\pi$ -Donors, Tetrathiafulvalenes

## Introduction

Derivatives of 1,3-dithiole-2-thione (vinylene trithiocarbonate) are good building blocks for constructing tetrathiafulvalenes, precursors of organic conductors and superconductors (see [1, 2]). They can be prepared by several methods, depending on the nature of the additional heteroatoms and alkyl groups. For example, the compound tetrahydro-[1,4]diselenino[2,3-*d*][1,3]dithiole-2-thione (**4c**) is obtained in good yield by treating the zincate **1** or the disodium salt of 4,5-bis-selanyl-[1,3] dithiole-2-thione (**3**) with 1,2-dibromoethane [3]. However, using 1,2-dibromopropane or 2,3-dibromobutane instead of 1,2-dibromoethane, traces of 5-methyl-5,6-dihydro-[1,4]diselenino[2,3-*d*][1,3]dithiole-2-thione (**4b**) and 5,6-dimethyl-5,6-dihydro-[1,4]diselenino[2,3-*d*][1,3] dithiole-2-thione (**4a**) were obtained, respectively.

In this paper, the preparation of **4a**, **4b**, and **4c**, using the cyclic sulfates **5a**, **5b**, **5c**, instead of the corresponding dibromides, is described. The chemical procedure is outlined in Scheme 1. The compounds were characterized analytically and spectroscopically.



i =  $\text{PhCOCl}$ , in acetone; ii =  $\text{Na} + \text{C}_2\text{H}_5\text{OH}$ ; iii = **5** in THF  
i' =  $\text{Br}_2$ , in  $\text{CH}_2\text{Cl}_2$ ; ii' =  $\text{NaBH}_4$ , in acetone  
(a)  $\text{R}_1 = \text{R}_2 = \text{CH}_3$ ; (b)  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{H}$ ; (c)  $\text{R}_1 = \text{R}_2 = \text{H}$

Scheme 1.

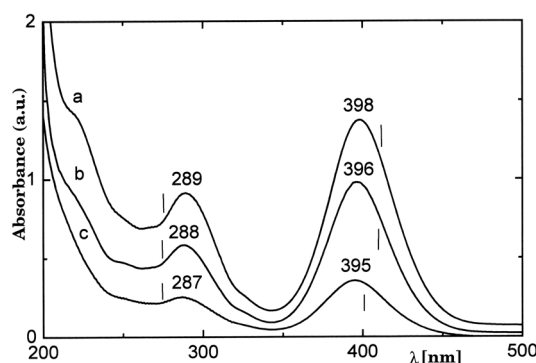


Fig. 1. UV/vis spectra of **4a** (a), **4b** (b) and **4c** (c) in  $\text{CH}_3\text{CN}$ . Vertical bars indicate the peak positions of the corresponding all-sulfur analogs.

## Experimental Section

Compounds **2** were prepared from the zincate **1**, almost quantitatively, by methods reported in [3, 4]. The disodium salt **3** was obtained in a yield of 95–98% from **2**, in Ar atmosphere, by a method similar to that reported for the preparation of the all sulfur analog [5] (see also [3, 4]). Cyclic sulfates **5a**, **5b**, and **5c** were synthesized from the corresponding diols, i.e., (2*R*,3*R*)-2,3-butanediol (Aldrich 23,763-9), 1,2-propanediol (Aldrich 39,803-9) and 1,2-ethanediol (Aldrich 10,246,6), by methods reported in [6–8].

Compound **4a** was prepared as follows: To a freshly prepared red-brown solution of **3**, obtained from **2A** (1.75 g, 3.5 mmol) in dry THF (50 ml) under an Ar atmosphere, a solution of **5a** (0.532 g, 3.5 mmol) in dry THF (5 ml) was

added dropwise, stirring within 15 min. The mixture was stirred overnight at *ca.* 55 °C under Ar atmosphere. The obtained reaction mixture was evaporated and the residue extracted with methanol (3 × 30 ml). The extracts were evaporated to leave a crude product, which was washed with water and dried in air. Subsequently, it was chromatographed on a silica gel column, using CH<sub>2</sub>Cl<sub>2</sub> as eluent, to give 135 mg of **4a** (a yield of 11% based on **2A**) as yellow needles; m.p. 88 °C. – MS: *m/z* = 348. – C<sub>7</sub>H<sub>8</sub>S<sub>3</sub>Se<sub>2</sub> (346.2): calcd. C 24.28, H 2.33; found C 24.22 H 2.19. –  $[\alpha]_D^{20} = -278^\circ$  (*c* 1, CHCl<sub>3</sub>).

Compound **4b** was prepared by the same method in a yield of 17% based on **2A**; m.p. 98 °C. – MS: *m/z* = 334. – C<sub>6</sub>H<sub>6</sub>S<sub>3</sub>Se<sub>2</sub> (332.1): calcd. C 21.69, H 1.82; found C 21.74, H 1.69.

Compound **4c** was prepared by the same method in a yield of 52% based on **2A**. The analytical data are identical to those of an authentic sample [3].

The UV/vis spectra of **4a-c** are shown in Fig. 1.

## Discussion

Compound **4a** was prepared in a chiral form (*i.e.*, in the *S,S*-configuration), but in a lower yield than that of the all-sulfur analog [8, 9]. Compound **4b** was also prepared in low yield, but **4c** was prepared in a yield comparable to that obtained by using 1,2-dibromoethane instead of the sulfate **5c** [3]. The peak positions of the UV/vis spectra of **4a-c** (Fig. 1) are close to those of the corresponding all-sulfur analogs. Compounds **4a-c** could be easily reconverted to **3** by treating them with NaOC<sub>2</sub>H<sub>5</sub> or NaBH<sub>4</sub> in an organic solvent, but in the case of the all-sulfur analogs, the five-membered ring is opened by these reagents [1, 2]. As for other derivatives of vinylene trithiocarbonate, treatment of **4** with (EtO)<sub>3</sub>P gives the corresponding tetrathiafulvalenes. The preparation and properties of these compounds and their conducting salts will be reported elsewhere.

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