



## Synthesis and Characterization of Tetrathiatetraasterane

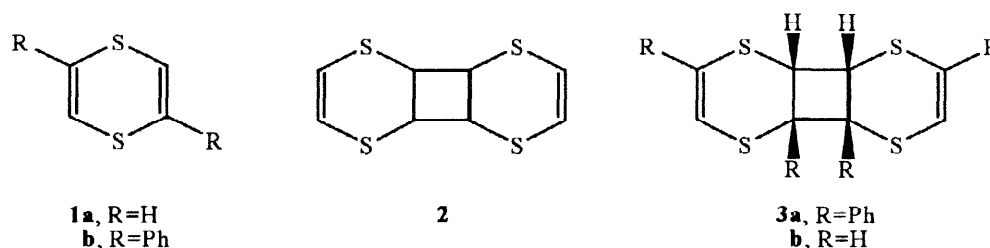
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Received 5 August 1998; accepted 22 September 1998

**Abstract:** Irradiation of 1,4-dithiin gives the *cis, syn, cis*-photodimer in 70–80% yield whose structure has been unequivocally established by X-ray crystallographic methods. A minor product is formed in this photodimerization which is shown to be the *trans, anti, trans*-photodimer by X-ray structural analysis. Irradiation of the *syn* photodimer produces tetrathiatetraasterane in 70% yield. The structure of this product is also proven by X-ray methods. © 1998 Elsevier Science Ltd. All rights reserved.

Gollnick and Hartmann<sup>1</sup> reported that irradiation of dithiin, **1a**, in degassed solvents produced [2+2]

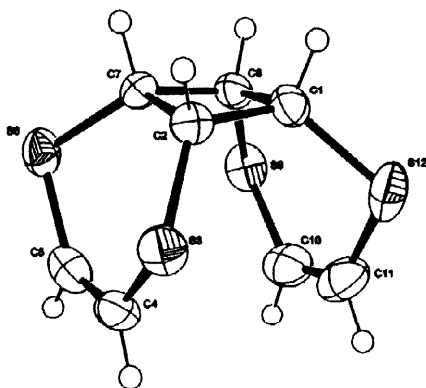


photodimer **2** in 80% yield. The stereochemistry of **2** could not be assigned and no further products were observed. Kobayashi and Ohi<sup>2</sup> reported that irradiation of 2,6-diphenyl-1,4-dithiin, **1b**, in ether using light from a high pressure mercury lamp filtered through Pyrex gave half-closed dimer **3a** and caged dimer **4a** in 2.5 and 13% yields, respectively. The structure of cage dimer **4a** was based solely on its elemental analysis and mass spectrum

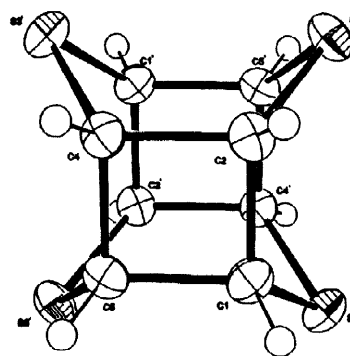


because its insolubility in organic solvents precluded further structural analysis. This structural assignment has also been questioned.<sup>1</sup> Irradiation of derivatives of **1b** failed to give soluble cage dimers under comparable conditions and irradiation with 254 nm light produced aryl acetylenes as the only characterizable products.<sup>3</sup> This letter reports a reinvestigation of the photochemistry of **1a** and **2**.

Irradiation of **1a** produced the [2+2] photodimer reported by Gollnick and Hartmann in 70–80% yield. Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into a chloroform solution of the photodimer. An ORTEP drawing of this *cis, syn, cis*-dimer **3b** is shown in Figure 1. Furthermore, irradiation of this dimer in dilute, degassed benzene solution with 350 nm light gave a precipitate in 70% yield which gave the following spectroscopic data: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.13 MHz) δ 4.21 (s); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.77 MHz) δ 39.54; UV (CH<sub>2</sub>Cl<sub>2</sub>) 230 (ε 600), 274 nm (sh, ε 18); MS *m/z* 232, 116, 103, 97, 84, 77, 71. HRMS Calcd for C<sub>8</sub>H<sub>8</sub>S<sub>4</sub>: 231. 9509 Found: 231. 9510 An X-ray crystallographic structure study was done on



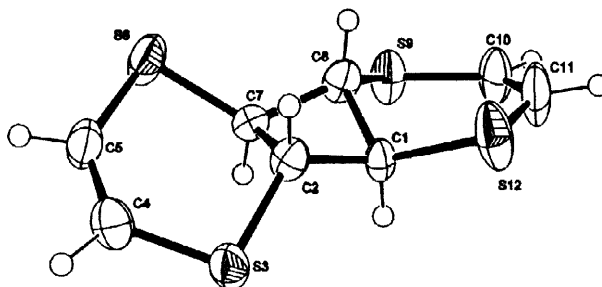
**Figure 1.** ORTEP Drawing of **3b**.



**Figure 2.** ORTEP Drawing of **4b**.

a crystal of this material grown from dichloromethane solution. The ORTEP drawing of the tetrathiatetraasterane **4b** is shown in Figure 2.

Irradiation of **1a** formed, in addition to photodimer **3b**, a minor isomeric product. The ratio of these two products was 20:1, respectively. The minor product gave the following spectroscopic data:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 250.13 MHz)  $\delta$  3.54 (s, 4), 6.15 (s, 4);  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 125.77 MHz)  $\delta$  45.96, 114.92; UV ( $\text{CH}_2\text{Cl}_2$ ) 234 ( $\epsilon$  3100), 274 ( $\epsilon$  2350), 318 nm ( $\epsilon$  90); MS  $m/z$  232, 116, 103, 97, 71; HRMS Calcd for  $\text{C}_8\text{H}_8\text{S}_4$ : 231.9509. Found 231.9504. The structure of this minor product was unequivocally established by X-ray methods to be the unusual, strained trans, anti, trans photodimer **5**. An ORTEP drawing of this molecule is shown in Figure 3.



**Figure 3.** ORTEP Drawing of **5**.

Tetrathiatetraasterane is a member of the class of compounds whose molecular shape resembles a four-pointed star. Tetraasteranes consisting of all carbon cages have also been synthesized and characterized.<sup>4-6</sup>

In conclusion, the photodimer obtained by irradiation of 1,4-dithiin, first reported by Gollnick and Hartmann, is unequivocally established to have cis, syn, cis stereochemistry. Furthermore, irradiation of this dimer results in intramolecular [2+2] photocyclization to tetrathiatetraasterane **4b**.

**Acknowledgment.** The authors gratefully acknowledge support of this work by the National Science Foundation (CHE-9422200). The X-ray crystallographic structures were determined at the Molecular Structure Laboratory of the University of Arizona.

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