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Synthesis and Structure of Thianthrene Derivatives Bearing Cyclic Polysulfide Rings

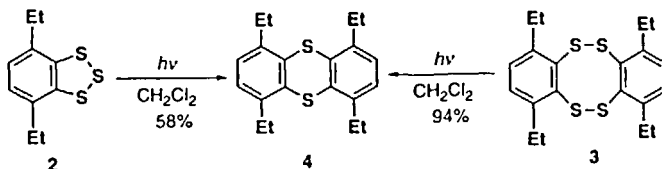
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Photolytic preparation and electrochemical properties of thianthrene derivatives bearing trithiole or dithian rings are reported.

Recently, we have reported preparation, structure and reactivities of several cyclic polysulfides.^{1, 2} In the course of our studies with respect to cyclic polysulfides, photolytic desulfurization of **1** were examined. Here, we report the results of the novel photolytic reaction of cyclic polysulfides, the structure of **6** and the oxidation potentials of **4-10**.

Typically, photolysis of **2** was performed by 100 W high pressure Hg lamp in CH₂Cl₂ under Ar. Dibenzotetrathiocin **3** was photolyzed in the similar condition. In these photolysis, desulfurization-cyclization and ring contraction reactions proceeded to give **4** in 58% and 94% yields, respectively.



These results prompted us to apply the novel photoreaction into double polysulfide ring systems. On the photolysis of **5**, **6** was obtained in 13% yield. The structure of **6** was verified by X-ray crystallography, revealing that **6** has two trithiole rings.

The compound **7** was photolyzed similarly to produce **8** in 59% yield. Meanwhile, tetrathiocin derivative **9** which was synthesized by treatment of **5** with one equivalent of NaBH₄ and H₂O₂ was irradiated to produce **6** in 51% yield. The results of redox potentials and UV spectra of these new compounds are summarized in Table 1.

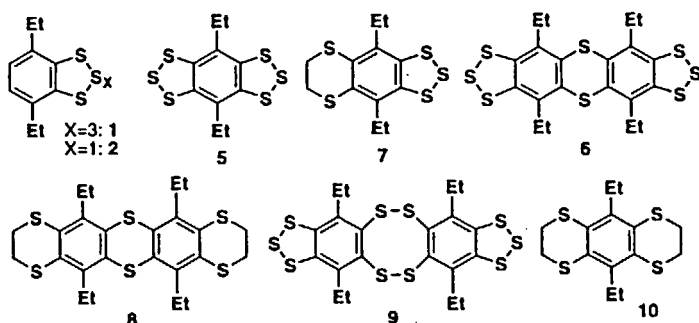


Table 1. Oxidation Potentials, and UV Spectra.

$E_{1/2}$ -V		UV	
		λ_{maxnm} (ϵ)	
1		299 (3600)	355 (1200, sh)
2		274 (7100)	325 (1500)
3		317 (7500)	350 (2500, sh)
4	0.89	261 (28000)	287 (4700)
5	0.78 0.87		295 (4300)
6^a	0.88 ^b		297 (17000)
7	0.70 1.00		353 (2500)
8	0.78 0.89	282 (68000)	294 (37000)
9			341 (6200)
10	0.74	272 (26000)	288 (18000)
			341 (2800, sh)
			313 (11000, sh)
			326 (7500, sh)
			300 (36000)
			361 (12000)
			291 (4700, sh)
			326 (1800, sh)

The oxidation potentials were determined by the cyclic voltammetry in CH₃CN using Ag/0.01 M AgNO₃ as a reference electrode; ^aMeasured in PhCN; ^bQuasi reversible, Ep (V). The UV spectra were measured in CH₂Cl₂ as a solvent.

References

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