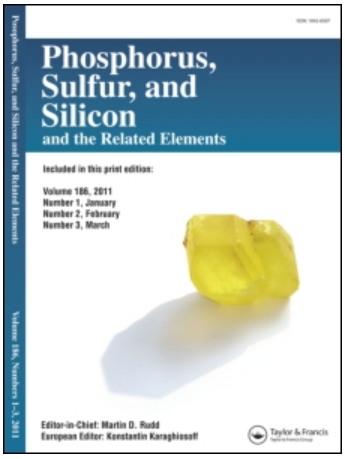

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Synthesis and Structure of Thianthrene Derivatives Bearing Cyclic Polysulfide Rings

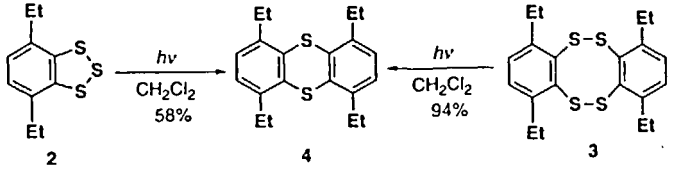
TAKESHI KIMURA[a], KAZUHIKO TSUJIMURA[a], SUSUMU MIZUSAWA[a], YASUSHI KAWAI[b], SATOSHI OGAWA[a] and RYU SATO[a]

[a]*Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka, Iwate 020, Japan and* [b]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan*

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 CH_2Cl_2 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.



2 **4** **3**

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 $NaBH_4$ and H_2O_2 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.

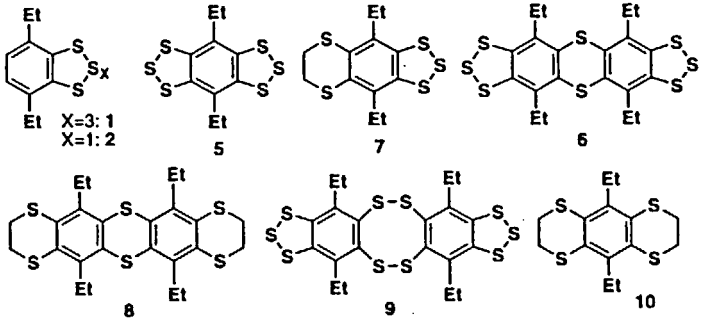


Table 1. Oxidation Potentials, and UV Spectra.

	$E_{1/2}$ V		UV		
				λ_{max}nm (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)	295 (4300)
5	0.78	0.87		297 (17000)	353 (2500)
6[a]	0.88[b]			294 (37000)	341 (6200)
7	0.70	1.00		288 (18000)	341 (2800, sh)
8	0.78	0.89	282 (68000)	313 (11000, sh)	326 (7500, sh)
9				300 (36000)	361 (12000)
10	0.74		272 (26000)	291 (4700, sh)	326 (1800, sh)

The oxidation potentials were determined by the cyclic voltammetry in CH_3CN using Ag/0.01 M $AgNO_3$ as a reference electrode; [a]Measured in PhCN; [b]Quasi reversible, Ep (V); The UV spectra were measured in CH_2Cl_2 as a solvent.

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