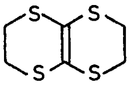
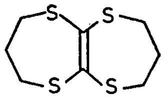
Tetrathioethylene Dications: Endocyclic to Exocyclic Rearrangement

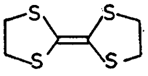
By Robert M. Harnden, P. Ricker Moses, and James Q. Chambers*
(*Department of Chemistry, University of Tennessee, Knoxville*, TN 37916)

Summary Electrogenerated dications of 2,5,7,10-tetrathiabicyclo[4.4.0]dec-1(6)-ene (**1**) and 2,6,8,12-tetrathiabicyclo[5.5.0]dodec-1(7)-ene (**2**) undergo a novel endocyclic to exocyclic rearrangement in acetonitrile solutions at room temperature.

The chemistry of tetrathioethylenes is dominated by their electron-donor properties and reversible oxidation to form radical cations and dications. While the neutral donor molecules are relatively inert chemically when compared to other electron-rich ethylenes,[1] the oxidised forms are susceptible to reactions such as fragmentation and nucleophilic attack. We report here a novel rearrangement of the dications electrogenerated from the tetrathioethylenes (**1**) and (**2**).


(1)


(2)


(3)

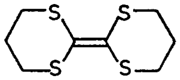

(4)

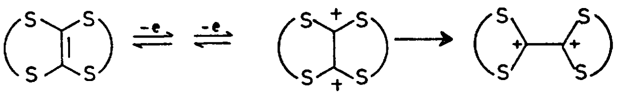
Table. Half-wave potentials (V *vs.* S.C.E.) of the tetrathioethylenes (**1**)—(**4**).

	$E^1_{1/2}$	$E^2_{1/2}$
(**1**)	0·90[a]	1·28[a]
(**3**)	0·71[a]	1·17[a]
(**2**)	0·90	1·03
(**4**)	0·72	0·90

[a] Corrected to S.C.E. scale from Ag-Ag$^+$ by addition of 0·30 V.

Compounds (**1**)[2] [m.p. 151·5—153 °C, δ (CDCl$_3$) 3·25 (8H, s, CH$_2$)] and (**2**) [m.p. 121—122 °C; δ (CDCl$_3$) 3·1 (8H, t, SCH$_2$) and 2·2 (4H, m, CH$_2$)] were prepared *via* electrochemical reduction of CS$_2$[3] followed by alkylation and isolation of the thione. Hydrolysis or electrochemical reduction of the thione and a second alkylation gave (**1**) and (**2**).†

Cyclic voltammograms of (**1**) and (**2**) (see Figure) show the expected reversible one-electron oxidation waves corresponding to radical cation and dication formation. When the platinum electrode potential is swept into the region in which either (**1**)$^{2+}$ or (**2**)$^{2+}$ is formed, a new one-electron wave appears on subsequent cycles which can be assigned to known exocyclic tetrathioethylene radical cation couples of (**3**) and (**4**). These new waves grow on repeated cycling of the potential and match the (**3**)$^{\dot{+}}$/(**3**) and (**4**)$^{\dot{+}}$/(**4**) couples. The indicated electrode reaction is shown in the Scheme. Half-wave potentials are given in the Table.



Scheme

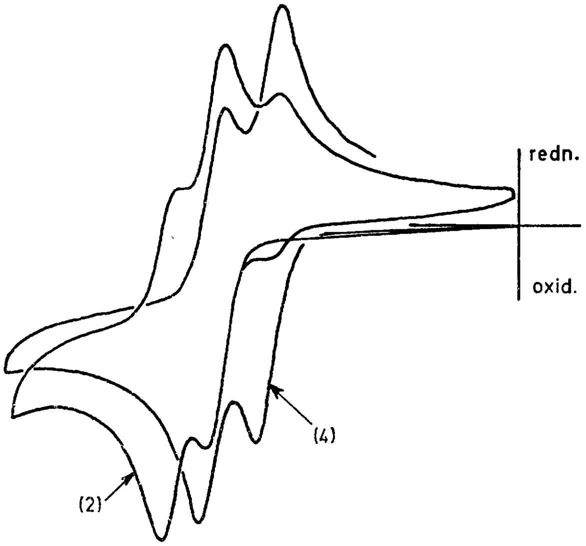


Figure. Cyclic voltammograms of (**2**) (5 × 10^{-4} M) and (**4**) (5 × 10^{-4}M) in MeCN with 0·1 M Et$_4$NClO$_4$, at a platinum disc electrode. Sweep rate: 0·104 V s^{-1}; initial potential: 0·00 V; switching potential: 1·50 V *vs.* S.C.E.

---

† Elemental analyses, and i.r. and mass spectra were consistent with these structures.

Support for the above assignments comes from e.s.r. spectra of radical cations electrogenerated form (**1**)—(**4**). Radical cation spectra obtained from solutions of (**2**) and (**4**) were identical within experimental uncertainty; both solutions gave a single nine-line spectrum due to a radical species with eight equivalent hydrogen atoms (a_H 3·15 G, g 2·0089). While both (**2**)$^{\dot{+}}$ and (**4**)$^{\dot{+}}$ would be expected to have similar spectra, it is also possible that the more stable (**4**)$^{\dot{+}}$ is formed in the diffusion layer under the conditions of the electrolysis (*ca.* 15 min electrolysis time). Electrolysis of solutions of (**1**) in the e.s.r. cavity gave a signal which was initially composed of two spectra. After *ca.* 15 min the signal due presumably to (**1**)$^{\dot{+}}$ was absent and the remaining spectrum was similar to the known spectrum of (**3**)$^{\dot{+}}$ (a_H 2·26 G, g 2·00647).[1,4]

A major contribution to the driving force for the rearrangement is the minimization of the coulombic interactions between positive sulphur atoms which is possible by rotation about the central carbon–carbon bond in the exocyclic but not in the endocyclic dications. The mechanism of the rearrangement is open to speculation, but it should possibly be included in the class of rearrangements in which two σ bonds simultaneously migrate intramolecularly, the 'dyotropic' rearrangements described by Reetz.[5]

We thank the Research Corporation, the National Science Foundation, and the University of Tennessee for support of this research, and Professor T. F. Williams of this department for e.s.r. facilities.

(*Received*, 12*th October* 1976; *Com.* 1158.)

---

[1] D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Amer. Chem. Soc.*, 1971, **93**, 2258.

[2] M. Mizuno, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, 1976, **41**, 1484; S. Wawzonek and S. M. Heilmann, *ibid.*, 1974, **39**, 511.

[3] P. R. Moses and J. Q. Chambers, *J. Amer. Chem. Soc.*, 1974, **94**, 945.

[4] J. Q. Chambers, N. D. Canfield, D. R. Williams, and D. L. Coffen, *Mol. Phys.*, 1970, **19**, 581.

[5] M. T. Reetz, *Angew. Chem. Internat. Edn.*, 1972, **11**, 129, 130; *Tetrahedron*, 1973, **29**, 2189.