Journal of
The Chemical Society,
Chemical Communications

NUMBER 19/1978 4 OCTOBER

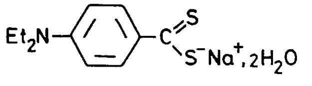
Electrochemical Formation of a Tetrathian Ring

By GEORGES CAUQUIS* and ALAIN DERONZIER

[*Laboratoire d'Electrochimie Organique et Analytique, E.R.A.(C.N.R.S.)* 675, *Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble,* 85X, 38041 *Grenoble Cedex, France*]

Summary The electrochemical generation of a stable dication, forming a tetrathian ring, from the *p*-diethylaminodithiobenzoate anion in acetonitrile is reported; this constitutes a new example of the oxidative cyclisation of a dithio-ligand.

THE oxidation of a dithio-ligand leading to a stable cyclic dicationic species is very seldom observed, the only real example being that of dithiocarbamates.[1] (The 1,2-dithiolium ion resulting from oxidation of some dithioacetylacetonato complexes is a monocation.[2]) We now report a second example of this type of cyclisation. We have synthesised by the standard method, with the appropriate Grignard reagent[3] the novel dithiobenzoato sodium salt (**1**),† with a stabilizing substituent on the phenyl ring.



(1)

Electrochemical oxidation in acetonitrile with 0·1 M Et_4NClO_4 transforms the anion (**1**) into the expected disulphide† (**2**) (S–S in the Scheme) by an e.dim (electron transfer followed by dimerisation) mechanism, as for the dithiocarbamate anion.[4] The dimer (**2**) in turn may be reduced back to (**1**). The cyclic voltammogram shows that the electron transfers are slow, but that the overall transformation is a reversible process. Half-wave potentials are summarized in the Table.

TABLE. Half-wave potentials at a platinum rotating disc electrode (V *vs.* Ag–Ag$^+$, 0·01M) of (**1**), (**2**), and (**3**)

	Oxidation	Reduction
(**1**)	−0·19, 0·46, 0·60	—
(**2**)	0·38, 0·60	−1·30
(**3**)	—	−0·10

However, the disulphide (**2**) shows more interesting electrochemical behaviour. It is oxidized in two successive one-electron exchanges corresponding to the formation of the unstable monocation $S^{\bullet+}$–S and the dication diradical $S^{\bullet+}$–$S^{\bullet+}$. The process is irreversible up to scan rates of 30 V s^{-1} but the cyclic voltammogram (Figure) shows a new cathodic peak at −0·10 V.

Coulometry by exhaustive electrolysis at the potential of the second peak P_2 shows that the number of electrons involved in the oxidation is two. Successive u.v.–visible absorption curves of the solution, recorded during electrolysis, pass through a series of isosbestic points at 385, 482, and 675 nm. The electrolysed solution shows no e.s.r. signals. The absorption band maximum (λ_{max} 537 nm) of the non-paramagnetic oxidized species is at long wavelength in comparison with that of (**2**) (λ_{max} 456 nm). This value (537 nm) approaches that observed for the absorption maximum of other conjugated quinone di-imine cation systems.[5] The most likely formula consistent with these results is the dicationic species $S^+{=}S^+$ containing a tetrathian ring.

Isolation of (**3**) is not possible by preparative electrolysis owing to the low solubility of (**2**) in acetonitrile and the extreme sensitivity of (**3**) to hydrolysis. However, the

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† Satisfactory analyses were obtained for these compounds.

tetrathian (**3**) can be obtained, not in a pure form, by oxidation with iodine in methylene chloride. As for bis-(diethyldithiocarbamoyl) disulphide [1d,e] chemical oxidation of the disulphide (**2**) leads to the I_3^- salt of (**3**), but it is accompanied by decomposition products which have not been identified. It is so insoluble in organic solvents that its ^{1}H n.m.r. spectra cannot be recorded. However, i.r. studies show a strong increase in the ν(C–S) vibration at 825—820 cm^{-1} and a disappearance of ν(C=S)[6] at 1030 cm^{-1} on oxidation of (**2**) into (**3**).

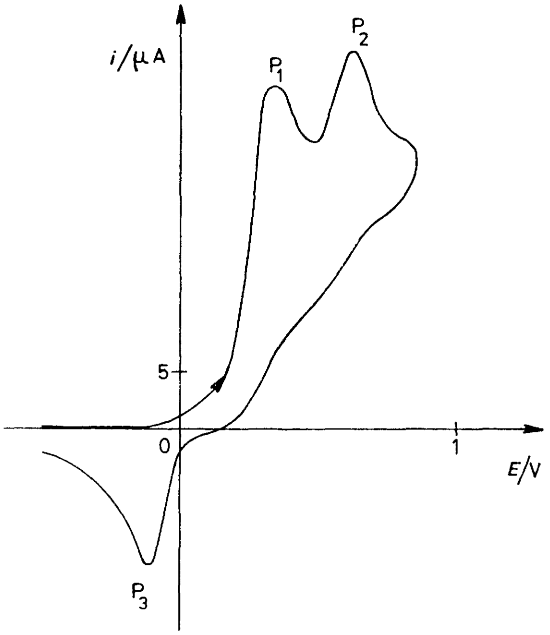
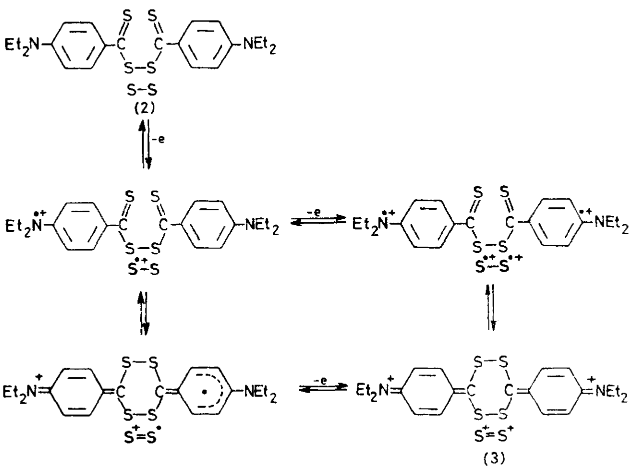


FIGURE. Cyclic voltammogram of (**2**) (5 × 10^{-4} M) in MeCN with 0·1 M Et$_4$NClO$_4$ at a platinum disc electrode; sweep rate 0·08 V s^{-1}; initial potential −0·5 V *vs.* Ag-Ag$^+$ 0·01 M.

The structure of (**3**) is also supported by the fact that it is easily reduced to the disulphide (**2**) at the same potential as that of the cathodic peak P$_3$ in the Figure, and the anionic compound (**1**) is almost completely restored by another exhaustive reduction, proving that there is no loss of sulphur during the oxidation procedure. This is not the case for the chemical oxidation of the dithiocarbamate anion.[1c]



SCHEME

Controlled potential oxidative electrolysis at the potential of the first voltammetric peak P$_1$ also produces (**3**): the cation radical $S^{\cdot+}$–S produced at the first peak P$_1$ potential is not stable, and cyclises slowly, on the time-scale of the cyclic voltammogram experiments, into the intermediate species S^+=$S^{\cdot}$ which itself is oxidized into the dication S^+=S^+ at the same potential. This e.c.e. mechanism, of course, competes with the disproportionation (1). At the potential of the second peak P$_2$ the cyclisation takes place after a second electron transfer to give S^+=S^+ *via* formation of $S^{\cdot+}$–$S^{\cdot+}$ species (e.e.c. mechanism).

$$S^{\cdot+}\text{–}S + S^{+}\text{=}S^{\cdot} \rightleftharpoons S\text{–}S + S^{+}\text{=}S^{+} \qquad (1)$$

Thus, depending on the potential, the anodic formation of the tetrathian compound occurs by means of two distinct mechanisms and the three compounds (**1**), (**2**), and (**3**) make up a set in which all constituents are electrochemically mutually exchangeable.

(*Received, 28th December* 1977; *Com.* 1305.)

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[1] (a) J. Willemse and J. J. Steggerda, *Chem. Comm.*, 1969, 1123; (b) P. T. Beurskens, W. P. J. H. Bosman, and J. A. Cras, *J. Cryst. Mol. Struct.*, 1972, **2**, 183; (c) J. Willemse and J. A. Cras, *Rec. Trav. chim.*, 1972, **91**, 1309; (d) E. W. Ainscough and A. H. Brodie, *J.C.S. Dalton*, 1977, 565; (e) S. H. Wheeler, B. M. Mattson, G. L. Miessler, and L. H. Pignolet, *Inorg. Chem.*, 1978, **17**, 340.

[2] G. A. Heath, R. L. Martin, and I. M. Stewart, *Austral. J. Chem.*, 1969, **22**, 83; A. Furuhashi and A. Ouchi, *Bull. Chem. Soc. Japan*, 1969, **42**, 260; A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Amer. Chem. Soc.*, 1973, **95**, 1449.

[3] J. Houben, *Chem. Ber.*, 1906, **39**, 3219.

[4] G. Cauquis and D. Lachenal, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1973, **43**, 205.

[5] D. Serve, *Electrochim. Acta*, 1976, **21**, 1171; P. J. Grossi, L. Marchetti, R. Ramasseul, A. Rassat, and D. Serve, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1978, **87**, 353.

[6] O. Piovesana, C. Furlani, A. Flamini, A. Sgamellotti, and C. Bellitto, *Atti Accad. naz. Lincei, Rend. Classe Sci, fis. mat. nat.*, 1973, **54**, 763.