

Tetrathiadiazafulvalenes; Preparation and Characterisation of *cis*- and *trans*-[RCNS₂C=CS₂NCR] (R = Me, Ph)

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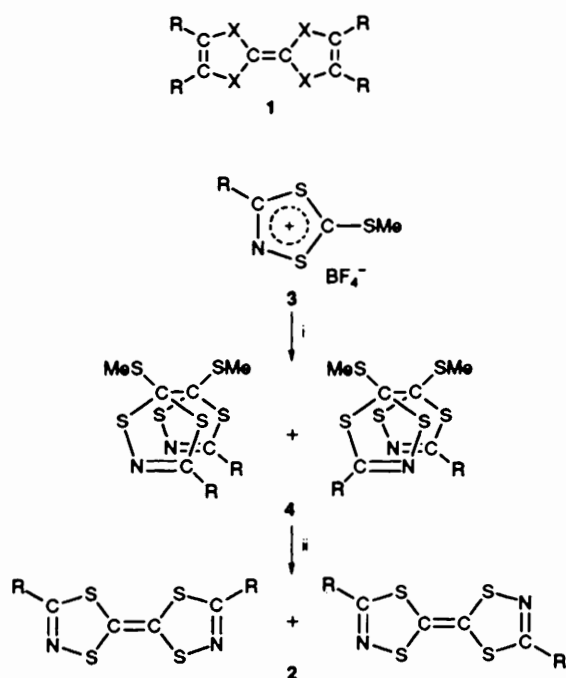
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Tetrathiadiazafulvalenes can be prepared by the reductive coupling of 5-methylthio-1,4,2-dithiazolium salts, and thermolysis of the resulting hexathiooxalates; oxidation of tetrathiadiazafulvalenes affords the corresponding radical cations.

The tetrachalcogenofulvalenes **1** (X = S, Se) have played an important role as electron donors in conducting organic charge-transfer salts.¹ Derivatisation of **1**, which is essential to varying its electronic properties, has generally been achieved by altering the substituents R or by chalcogen exchange. Herein we report the preparation, characterisation, crystal structures and electrochemical behaviour of the first tetrathiadiazafulvalenes **2**, in which the central C₂X₄ moiety and unsaturated framework of **1** is retained, but two peripheral CR units are replaced by nitrogen atoms.

Reduction of the 5-methylthio-1,4,2-dithiazolium tetrafluoroborate salts **3** (3 mmol),² with zinc dust (15 mmol) in acetonitrile (30 ml) for 1 h, affords an isomeric mixture of the dimeric hexathio-oxalates **4** (Scheme 1). The isomeric mixtures can be purified by chromatography (silica gel, benzene eluent), and isolated as pale-yellow oils in good yield (>90%). In the case of **4.Me** the two isomers can be distinguished by ¹H NMR [δ (C₆D₆) 2.097, 2.084 (SCH₃); 1.696, 1.685 (CCH₃)], while for **4.Ph** they can be observed by TLC (silica gel, CH₂Cl₂-hexane, 1:1). The reductive dimerisation of **3** is analogous to that of the 1,3-dithiolium salts, but in contrast to the behaviour of 1,3,2-³ and 1,2,3-dithiazolium⁴ salts, which reduce to the corresponding dithiazolyl radicals.

Similar to the formation of tetrathiafulvalenes *via* the thermolysis of the carbon based hexathio-oxalates,⁵ when solutions of **4** in tetrachloroethane (30 ml) are heated to 140–145 °C, the colour of the solution turns from yellow to orange-red, and TLC analysis indicates almost complete conversion of **4** to the tetrathiadiazafulvalenes **2** within 10–15



Scheme 1 Reagents and conditions: i, Zn; ii, 140–145 °C, C₂H₂Cl₄.

min.[†] The products can be isolated (after solvent removal), by chromatography (**2.Me**; CH₂Cl₂-hexane 3:7) or by washing with boiling acetonitrile (**2.Ph**), in good yield (based on **3**: **2.Me**, 68%; **2.Ph**, 85%) as isomeric mixtures. The *trans* isomers of **2** were obtained by preferential crystallisation from CH₂Cl₂-hexane (**2.Ph**; m.p. 212–214 °C) or toluene (**2.Me**; m.p. 146–148 °C) and *cis*-**2.Me** (m.p. 114 °C) could be separated by chromatography (CH₂Cl₂-hexane, 1:1) of isomerically enriched samples [¹H NMR, **2.Me**, δ (C₆D₆): *trans*, 1.575; *cis*, 1.595]. *cis*-**2.Ph** can be distinguished from the *trans* isomer by TLC (CH₂Cl₂-hexane, 1:9), but it has not been isolated in a pure form.

The structures of *cis*-**2.Me** and *trans*-**2.Ph** have been confirmed by X-ray crystallography;[‡] ORTEP views are shown in Figs. 1 and 2, along with selected bond lengths and angles. The C–C and C–S distances are similar to those seen in, e.g. tetrathiafulvalene (TTF).⁶ In contrast to *trans*-**2.Ph**, *cis*-**2.Me** is markedly non-planar; the least-squares planes of the S(1)–N(1)–C(2)–S(2) and S(3)–N(2)–C(5)–S(4) units make angles of 24.7 and 19.0°, respectively, with the plane of the central C₂S₄ unit. In keeping with the more electronega-

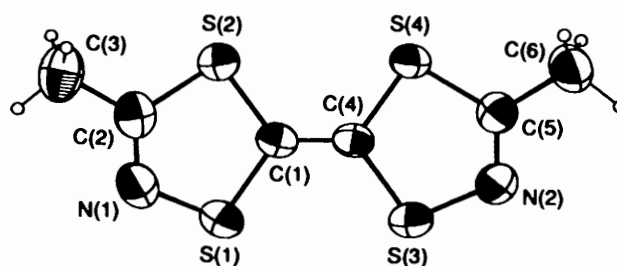


Fig. 1 ORTEP perspective view of *cis*-**2.Me**. Selected average (chemically equivalent) bond lengths (Å) and angles (°): C(1)–C(4) 1.333(3), S(1)–C(1) 1.753(2), S(2)–C(1) 1.747(2), S(1)–N(1) 1.687(2), S(2)–C(2) 1.769(2), N(1)–C(2) 1.270(3), C(2)–C(3) 1.490(3); C(4)–C(1)–S(1) 124.6(2), C(4)–C(1)–S(2) 124.7(2), S(1)–C(1)–S(2) 110.7(1), C(1)–S(1)–N(1) 97.5(1), S(1)–N(1)–C(2) 115.7(2), N(1)–C(2)–S(2) 119.9(2), C(2)–S(2)–C(1) 92.9(1).

[†] Compounds **2** have been characterised by elemental (C, H and N) analysis and mass spectrometry.

[‡] Crystal data for *cis*-**2.Me**: C₆H₆N₂S₄, *M* = 234.38, monoclinic, *P*2₁/*n*, *a* = 11.340(4), *b* = 9.055(2), *c* = 9.795(3) Å, β = 105.38(2)°, *V* = 969.6 Å³, *Z* = 4, *D*_c = 1.61 g cm⁻³, μ = 8.9 cm⁻¹, data collected to $2\theta_{\max}$ = 50.0° using Mo-K α radiation (λ = 0.7107 Å). The structure converged with *R* = 0.023, *R*_w = 0.024 for 1536 data having *I*_o > 3 σ (*I*_o) and 134 variables.

Crystal data for *trans*-**2.Ph**: C₁₆H₁₀N₂S₄, *M* = 358.53, monoclinic, *C*2/*c*, *a* = 12.080(4), *b* = 3.594(2), *c* = 31.596(13) Å, β = 92.05(2)°, *V* = 1508.1 Å³, *Z* = 4, *D*_c = 1.58 g cm⁻³, μ = 6.0 cm⁻¹, data collected to $2\theta_{\max}$ = 50.0° using Mo-K α radiation (λ = 0.7107 Å). The structure converged with *R* = 0.029, *R*_w = 0.031 for 1159 data having *I*_o > 3 σ (*I*_o) and 116 variables. A crystallographic centre of inversion is imposed upon the molecule.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

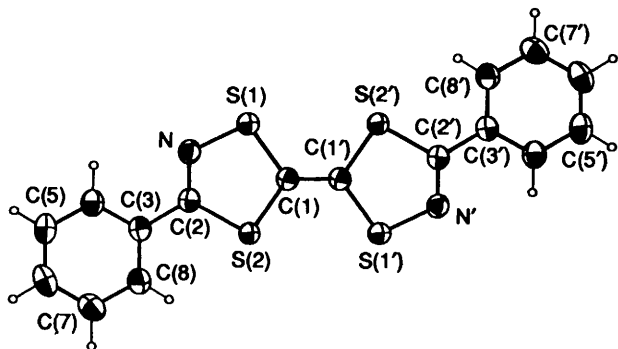


Fig. 2 ORTEP perspective view of *trans*-2.Ph. Selected bond lengths (Å) and angles (°): C(1)–C(1') 1.338(3), S(1)–C(1) 1.765(2), S(2)–C(1) 1.751(2), S(1)–N 1.663(2), S(2)–C(2) 1.768(2), N–C(2) 1.282(3), C(2)–C(3) 1.470(3); C(1')–C(1)–S(1) 124.6(2), C(1')–C(1)–S(2) 124.1(2), S(1)–C(1)–S(2) 111.3(1), C(1)–S(1)–N 98.4(1), S(1)–N–C(2) 116.9(2), N–C(2)–S(2) 119.4(2), C(2)–S(2)–C(1) 94.0(1).

tive framework, derivatives of **2** are less potent electron donors than those of TTF. Cyclic voltammetry on derivatives of **2** [in MeCN, with tetrabutylammonium hexafluorophosphate (0.1 mol dm⁻³) as supporting electrolyte] reveals two reversible oxidation waves [*trans*-2.Me, 0.59 and 0.95 V; *trans*-2.Ph, 0.65 and 1.01 V (vs. saturated calomel electrode); cf. TTF,⁷ 0.30 and 0.66 V] for the formation of radical cation and dication species. The stable radical cation **3**^{•+} (R = Me, *trans*) can be observed by EPR spectroscopy, and exhibits a spectrum consisting of a broad triplet with $g = 2.0062$, $a_N = 1.56$ mT. We are currently investigating the use of these and other derivatives of **3** in the design of new molecular conductors.

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