

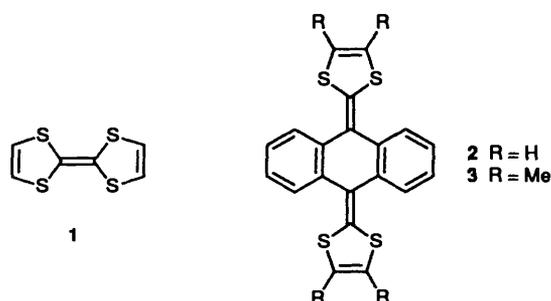
## Highly Functionalised Analogues of Tetrathiafulvalene: New 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Donors

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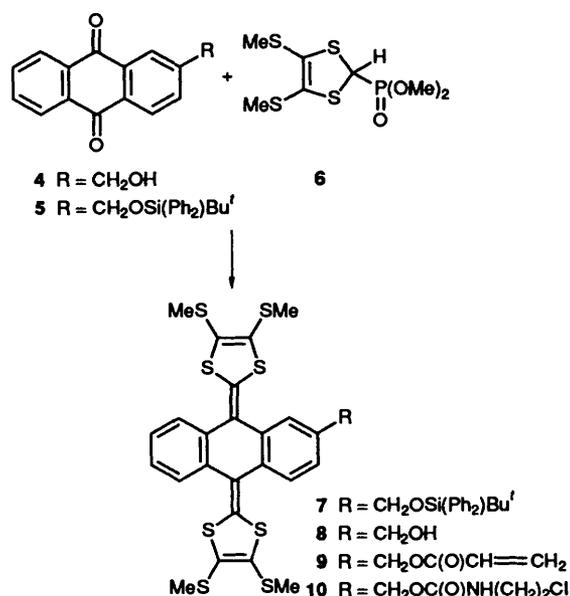
We describe the efficient synthesis and solution redox chemistry of the first highly functionalised derivatives of the  $\pi$ -electron donor 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene.

The synthesis of redox-active building blocks with reactive functional groups are of importance in supramolecular chemistry.<sup>1</sup> In this context the tetrathiafulvalene (TTF) ring system **1** is of current interest, and several derivatives with hydroxy<sup>2</sup> and amino substituents<sup>3</sup> have been reported. However, the synthesis of functionalised TTF systems is not straightforward: direct substitution onto the TTF ring (*via* lithiated species) frequently yields a mixture of products, and very few methods are available for constructing the TTF ring from highly substituted components.<sup>4</sup> There is, therefore, a need to explore new  $\pi$ -electron donor systems that can be readily functionalised.



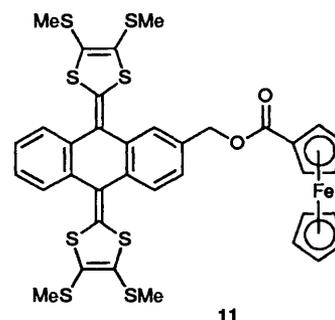
From this viewpoint we were attracted to 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **2**, which is an analogue of TTF with extended conjugation between the two 1,3-dithiole rings. The parent system **2** and the tetramethyl derivative **3** have recently been studied as new  $\pi$ -donor components for the formation of organic metals.<sup>5</sup> We have now synthesised the first functionalised derivatives of system **2**. Compound **8** is our key intermediate with the hydroxymethyl substituent providing a versatile 'handle' for further elaboration. We chose to prepare system **8** with methylthio substituted 1,3-dithiole rings for two reasons: (i) the Horner–Wittig reagent **6** is readily available in 10–20 g batches from cheap starting materials,<sup>6</sup> and (ii) compounds **2** and **3** are both very easily oxidised;<sup>5a,c</sup> further, the methylthio substituents have the benefit of raising the oxidation potential and thereby increasing the stability of the anthracenediylidene system in air.

2-(Hydroxymethyl)anthraquinone **4** reacted with *tert*-butyldiphenylsilyl chloride in the presence of imidazole to yield the silylated derivative **5** (50%).<sup>†</sup> Two-fold reaction of the quinone **5** with the phosphorus-stabilised carbanion generated from reagent **6** (BuLi, THF, 20 °C) yielded the anthracenediylidene derivative **7** (50%), deprotection of which (Bu<sub>4</sub>NF, THF, 20 °C) gave the alcohol **8** (91%). The suitability of compound **8** as a building unit for highly functionalised  $\pi$ -donor systems was



demonstrated by efficient reactions with both acryloyl chloride and 2-chloroethyl isocyanate (Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, for both reactions) to afford the acrylate and urethane derivatives **9** (84%) and **10** (70%) respectively.

The alcohol **8** reacted with ferrocenecarbonyl chloride (Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C) to furnish the multi-stage redox assembly **11** (60%), the solution electrochemistry of which has been studied by cyclic voltammetry. Oxidation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moiety to yield the dication occurs as a single, two-electron, quasi-reversible wave ( $E_{ox} = +0.59$  V,  $E_{red} = +0.25$  V).<sup>7</sup> The ferrocene/ferrocinium redox couple is seen as a cleanly reversible wave at  $E^{1/2} = 0.67$  V.



In conclusion, we have developed straightforward methodology for the preparation of compounds **8–11**, which are highly functionalised analogues of TTF. These are versatile electron donor systems and we are currently pursuing their incorporation into novel redox assemblies.

<sup>†</sup> All new compounds gave satisfactory elemental analyses, mass spectra and <sup>1</sup>H NMR spectra.

## Experimental

**Cyclic Voltammetric Data for Compound 11.**—Experimental conditions: compound **11** (ca.  $1 \times 10^{-5}$  mol dm<sup>-3</sup>), electrolyte Et<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (ca.  $1 \times 10^{-1}$  mol dm<sup>-3</sup>) in dry dichloromethane under argon, 20 °C, versus Ag/AgCl, Pt working electrode, scan rate 100 mV s<sup>-1</sup> using a BAS 100 Electrochemical Analyser.

**Synthesis of Compound 7.**—Butyllithium (1.6 mol dm<sup>-3</sup> in hexane; 1.6 cm<sup>3</sup>, 2.7 mmol) was added to a stirred solution of compounds **5** (0.59 g, 1.2 mmol) and **6** (0.78 g, 2.5 mmol) in dry tetrahydrofuran (75 cm<sup>3</sup>) at 20 °C and the resulting mixture stirred at 20 °C for 16 h. The solvent was evaporated under reduced pressure and diluted with water (40 cm<sup>3</sup>) and the residue was extracted into dichloromethane. The organic layer was dried (MgSO<sub>4</sub>) filtered and evaporated under reduced pressure. The product was purified by chromatography on a silica gel column, eluted with dichloromethane–hexane (1:1, v/v) to afford compound **7** as a yellow–orange oil (530 mg, 50%) which solidified slowly with time.

**Compound 8.**—A mixture of tetrabutylammonium fluoride (1 mol dm<sup>-3</sup> in THF; 0.45 cm<sup>3</sup>, 0.45 mmol) and compound **7** (400 mg, 0.48 mmol) in THF (50 cm<sup>3</sup>) was stirred at 20 °C for 16 h. The solvent was evaporated under reduced pressure and the residue chromatographed on a silica column, eluted initially with dichloromethane–hexane (1:3, v/v) to remove a small amount of an unidentified orange coloured compound, then with dichloromethane to yield compound **8** as a yellow solid (260 mg, 91%), m.p. 110 °C (Found: C, 50.7; H, 3.9. C<sub>25</sub>H<sub>22</sub>OS<sub>8</sub> requires C, 50.47; H, 3.72%); *m/z*: (EI) 594 (M<sup>+</sup>); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.57–7.54 (4 H, m), 7.31–7.29 (3 H, m), 4.76 (2 H, s), 3.71 (1 H, br, exchangeable) and 2.38 (12 H, s).

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