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Bis(tetrathiafulvalenyl)sulphide [(TTF)$_2$S] : Synthesis and X-Ray Crystal Structure

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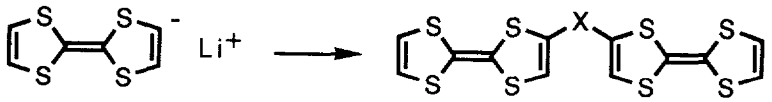
Abstract. Bis(tetrathiafulvalenyl)sulphide [(TTF)$_2$S] has been synthesised by reaction of mono-lithiated TTF with di(phenylsulphonyl)sulphide, and characterised by cyclic voltammetry and single crystal X-ray analysis, which reveals a remarkably close two-dimensional chalcogen network in the solid state. The synthesis of (TTF)$_2$Se, using the selenating reagent di(phenylsulphonyl)diselenide, is also reported.

In the quest for new organic metals and organic superconductors, the preparation of covalently linked dimers (and higher multiples) of tetrathiafulvalene (TTF) is of burgeoning interest.[1-8] Such electron-donor systems should display novel multi-stage redox behaviour with high oxidation states being accessible at relatively low potentials (e.g. the tetracation for a dimeric TTF).[3] Furthermore, they offer unique potential for controlling the stoichiometry, band filling and superstructure in derived charge-transfer complexes and ion radical salts, as the juxtaposition of adjacent TTF molecules can be modified by the nature of the linking group. From this viewpoint, TTF moieties have been bridged by aromatic rings,[2,3,7] alkyl chains[3,4,5,8] and by tellurium[1] and phosphorus atoms.[6] The use of sulphur and selenium as linking atoms was particularly attractive to us, as it is well known that these heteroatoms readily participate in intra- and inter-stack interactions in other donor systems, thereby increasing the dimensionality and suppressing Peierls distortions.[9] Herein we report the one-pot synthesis and solution electrochemistry of bis(tetrathiafulvalenyl)sulphide [(TTF)$_2$S] (2) and the analogous selenide [(TTF)$_2$Se] (3). The X-ray crystal structure of sulphide (2) reveals a remarkable network of very close, intermolecular S---S interactions in the solid state.

Monolithiated TTF species (1)[10] reacted with di(phenylsulphonyl)sulphide (5)[11] to afford compound (2) which was isolated as an air-stable crystalline solid.[12] In a bid to obtain the analogous disulphide, (TTF)$_2$S$_2$, di(phenylsulphonyl)disulphide (6),[13] was reacted with anion (1). However,



(1)

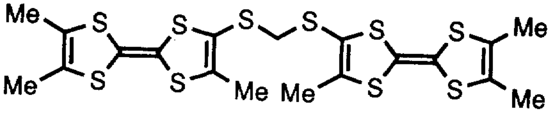
(2) X = S
(3) X = Se
(4) X = Te

$PhSO_2$-S-SO_2Ph

(5)

$PhSO_2$-X-X-SO_2Ph

(6) X = S
(7) X = Se



(8)

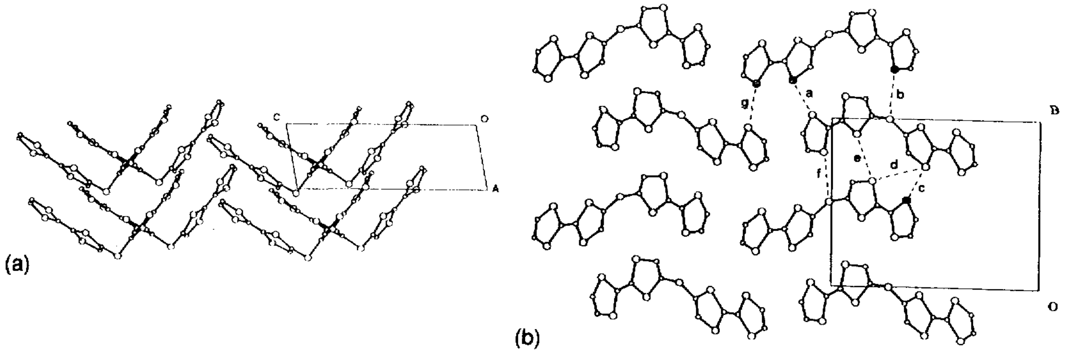


Figure 1. Single crystal X-ray structure of compound (2): (a) view along the *b* axis; (b) view along the *a* axis showing the network of intermolecular S--S contacts, many of which are shorther than the sum of the Van der Waals radii (3.8 Å). Distance a = 3.449, b = 3.658, c = 3.497, d = 3.815, e = 3.517, f = 3.662, g = 3.918 Å. The non-bonded interactions are coded as follows: O---O (same plane), O---⊘ (next molecule below), O---● (next molecule above).

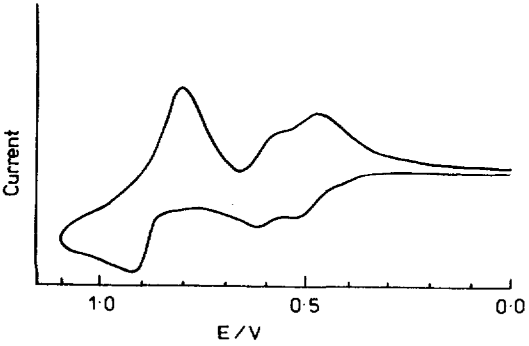


Figure 2. Cyclic voltammogram of compound (2). Experimental conditions: compound (2) (*ca.* 1 x 10^{-5} mol dm^{-3}), electrolyte $Et_4N^+PF_6^-$ (*ca.* 1 x 10^{-1} mol dm^{-3}) in dry dichloromethane under nitrogen, 20°C, *versus* Ag/AgCl, Pt electrode,scan rate 100 mV s^{-1}.

sulphide (2) was the only isolated product (8% yield). In a similar reaction, di(phenylsulphonyl) diselenide (7)[13] yielded bis(tetrathiafulvalenyl)selenide (3).[12]

The X-ray crystal structure of $(TTF)_2S$ (2) is shown in Figure 1.[14] There are two independent molecules per unit cell. The molecule is bent about the bridging sulphur atom with a C(6)-S(5)-C(7) angle of 100.6(5)°. A view along the *b* axis (Figure 1a) shows that each TTF unit in $(TTF)_2S$ is slightly distorted into a chair conformation (similar to TTF itself[17]) and that the molecules of $(TTF)_2S$ pack in a manner reminiscent of a flock of flying seagulls. The stacks are 'tied' together by a two-dimensional network of intermolecular S---S contacts that are considerably shorter than the Van der Waals distance, as shown in Figure 1b. There is also a weaker three-dimensional interaction in the structure [non-bonded interaction g (Figure 1b)]. Such tight packing of a neutral TTF donor is observed in a very few other structures, notable examples being bis(ethylenedithio)-TTF (BEDT-TTF)[18] and TTF_2Te (4)[1] for which the closest intermolecular S---S distances are 3.482 and 3.53 Å, respectively.

The solution electrochemistry of $(TTF)_2S$ (2) and $(TTF)_2Se$ (3) has been studied by cyclic voltammetry. The data are identical for both compounds; the cyclic voltammogram of compound (2) is shown in Figure 2. Three distinct oxidation waves are observed. The first two oxidations ($E_1^{1/2} = 0.49$ V and $E_2^{1/2} = 0.61$ V) are both one-electron processes, and repeated cycling between 0.0 V and 0.7 V established that these two waves are reversible. These data are consistent with the sequential formation of mono- and di-cationic species $TTF\text{-}S\text{-}TTF^{+\cdot}$ and $TTF^{+\cdot}\text{-}S\text{-}TTF^{+\cdot}$, respectively. Further oxidation to tri- and tetra-cationic species, $(TTF)_2S^{3+\cdot}$ and $(TTF)_2S^{4+}$, is observed as a single, irreversible, two-electron wave at $E^{1/2} = 0.86$ V. (*Cf.* For TTF, $E_1^{1/2} = 0.34$ V and $E_2^{1/2} = 0.78$ V under identical conditions). The separation between the potentials of $E_1^{1/2}$ and $E_2^{1/2}$ for compounds (2) and (3) ($\Delta E = 0.12$ V) is probably due to intra- (or inter-) molecular Coulombic effects. This value is different from that reported by Becker *et al* for the telluride analogue (4) ($\Delta E = 0.34$ V versus Ag/AgCl, glassy carbon electrode, in MeCN-THF),[1] yet it is very similar to that reported by Bechgaard and coworkers for the bis(trimethylTTF) derivative (8) ($\Delta E = 0.135$ V) in which the TTF moieties are electronically isolated by the methylene linkage.[3,19] The bridging chalcogen atom of compounds (2)-(4) could, conceivably, electronically couple the two TTF rings to a limited extent. However, recent extended Hückel calculations suggest that through-bond (intramolecular) interactions between TTF units in dimers, $(TTF)_2X$, will be very weak, irrespective of the nature of the linking group X:[6] the very similar electrochemical results for systems (2) and (8) support these calculations.

In conclusion, we have synthesised the new bis-TTF derivatives (2) and (3): their multistage redox behaviour and the extensive sulphur-sulphur network that exists in the solid state structure of (2) are particularly interesting features of these new donors.

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12. Compound (2), 14% yield, m.pt. 144-147 °C (recrystallised from CS_2/hexane);

    Compound (3), 9% yield, m.pt. 161-164°C [purified by silica column chromatography, eluent cyclohexane/toluene (3:1 v/v)]. Compounds (2) and (3) both gave elemental analyses and mass spectra consistent with their formulae.
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14. Crystal data for (2): $C_{12}H_6S_9$, triclinic space group P 1, a = 5.107(1), b = 11.978(2), c = 14.056(2) Å, α = 89.22(3), β = 100.45(7), γ = 94.36(1)°, U = 843.17 Å^3, Z = 2, F(OOO) = 444, Mo-Kα radiation, λ = 0.71069 Å. The structure was solved by direct methods (SHELXS 86)[15] and refined by least-squares analysis[16] (anisotropic for non-hydrogens) to R = 0.043 for 2747 observed ($F_o > 2\sigma F_o$) reflections from 3145 unique data. The data were collected on an Enraf-Nonius FAST area detector diffractometer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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19. This similarity was confirmed by obtaining the cyclic voltammograms of both compounds (2) and (8) under identical conditions at the University of Copenhagen.

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