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# Bis(trisubstituted tetrathiafulvalenyl) disulfides : Disulfide-bridged TTF Dimers

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***Abstract*** : The title compounds are synthesized, using the oxidative coupling of TTF thiolates. The disulfide linkage induces approximate orthogonality between the two TTF units, while maintaining virtually unchanged their electrochemical properties.

The design of pluridimensional networks is one of the main research trends in the field of tetrathiafulvalenes (TTFs) based materials, in order to improve their electroconductive properties (suppression of Peierls distorsions).[1] Additionally, the construction of systems of orthogonal spins has been suggested as a possible way towards organic ferromagnets[2]. Disulfide brigded bis-tetrathiafulvalenes of the TTF-S-S-TTF type are good candidates as precursors of such pluridimensional materials since the rather strictly defined conformational behaviour of the disulfide linkage is expected to induce a non-coplanarity of the two TTF sub-units.[3]

Several related dimeric TTFs,[4-6] especially the monosulfide[5] TTF-S-TTF and the ditelluride[6] TTF-Te-Te-TTF, have been synthezised recently, however, attempts to obtain the disulfide TTF-S-S-TTF have been, to our knowledge, unsuccessful.[5]

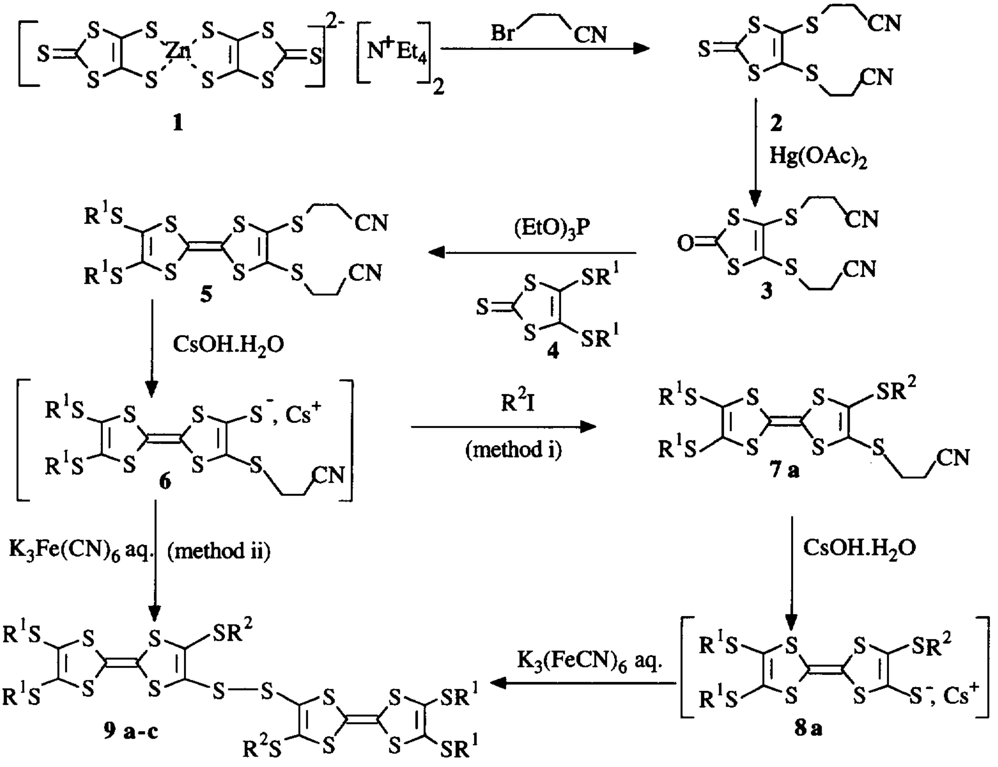
We present here the synthesis of bis(tris(methylthio)tetrathiafulvalenyl)disulfide **9a,** as well as its X-ray structure results and electrochemical properties which agree with its behaviour as a π-donor capable to afford new materials of enhanced dimensionality.

The target compound **9a** was prepared according to scheme 1,[7] by starting from the bulk obtainable zinc complex **1**.[8] Our synthetic methodology mainly lies on the use of the cyanoethyl group as an easily removable thiolate protector.[9,10] The final oxidative coupling[11] of two thiolates **8a** was efficiently (recrystallized yield : 87%) achieved by action of aqueous potassium hexacyanoferrate(III) $K_3Fe(CN)_6$ and it should be noted that, under these conditions, unwanted oxidation of the TTF core is apparently completly avoided.[12]

Additionally, we have also prepared, using a similar strategy (scheme 1), the bis(tetrathiafulvalenyl) disulfides **9b,c**,[13] which still possess cyanoethyl groups, susceptible of further chemical transformations and thus confirming that this synthetic strategy is very versatile.

The molecular structure of **9a**, drawn from X-ray diffraction data, is displayed in Fig. 1. In agreement with the general conformational patterns of disulfides,[3] the C(1) S(5) S(5') C(1') (see Fig. 1 for the labelling scheme) dihedral angle in compound **9a** adopts a value of 70°. The relative positioning of the two tetrathiafulvalenyl moieties may be, at first, roughly outlined by stating that they tend to lie in parallel planes and that their longitudinal axis tend to be orthogonal; more precisely the angle of the mean planes defined respectively by S(1), S(2), C(3), C(4), S(3), S(4) and S(1'), S(2'), C(3'), C(4'), S(3'), S(4') is, in fact, 36° and the angle between the C(3)-C(4) and C(3')-C(4') directions is 112°.

**Scheme 1**



a : $R^1 = R^2 =$ Me (obtained through method i)
b : $R^1 = n\text{-}C_5H_{11}$, $R^2 = CH_2\text{-}CH_2\text{-}CN$ } (obtained through method ii)
c : $R^1 = CH_2\text{-}CH_2Ph$ , $R^2 = CH_2\text{-}CH_2\text{-}CN$

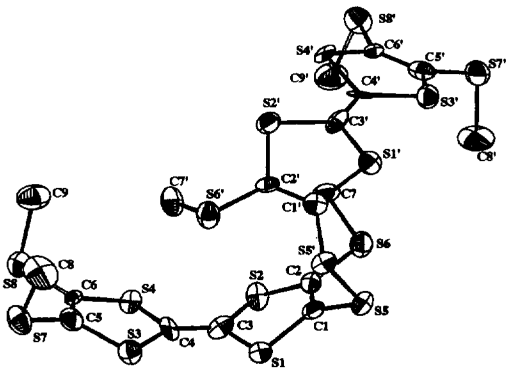


Fig. 1. Molecular structure of **9a**

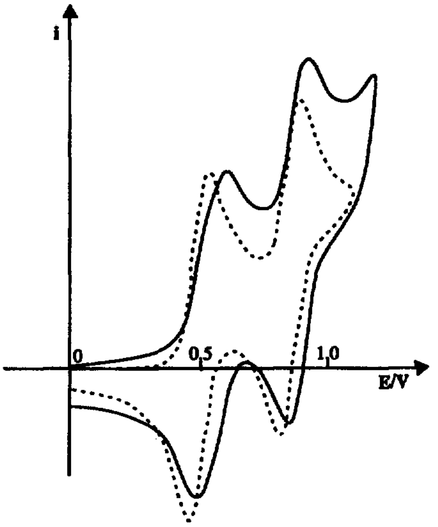


Fig. 2 : Cyclic voltammograms of **9a** (full line) and TMT TTF (dotted line).

*Experimental conditions* : working electrode : Pt, reference : SCE, **9a** or TMT TTF : 2.5 $10^{-4}$ mol $L^{-1}$ , supporting electrolyte : $Bu_4NPF_6$ 0.1 mol $L^{-1}$, solvent : $CH_2Cl_2$ , scan rate 100 mV $s^{-1}$.

The cyclovoltammogram of **9a** (Fig. 2) is archetypal of a TTF derivative and thus exhibits two oxidation peaks at $E_{pa1}$ = 0.61V and $E_{pa2}$ = 0.93V versus SCE. The reversibility of these processes was established by repeated cycling. As it can be judged from Fig. 2, the cyclovoltammograms of **9a** and of tetra(methylthio)tetrathiafulvalene (TMT TTF) which can be considered as the "model monomer" of **9a**, are, in fact, quite similar (for TMT TTF : $E_{pa1}$ = 0.55V, $E_{pa2}$ = 0.90V).

In a double electron-donor system such as **9a,** the removing of one electron from one half of the molecule is *a priori* expected to influence the removing of one electron from the other half. Thus each of the two reversible oxidation steps of TTFs (TTF $\rightarrow$ $TTF^{\bullet +}$ and $TTF^{\bullet +}$ $\rightarrow$ $TTF^{2+}$) is expected to be splitted in two components, leading to a total of four oxidation peaks. The experimental voltammogram of **9a** (Fig. 2) shows that this is not the case and that only two waves are still observed. This leads to the conclusion that the mutual influence of the two tetrathiafulvalenyl moieties of **9a** is weak. Each of the two observed redox waves of **9a** corresponds in fact to the superposition of two nearly degenerate monoelectronic processes occuring on both halves of the molecule, thus leading only to a moderate broadening of the voltammogram of **9a** and a slight increase to higher potentials of the resulting observed $E_{pa1}$ and $E_{pa2}$, when compared to TMT TTF.

This behaviour can be understood from the molecular structure of **9a** (Fig. 1), if accepting the reasonable assumption that the general features of the solid state conformation of **9a** are kept in solution[3] : from previous studies[4,5,14] on related dimers TTF-X-TTF, it is generally concluded that through-bond interactions between the two TTF moieties are weak, irrespectively of the nature of the bridging group X; if geometrically allowed, through-space interactions (especially Coulombic repulsions) may be more important, but in the case of **9a** the relative positioning of the two TTF entities (Fig. 1 and above discussion) hardly seems to allow important spatial interactions.

Thus, it may be concluded, in first analysis, that the disulfide connector does not modify the redox properties of the two TTF halves of **9a**, which remain electrochemically independent, and that it acts purely as a structural director through its conformational effect. The obtention of compounds **9** provides a new example of the versatility of the cyanoethylthio group based synthetic strategy [9,10]. On the grounds of the above structural and electrochemical features, attempts at chemical and electrochemical oxidations of **9a** are actively carried out to obtain related cation (radical) salts. Besides, owing to the juxtaposition in **9** of oxydable (TTF-) and reductible (-S-S-) parts, we shall undertake a deeper electrochemical study of these compouds, especially in the cathodic region.

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7. Compounds **1-7** have been previously described [8,9].
Compound **9a** (via intermediate **8a**) : **7a** (250 mg, 0.58 mmol) was dissolved in DMF (0.9 mL) and CsOH.$H_2O$ (0.12 g, 0.71mmol) in MeOH (0.3 mL) was added. The mixture was stirred at 0°C, under nitrogen, for 1 h, then $K_3Fe(CN)_6$ (0.71 mmol) in water (6 mL) was added. Stirring was continued for 15 min, then the precipitated disulfide **9a** was filtered off, washed with water, dried over $P_2O_5$ and recrystallized from boiling toluene. Yield 191 mg (87%). m.p. 160-162°C. Anal. Calcd for $C_{18}H_{18}S_{16}$ : C 28.95 , H 2.41, S 68.63; Found : C 29.64, H 2.47, S 68.07 MS (EI): Parent Peak $M^+ = 746$ is not observed, presence of $(M/2)^+ = 373$. $^1$H-NMR (270 MHz, $CS_2$+ $CDCl_3$) : 2.48 (s), 2.45 (s), 2.44 (s). I R (KBr): 2982 (w), 2912 (w), 1462, 1410, 1312, 1299, 1007 (w), 992 (w), 962, 952, 888, 878 and 769 cm$^{-1}$ .

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12. We checked also that $(Bu_4N)_3 Fe(CN)_6$ does not react with tetrathiafulvalene in $CDCl_3$ solution.

13. Obtained from one-pot mono-decyanoethylation of the corresponding **5b-c** and subsequent oxidation of the formed thiolates :
**9b** : Yield 72%. m.p. 167°C. Anal. Calcd. for $C_{38}H_{52}N_2S_{16}$ : C 43.51, H 5.00, N 2.67, S 48.81; Found : C 43.33, H 4.89, N 2.98, S 46.65. MS (FAB): $M^+ = 1048$, $(M/2)^+ = 524$. $^1$H-NMR (270 MHz, $CDCl_3$): 3.07 (t, 4H), 2.83 (t, 8H), 2.71 (t, 4H), 1.65 (m, 8H), 1.38 (m,16H), 0.91(t, 12H).
**9c** : Yield 68%. m.p. 173°C. Anal. Calcd. for $C_{50}H_{44}N_2S_{16}$ : C 50.64, H 3.74, N 2.36, S 43.26; Found : C 50.38, H 3.80, N 2.42, S 43.95. MS (FAB): $M^+ = 1184$, $(M/2)^+ = 592$. $^1$H-NMR (270 MHz, $CDCl_3$): 7.25 (m, 20H); 3.06 (m, 12H), 2.97 (m, 8H), 2.69 (t, 4H).

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