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Tetrathiafulvalene (TTF) fused to acenaphthyleno[1,2*b*][1,4]dithiine: synthesis and X-ray crystal structure of a new π-electron donor system

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Abstract

The reaction of transient 1,3-dithiole-2,4,5-trithione **4** with acenaphthylene afforded the Diels-Alder adduct **5**, which was dehydrogenated to yield **6**; cross-coupling of **6** with **7** gave the tetrathiafulvalene (TTF) derivative **8**, which was converted into the di(methylsulfanyl) analogue **10**, the solution electrochemistry and X-ray crystal structure of which are reported.

New π-electron donors continue to attract great attention in the field of molecular materials, and tetrathiafulvalene (TTF) derivatives,[1] polycyclic arenes,[2] and thia-arenes[3] are amongst the most studied systems in this context. Recently, Tani *et al* reported the synthesis of the π-electron donor acenaphthyleno[1,2-*b*][1,4]dithiine **1**,[4] and we have described a substantially-modified route to **1**, along with syntheses of the benzo- **2** and thienyl-fused analogues.[5] These synthetic routes to the acenaphthyleno[1,2-*b*][1,4]dithiine skeleton used acenaphthylen-1-one,[4,5] or acenaphthylenequinone[5] as starting materials. We were unable to functionalise the dithiine ring of **1** by a lithiation / electrophilic substitution protocol (due to ring-opening reactions)[5] and the literature routes[4,5] were not readily adaptable to the synthesis of new derivatives of **1** for which functionalised 1,2-dithiols would be required. We now report an entirely different approach to derivatives of **1**, based on a cycloaddition reaction of acenaphthylene, which has led to the novel fused TTF system **10**.

Thermally-induced depolymerisation of oligo(1,3-dithiole-2,4,5-trithione) **4**[6,7] in refluxing toluene in the presence of acenaphthylene **3** afforded the cycloaddition product **5**[8] in 79% yield. Dehydrogenation of **5** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) readily afforded compound **6** (94% yield) which was cross-coupled with Becher's reagent **7**[9] under standard conditions in the presence of triethylphosphite[10] to afford the TTF system **8** in 17% yield, after chromatographic separation (silica gel, eluent dichloromethane) from self-coupled products. Deprotection of **8** using caesium hydroxide monohydrate in a mixture of THF and methanol[9,11] gave the transient dithiolate species **9** which reacted *in situ* with methyliodide to afford di(methylsulfanyl) derivative **10** in 96% yield (from **8**). Compound **10** is air-stable and shows good solubility in a range of organic solvents.

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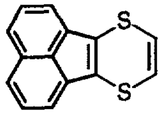

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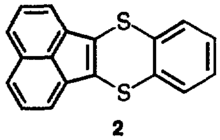

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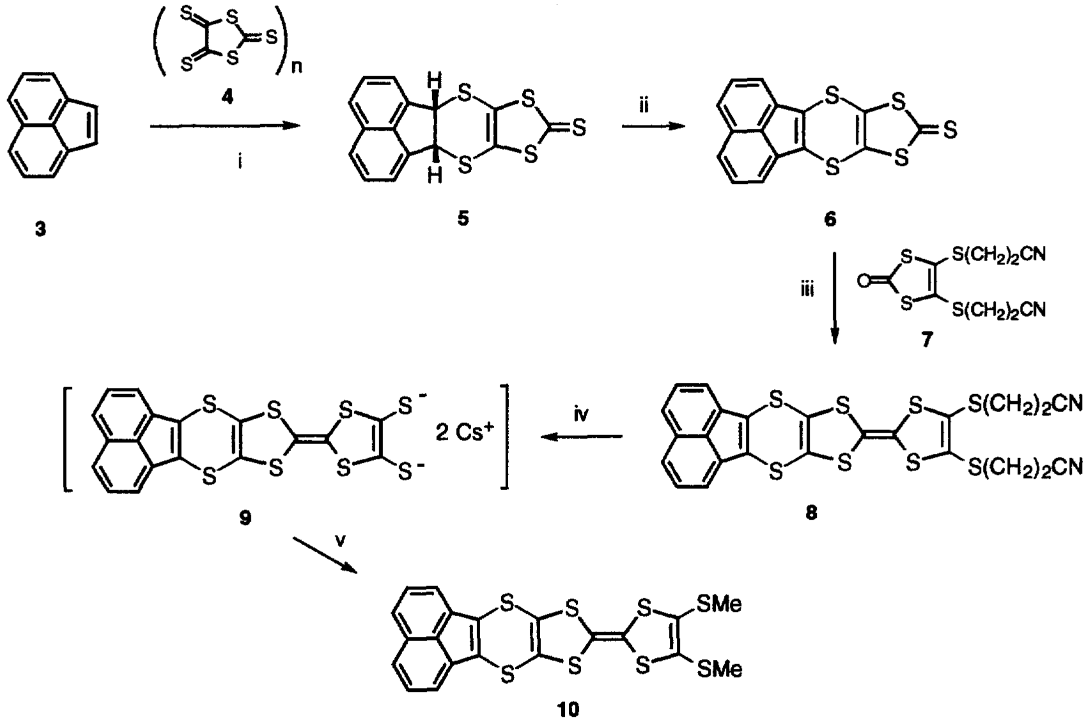

Scheme 1 *Reagents and conditions:* i, **5**, PhMe, reflux, 79%; ii, DDQ, PhMe, 94%; iii, **7**, $P(OEt)_3$, reflux, 17%; iv, $CsOH.H_2O$, THF/MeOH, 20 °C, 15 min; v, MeI, 20 °C, 96% (from **8**).

The cyclic voltammogram (CV) of compound **10**[12] showed two reversible, one-electron oxidation waves to form, sequentially, the radical cation and dication species ($E_1^{1/2}$ + 0.38, $E_2^{1/2}$ + 0.74 V) followed by a third irreversible wave at E_3^{ox} + 1.38 V. The first two waves are typical of the TTF system ($E_1^{1/2}$ + 0.34, $E_2^{1/2}$ + 0.71 V for TTF under the same conditions, and alkylsulfanyl substitution is known to anodically shift these values)[13] and the third wave is assigned to an oxidation of the fused acenaphthyleno[1,2-*b*][1,4]dithiine moiety, yielding the unstable trication radical species.

The X-ray molecular structure of **10**[14] reveals that the molecule adopts a boat conformation, folding by 46.5° along the (S1)...S(2) vector of the dithiine ring,[15] and by 17.0° along the S(5)...S(6) vector (Fig. 1). The fused 1,3-dithiole ring has an envelope-like distortion, with S(3) tilting out-of-plane by 6°. Molecules pack into a 'fir tree' stack, in which acenaphthyleno moieties overlap with TTF moieties (Fig. 2).

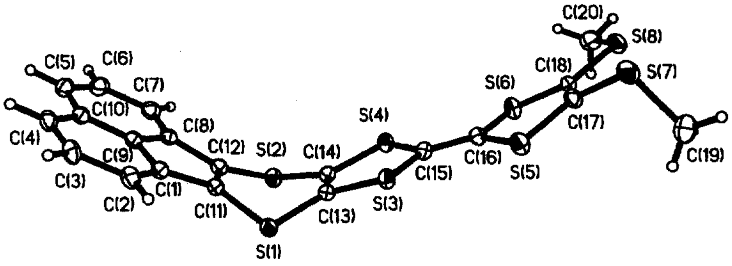

Figure 1 Molecular structure of **10**

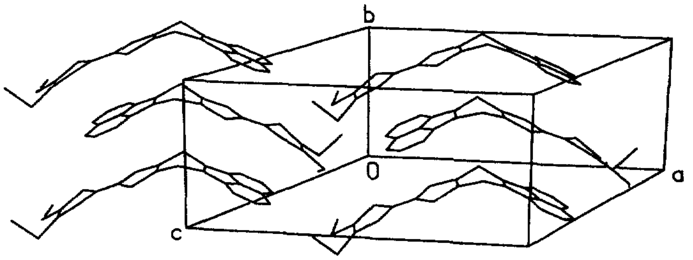

Figure 2 Packing of molecules of **10** in the crystal

In conclusion, new methodology for the preparation of functionalised acenaphthyleno[1,2-*b*][1,4]dithiine derivatives is reported. This should be versatile for a range of derivatives of **1** using cross-coupling reactions of **6** (to afford TTFs, as illustrated here by the synthesis of **10**) and transition metal coordination[16] to the dithiolate unit **9**. The good solubility of **10** contrasts with many other aromatic ring-annelated TTF systems which are insoluble,[17] or require long-chain substituents to provide solubility.[1a] This augers well for the formation of cation radical salts of **10**, which may combine the properties of the TTF and thia-arene families of π-donor molecules.

ACKNOWLEDGEMENTS

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8 All new compounds gave satisfactory elemental analysis, mass spectrometric and spectroscopic data. Selected data: compound **5**, yellow needles, m.p. 235-240°C; ν_{max} (KBr)/cm^{-1} 1065, 1041, 821, 775, 505; δ_H (400MHz; CS$_2$ / CDCl$_3$ 5:1) 5.74 (2H, s, *benzylic*), 7.45 (2H, d, *J* = 6.8, Ar-*H*), 7.57 (2H, m, Ar-*H*) and 7.72 (2H, d, *J* = 8.4, Ar-*H*); compound **6**, orange microcrystals, mp > 250°C, ν_{max} (KBr)/cm^{-1} 1423, 1073, 1032, 816, 763; δ_H (400 MHz; CS$_2$ / CDCl$_3$ 5:1v/v) 7.61 (4 H, m, Ar-*H*) and 7.86 (2 H, d, *J* = 7.6, Ar-*H*); compound **8**, dark purple needles, m.p. 174-177°C (from toluene) ν_{max} (KBr)/cm^{-1} 2922, 2248 (CN), 1475, 1457, 1425, 1133, 892, 816, 764; δ_H (200 MHz; CDCl$_3$) 2.75 (4H, t, *J* = 7.7, SC*H*$_2$CH$_2$), 3.09 (4H, t, *J* = 7.1, CH$_2$C*H*$_2$CN), 7.57 (4H, m, Ar-*H*) and 7.84 (2H, dd, *J* = 9.52 and 1.42, Ar-*H*); compound **10**, dark red needles, m.p. 187-190°C (from CS$_2$ / hexane); ν_{max} (KBr)/cm^{-1} 1424, 894, 815, 764 vs; δ_H (400 MHz; CDCl$_3$) 2.44 (6H, s, SC*H*$_3$), 7.54 (2H, dd, *J* = 7.0 and 8.0, Ar-*H*), 7.59 (2H, d, *J* = 6.4, Ar-*H*) and 7.82 (2H, dd, *J* = 8.8 and 0.4, Ar-*H*).

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14 Crystal data for **10**: C$_{20}$H$_{12}$S$_8$, M=508.8, monoclinic, space group P2$_1$/c (No.14), T=150 K, *a*=17.166(1), *b*=7.714(1), *c*=16.897(1) Å, β=115.71(1)°, V=2016.0(3) Å^3, Z=4, Dx=1.676 g cm^{-1}, $\bar{\lambda}$ (Mo-K_α)=0.71073 Å, μ=8.9 cm^{-1}, 15561 data (5452 unique) measured on a SMART 1K CCD area detector, 301 parameters refined on F^2, R=0.041 [4329 data with F^2>2σ(F^2)], wR(F^2)=0.096. The same structure was found at T=293 K.

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