

New, Extensively-Conjugated π -Electron Donors Combining both Tetrathiafulvalene (TTF) and 2,2'-Ethanediylidene-bis-(1,3-dithiole) Units: Synthesis and Solution Electrochemistry

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Abstract: New π -electron donor molecules have been prepared containing covalently linked tetrathiafulvalene (TTF) and 2,2'-ethanediylidene-bis-(1,3-dithiole); cyclic voltammetric studies establish that these extensively conjugated systems possess remarkably low oxidation potentials.

In the search for new organic conductors,¹ there is great interest in electron donors of the tetrathiafulvalene (TTF) family **1** that contain extended π -electron conjugation,² *e.g.* 2,2'-ethanediylidene-bis-(1,3-dithiole) derivative **2** has recently been synthesised independently by three groups.^{2d-f} Increased conjugation reduces intramolecular Coulombic repulsion in oxidised states leading to novel electrochemical behaviour, and may also increase interchain contacts between the donors, thereby enhancing the dimensionality in charge-transfer salts. Sulfur containing substituents (*e.g.* ethylenedithio groups) attached to TTF are known to increase significantly interchain reactions.¹ We now focus on the synthesis and solution redox properties of a new series of π -donors in which 1,3-dithiole rings and the 2,2'-ethanediylidene-bis-(1,3-dithiole) framework are attached to the periphery of TTF. Compounds **10-12** are especially interesting compounds, as they are the first examples of TTF linked to a vinylogous TTF framework. Key synthetic steps involve Wittig and Wittig-Horner reactions of the phosphorus ylids and phosphonate anions derived from reagents **5a-d** and **9b-d**, respectively.

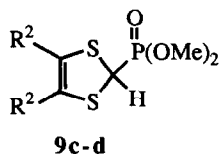
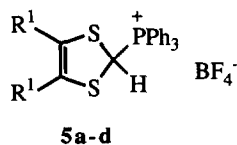
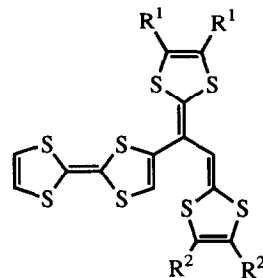
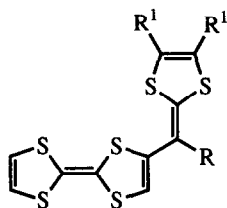
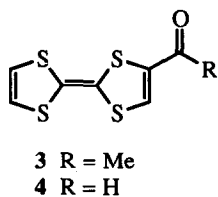
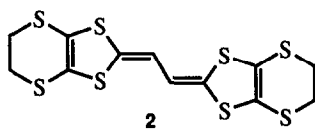
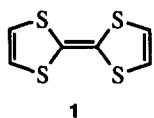
4-Acetyl-TTF **3**³ and 4-formyl-TTF **4**⁴ reacted cleanly with the ylids generated from phosphonium salts **5a-d**² (*n*-BuLi, -78°C, THF) to yield products **6a-d** and **7a-d**, respectively (60-90% yields). Construction of the vinylogous TTF framework from compounds **7c-d** was accomplished in two steps. Vilsmeier reaction of Me₂NCHCl⁺ (generated from oxalyl chloride and DMF) followed by treatment with sodium hydroxide gave aldehydes **8c-d** (25-35% yields). The efficiency of this step could not be improved, although different reaction conditions were tried. The anions generated by deprotonation of reagents **9c-d**² (*n*-BuLi, 20°C, THF)^{2h} reacted with aldehydes **8c-d** to yield the highly-conjugated π -electron donor systems **10-12** (*ca.* 60% yield). It is noteworthy that compounds **8c-d** did not undergo Wittig reactions using reagents **5**; the more reactive Wittig-Horner reagents **9** were required for this step.⁵

The donor ability of compounds **10-12** has been studied by cyclic voltammetry.⁶ Both donors **11** and **12** exhibit two fully reversible oxidation waves (E_{pa}^1 and E_{pa}^2) and a third irreversible wave (E_{pa}^3)⁷ at the following potentials: $E_{pa}^1 = +0.18$ V (**11**), +0.19 V (**12**); $E_{pa}^2 = +0.40$ V (**11**), +0.41 V (**12**) and $E_{pa}^3 = +1.18$ V (**11**) and +1.22 V (**12**). These data demonstrate the remarkably strong electron donor properties of compounds **11** and **12** which are formed by covalent attachment of TTF and its vinylogous derivative. It is

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striking that the oxidation potentials of **11** and **12** are significantly lower than those observed for the independent TTF and 2,2-ethanediylidene-bis-(1,3-dithiole) moieties,^{2e-8} with ΔE_{pa} values ($\Delta E_{pa} = E_{pa}^2 - E_{pa}^1$) in the same range (0.20 V) as the parent vinylogous TTF unit. (Cf. $E_{pa}^1 = +0.34$ (**1**), $+0.59$ (**2**); $E_{pa}^2 = +0.78$ (**1**), $+0.71$ (**2**) V, vs. Ag/AgCl.)^{2e} The good reversibility of the first two redox steps for **11** and **12** demonstrates that the oxidised species are stable. It is surprising, therefore, that we were unable to obtain the cyclic voltammogram of analogue **10** which appeared to decompose readily under electrochemical conditions.

The preparation of compounds **11** and **12**, which possess outstandingly low oxidation potentials (for TTF derivatives) is an important step forward.⁸ Such compounds, in which dication states are readily accessible, have been identified, from theoretical studies, to be promising systems for the discovery of new mechanisms of conduction and superconduction involving bipolarons.⁹ The preparation and characterisation of mixed valence salts of the new donors **11** and **12** is, therefore, a fascinating prospect.



For compounds **5-9**:

a; R¹ and R² = H

b; R¹ and R² = Me

c; R¹ and R² = SMe

d; R¹-R¹ and R²-R² = S(CH₂)₂S

Experimental¹⁰

General Procedure for Compounds 6a-d and 7a-d. A stirred solution of reagent 5a-d² (5.0 mmol) dissolved in dry tetrahydrofuran (THF) (15 ml) was cooled to -78°C and *n*-butyl lithium (5.0 mmol) was added. After 15 min. at -78°C, a solution of compound 3 or compound 4 (4.0 mmol) dissolved in THF (12 ml) was introduced dropwise. The reaction mixture was then allowed to warm to 20°C, with stirring for 16 h. Solvent was then evaporated *in vacuo* and the residual oil was chromatographed on a silica gel column eluted with toluene / cyclohexane (4:1 v/v) to yield the product. Representative data: compound 7d, a red solid, 83% yield, m.p. 174-176°C; δ_{H} (CDCl₃) 6.32 (2H, s), 6.08 (1H, s), 5.95 (1H, s) and 3.32 (4H, s) ppm.

General Procedure for Compounds 8c-d. Oxalyl chloride (0.175 ml, 2.0 mmol) was carefully added to dry dimethylformamide (DMF) (7.0 ml) at 0°C with stirring under nitrogen to precipitate a white salt. After 0.5 h, compound 7c-d (1.0 mmol) was added either as a solid or as a solution in DMF, and the temperature was raised to 20°C. After stirring for 2 h at 20°C, the reaction mixture was cooled to 0°C and cold aqueous sodium hydroxide solution (1M, 50 ml) was added. The mixture was stirred for 1 h at 20°C and extracted with dichloromethane. The organic layer was separated, washed thoroughly with water, dried (MgSO₄) and evaporated to give a black residue which was purified by chromatography on a silica column eluted with dichloromethane, to yield the product. Representative data: compound 8d, a black solid, 30% yield, m.p. 234-237°C; δ_{H} (CDCl₃) 9.69 (1H, s), 7.01 (1H, s), 6.35 (2H, s) and 3.36 (4H, s) ppm.

General Procedure for Compounds 10-12. *n*-BuLi (0.6 mmol) was added to a stirred solution of aldehyde 8c-d (0.4 mmol) and freshly prepared phosphonate ester 9c-d (0.6 mmol) dissolved in dry THF (10 ml). The solution immediately turned bright red and the mixture was stirred at 20°C under nitrogen. After 0.5 h, the solvent was evaporated and the residual oil was purified by preparative t.l.c. on a neutral alumina plate with toluene/hexane (7:3 v/v) as eluent. Representative data: compound 12, a dark red solid, 60% yield, m.p. 102-105°C; δ_{H} (CDCl₃) 6.31 (2H, s), 6.09 (2H, s), 3.31 (4H, s), 2.43 (3H, s) and 2.41 (3H, s) ppm.

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 4. Compound **4** was prepared by a modification of the literature route (ref. 3): J.Garin, J.Orduna, S.Uriel, A.J.Moore, M.R.Bryce, S.Wegener, D.S.Yufit and J.A.K.Howard, manuscript in preparation.
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 6. Cyclic voltammetric data were obtained using a PAR 273 Potentiostat/Galvanostat. Experimental conditions: donor, (1×10^{-3} M); electrolyte $\text{Bu}_4\text{N}^+\text{PF}_6^-$ (1×10^{-1} M); dry dichloromethane under nitrogen, 20°C, versus SCE, Pt electrode, scan rate 200 mV sec⁻¹.
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 10. Compounds **6-8** were pure as judged by elemental analysis, mass spectrometry and ¹H NMR spectroscopy. Molecular ion peaks could not be obtained for compounds **10-12** using EI, CI or FAB MS; their structural assignments are based on correct elemental analysis (for compound **11**) and unambiguous ¹H NMR spectra for **10-12**.

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