4,4′,5,5′-Tetrakis(2-thienyl)tetrathiafulvalene [TT-TTF]: synthesis and first X-ray crystal structure of a thiophene-substituted TTF electron donor

Adam Charlton,[a] Allan E. Underhill,[a] Gwion Williams,[a] Maher Kalaji,[a] Patrick J. Murphy,*[a] David E. Hibbs,[b] Michael B. Hursthouse[b] and K. M. Abdul Malik[b]

[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd, UK LL57 2UW*
[b] *Department of Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff, UK CF1 3TB*

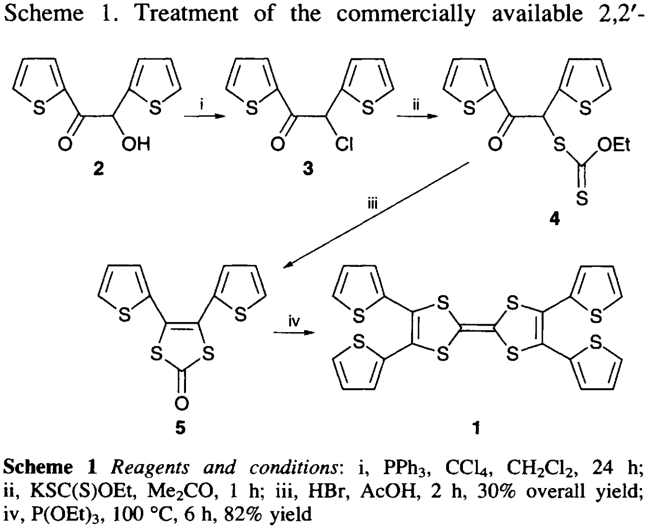
The synthesis, electrochemical properties, preliminary electropolymerisation studies and the single-crystal X-ray crystal structure of the title compound 1 (TT-TTF), a novel thiophene-substituted tetrathiafulvalene electron donor, are described.

The electron donor TTF, first reported by Wudl *et al.* in 1970,[1] and its analogues, are of central importance in the burgeoning field of molecular conductors.[2] Recently developed novel synthetic methodologies have also enabled TTFs to be incorporated into elaborate supramolecular architectures.[3] However, there are few reports regarding the synthesis of polymeric TTF systems, with a view to preparing electrically conducting, yet processable materials. Initial work by Wudl and coworkers[4] and Pittman *et al.*[5] in the 1970s focused on attempts to incorporate TTF moities into the backbone of methylacrylate and styrene polymers, resulting in products that were either poorly conducting or insoluble. In a more recent publication, Mullen and coworkers[6] described the syntheses of a variety of soluble main- and side-chain TTF polymers.

The concept of combining the high electrical conductivities observed in doped TTF molecular crystals with the ordered, high molecular mass polymers based on thiophene,[7] within a single polymer framework is an attractive one. In this regard, Bryce *et al.*[8] have reported details of electropolymerisation studies on a TTF monomer conjugated to thiophene *via* an ester linkage. Thobie-Gautier *et al.*[9] have also reported the electrosynthesis of a TTF-derivatised polythiophene, in which the electroactive units in the monomer were separated by a linear oxadecyl spacer.

Here we report the synthesis and the single-crystal X-ray structure of 1, a novel TTF conjugated directly to four thiophene units. It is anticipated that 1 may serve as a precursor to soluble polymeric systems, and to electrically conducting charge-transfer complexes.

The synthesis of the target molecule TT-TTF 1 is shown in Scheme 1. Treatment of the commercially available 2,2′-theonin 2 with triphenylphosphine in tetrachloromethane–dichloromethane yielded the chloride 3. This somewhat unstable intermediate was allowed to react immediately with potassium ethyl xanthate to yield 4, which on treatment with a solution of HBr in acetic acid gave bis-4,5-(2-thienyl)-1,3-dithiole-2-one 5, in 30% overall yield. The reaction of 5 in freshly distilled triethylphosphite under argon, yielded 1† as a red microcrystalline solid (82%).



Scheme 1 *Reagents and conditions*: i, PPh_3, CCl_4, CH_2Cl_2, 24 h; ii, KSC(S)OEt, Me_2CO, 1 h; iii, HBr, AcOH, 2 h, 30% overall yield; iv, $P(OEt)_3$, 100 °C, 6 h, 82% yield

Single crystals of 1 were grown by slow evaporation of a concentrated dichloromethane solution. X-Ray single-crystal analysis‡ of 1 showed that the molecule (Fig. 1) is centrosymmetric. The central $S_2C_2S_2$ moiety is exactly planar, but the C(1)C(2)C(3)S(1)S(2) ring is buckled, with a fold angle of 9.2(4)° about the S(1)···S(2) axis. The thiophene substituents are disordered between two orientations, one with 0.91 : 0.09 and the other with 0.67 : 0.33 occupancy ratios, and seem to be quite flexible as shown by the values −18.0(4) and 93.5(3)° for the torsion angles S(1)–C(3)–C(8)–S(4) and S(2)–C(2)–C(4)–S(3), respectively. The packing of t–he molecules in the unit cell is fairly loose, with all intermolecular contacts (non-H) > 3.50 Å (Fig. 2).

The electrochemical properties of 1 were investigated using cyclic voltammetry in dichloromethane (Table 1). The cyclic voltammogram of 1 showed two reversible redox processes, at potentials more positive than for the parent TTF, measured under similar conditions. This is as expected, with the presence of the four electron-withdrawing thiophene units attached to the TTF core stabilising the $TTF^{\cdot+}$ and TTF^{2+} species respectively.

These results are consistent with the cyclic voltammetric data reported by Iyoda *et al.*[10] for compounds 6 and 7. Compound 6, the mono(2-thienyl) substituted TTF is intermediate, in terms of electron-donating ability, between TTF and 1, this being reflected in the decreased level of thiophene substitution in 6. It was noted that 7 shows only two redox waves, implying that it is oxidised in two two-electron steps.

Preliminary electropolymerisation studies on compound 1 were carried out in nitrobenzene, using a 0.1 M solution of NBu_4BF_4 (*vs.* Ag/Ag^+, Pt electrode). Continuous cycling between 0 and +0.22 V for 50 min resulted in the formation of a thin film on the platinum electrode, which displayed redox behaviour characteristic of a conducting polymeric material.

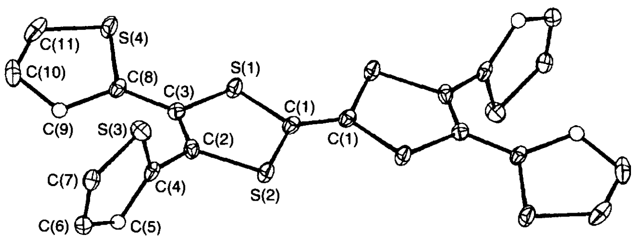


Fig. 1 Molecular structure of centrosymmetric TT-TTF 1. Only one orientation for each thiophene substituent [91% for S(3)/C(5) and 67% for S(4)/C(9)] is shown for clarity.

The complex redox properties and the electrical conductivity of the film are being studied at present.

The electrochemical properties of related derivatives are also under investigation, and these results, along with more extensive electropolymerisation studies on compound **1**, and details of the preparation of charge-transfer complexes will be reported in due course.

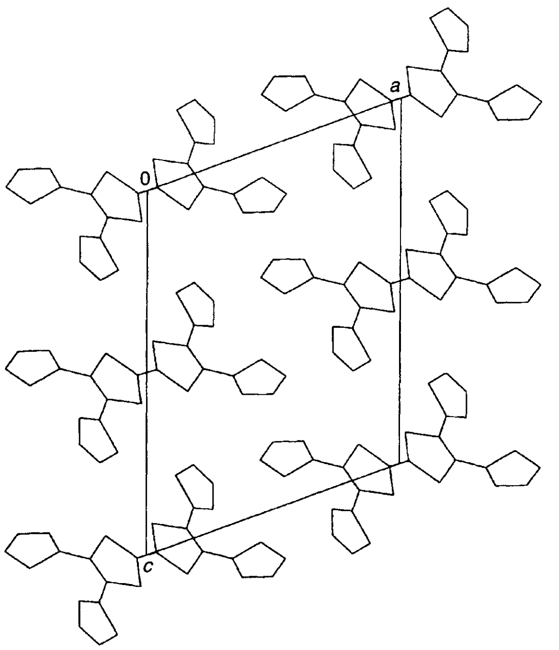
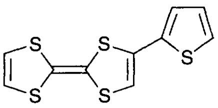


Fig. 2 Crystal packing diagram of TT-TTF **1** with projection of the *ac* plane

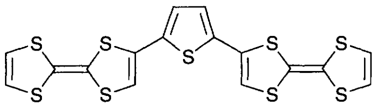
Table 1 Cyclic voltammetric data for the TTF derivatives

Compound	$E_1{}^{1/2}$/V	$E_2{}^{1/2}$/V
TTF[a]	+0.36	+0.74
1[b]	+0.48	+0.87
6[a]	+0.41	+0.80
7[a]	+0.38	+0.81

[a] NBu_4ClO_4 (0.1 mol dm^{-3}) in dry benzonitrile under argon at 20 °C., *vs.* Ag/AgCl, Pt electrode (see ref. 10). [b] NBu_4BF_4 (0.1 mol dm^{-3}) in dry dichloromethane under nitrogen at 20 °C. *vs.* Ag wire, Pt electrode.



6



7

Footnotes

† Compound **1**, red needles (from dichloromethane), mp 242–243 °C. Analysis: found C, 49.47; H, 2.13; S, 47.88. $C_{22}H_{12}S_8$ requires C, 49.60; H, 2.25; S, 48.14%; *m/z* (FAB) 532 (M$^+$); δ_H ($CHCl_3$) 7.33 (4 H, dd, *J* 1.2, 5.1 Hz, CH-5), 7.10 (4 H, dd, *J* 1.2, 3.7 Hz, CH-3), 7.00 (4 H, dd, *J* 3.7, 5.1 Hz, CH-4).

‡ *Crystal data* for **1**: $C_{22}H_{12}S_8$, M_w = 532.80, monoclinic, space group $P2_1/c, a$ = 12.3700(14), b = 5.5090(7), c = 16.750(3) Å, β = 110.25(2)°, U = 1070.9(3) Å^3, Z = 2, D_c = 1.652 Mg m^{-3}, μ(Mo-Kα) = 0.843 mm^{-1}, $F(000)$ = 544, crystal size = 0.35 × 0.22 × 0.16 mm, radiation Mo-Kα (λ = 0.710 69 Å), T = 150(2) K. All crystallographic measurements were made using a FAST area detector diffractometer following previously described procedures.[11] The structure was solved by direct methods (SHELXS86)[12] and refined on F^2 by full-matrix least squares (SHELXL93)[13] using all unique data. The thiophene moieties were disordered between two orientations. The S atoms of minor and carbon atoms of both major and minor occupancies in the disordered positions were isotropic; other non-H atoms anisotropic. The H-atoms were included in calculated positions (riding model). Final R [on $F, F_o > 3\sigma(F_o)$] and wR (on all F^2) were 0.0438 and 0.1064 respectively. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/245.

References

1 F. Wudl, G. M. Smith and E. J. Hufnagel, *Chem. Commun.*, 1970, 1453.

2 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Wangbo, *Organic Superconductors (Including Fullerenes)*, Prentice Hall 1992; *J. Mater. Chem.*, (Special Issue on Molecular Conductors), 1995, **5**, 1469–1760.

3 *Molecular Engineering for Advanced Materials*, ed. J. Becher and K. Schaumberg, NATO ASI Series, Kluwer Academic, Dardrecht, 1994.

4 M. L. Kaplan, R. C. Haddon, F. Wudl and E. D. Feit, *J. Org. Chem.*, 1978, **43**, 4642.

5 C. U. Pittman, M. Ueda and Y. F. Liang, *J. Org. Chem.*, 1979, **44**, 3639.

6 S. Frenzel, S. Arndt, R. Ma Gregorious and K. Mullen, *J. Mater. Chem.*, 1995, **5**, 1529 and references therein.

7 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.

8 M. R. Bryce, A. D. Chissel, J. Gopal, P. Kathirgamanathan and D. Parker, *Synth. Met.*, 1991, **39**, 397.

9 C. Thobie-Gautier, A. Gorgues, M. Jubault and J. Roncali, *Macromolecules*, 1993, **26**, 4094.

10 M. Iyoda, Y. Kuwatani, N. Ueno and M. Oda, *J. Chem. Soc., Chem. Commun.*, 1992, 158.

11 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

12 G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1990, **46**, 467.

13 G. M. Sheldrick, SHELXL93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

Received, 23rd July 1996; Com. 6/05146D