

Improved Synthesis and Crystal Structure of Tetrakis(benzoylthio)-tetrathiafulvalene. A Useful Precursor to Functionalised Bis(ethylenedithio)tetrathiafulvalene Derivatives

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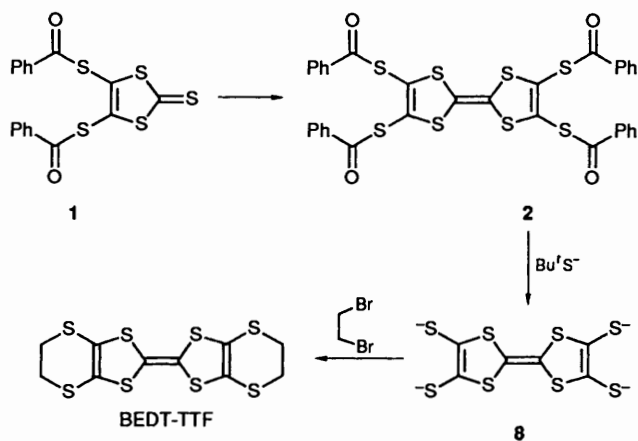
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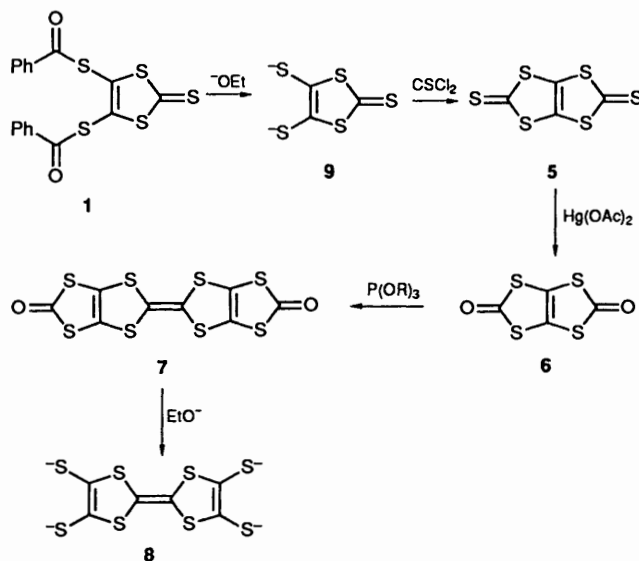
A simple one-step procedure is reported for the preparation of tetrakis(benzoylthio)tetrathiafulvalene (**2**) using octacarbonyldicobalt. The crystal structure of **2** is discussed and the preparation of some charge-transfer salts of **2** and their electrical conductivity has been determined. The use of **2** as a synthon for functionalised bis(ethylenedithio)tetrathiafulvalene derivatives is described.

In attempts to prepare symmetrical tetrakis(alkylthio)tetrathiafulvalene derivatives such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) a variety of methods have been developed.¹ The most common of these is the coupling of 4,5-bis-alkylthio-1,3-dithiol-2-ones or the corresponding thiones or selones using trivalent phosphorus compounds. Depending on the nature of the alkylthio substituents, this route sometimes fails to give the desired product or gives it in very low yield. We sought to synthesise derivatives of BEDT-TTF with extensive functionalisation of the outermost 1,4-dithiine rings including oxo substituents which are incompatible with trivalent phosphorus based coupling reagents.

An obvious way to overcome this problem is to use the TTF tetrathiolate **8** in which the central double bond is already present, as a substrate for the reaction with electrophiles. The tetrathiolate **8** is easily formed from the tetraester **2** by deprotection of the ester groups with sodium *tert*-butyl thiolate. Previously the tetraester **2** has only been prepared in very low yield (<1%) via the phosphite coupling of **1**^{2,3} (Scheme 1).



Tetrathiolate **8** can be obtained in better yield by the route outlined in Scheme 2. Reaction of **9** with thiophosgene^{3,4} gives dithione **5**, which in turn gives dione **6** on treatment with mercuric acetate. Dione **6** is also available by the method of Schumaker and Engler.⁵ Self-coupling of **6** can be effected with trimethyl phosphite to give **7** which can then be ring opened with methoxide ion to give **8**.^{4,5} This route to **8** involves many steps and is neither easy nor convenient.



Results and Discussion

We now report an improved method for the synthesis of **2** involving the facile coupling of **1** to **2** (Scheme 1) using dicobalt octacarbonyl in refluxing benzene, in a modification of the method reported by Le Costumer and Mollier.⁶ The yield is 25%, and may be improved by using different ester substituents on **1**.

Tetraester **2** contains a tetrathiafulvalene (TTF) donor unit and was expected to form charge-transfer complexes with organic acceptors and inorganic ions. Cyclic voltammetry of **2** showed two reversible oxidation waves at +0.66 V and +0.87 V [saturated calomel electrode (SCE)] (Pt electrodes, 0.1 mol dm⁻³ tetrabutylammonium hexafluorophosphate in CH₂Cl₂, 100 mV s⁻¹). These values are higher than those for TTF [+0.37 V and +0.75 V (SCE)] under the same conditions reflecting the electron-withdrawing nature of the thiabenzoyl substituents. Reaction of **2** in solution with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gives **2**-(TCNQ)₂ and **2**-DDQ, respectively. Compressed pellets of these complexes exhibited four probe direct current (dc) conductivities of 0.15 and 2 × 10⁻⁴ S cm⁻¹ respectively at room temperature and exhibited the temperature dependence of a semiconductor. Electrochemical

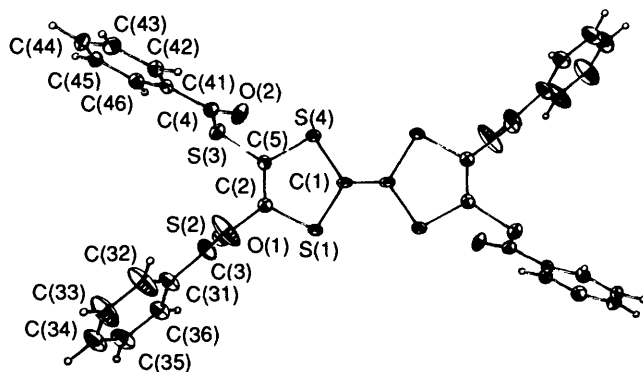


Fig. 1

Table 1 Bond lengths (Å) and angles (deg) in **2**

C(1)–C(1')	1.341(6)	C(2)–C(5)	1.337(4)
C(1)–S(1)	1.761(3)	C(1)–S(4)	1.762(3)
S(1)–C(2)	1.756(3)	S(2)–C(5)	1.745(3)
C(2)–S(2)	1.753(3)	C(5)–S(3)	1.759(3)
S(2)–C(3)	1.794(3)	S(3)–C(4)	1.822(3)
C(3)–O(1)	1.208(4)	C(4)–O(2)	1.189(4)
C(3)–C(31)	1.481(5)	C(4)–C(41)	1.499(4)
S(1)–C(1)–S(4)	114.6(2)	S(4)–C(1)–C(1')	122.7(3)
S(1)–C(1)–C(1')	122.7(3)	C(1)–S(4)–C(5)	95.00(14)
C(1)–S(1)–C(2)	94.82(14)	S(4)–C(5)–C(2)	117.9(2)
S(1)–C(2)–C(5)	117.5(2)	S(4)–C(5)–S(3)	118.2(2)
S(1)–C(2)–S(2)	116.2(2)	C(2)–C(5)–S(3)	123.7(2)
C(5)–C(2)–S(2)	126.3(2)	C(5)–S(3)–C(4)	99.85(14)
C(2)–S(2)–C(3)	100.5(2)	S(3)–C(4)–O(2)	122.3(2)
S(2)–C(3)–O(1)	121.6(3)	O(2)–C(4)–C(41)	124.8(3)
O(1)–C(3)–C(31)	124.8(3)	S(3)–C(4)–C(41)	113.0(2)
S(2)–C(3)–C(31)	113.5(3)		

oxidation of solutions of **2** in 1,1,2-trichloroethane (TCE) in the presence of BF_4^- gives $\text{2}_3^+(\text{BF}_4)_5$ which exhibited a compressed pellet conductivity of $6 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.

Compound **2** can be used as a synthon for the synthesis of BEDT-TTF and BEDT-TTF derivatives. Treatment of **2** with four equivalents of sodium *tert*-butanethiolate in tetrahydrofuran (THF) at -10°C resulted in the formation of **8** as a pink solid. Reaction with a small excess of 1,2-dibromoethane gave a product which showed identical spectroscopic data (IR, ^1H NMR, MS) and R_f value compared with authentic BEDT-TTF [Yield: 71%, m.p. $236\text{--}240^\circ\text{C}$ (decomp.); (lit.,⁷ $246\text{--}248^\circ\text{C}$ (decomp.))].

Other synthetically useful methods that do not require coupling of a thione in the final step are available. These include the lithiation of TTF followed by a sulfur (or selenium) insertion reaction generating the tetraanion **8** and the already-mentioned tetrathiapentalenedione route by Shumaker and later improvements.⁵ The method of choice will probably depend on the availability of starting materials since all three methods are capable of generating the tetrathiaanion **8** in acceptable yields, however our method appears to be relatively short and easy to carry out.

The tetraester **2** was further characterized by X-ray crystallographic methods. The compound crystallized with the molecule on a crystallographic twofold axis. The molecule **2** viewed along this symmetry axis is displayed in Fig. 1. The two thiabenzoyl groups attached to the same five-membered ring have the oxygen atom placed similarly with respect to the plane of the nearly planar TTF fragment pointing towards C(44) from a molecule related by the *c* glideplane. But, as is obvious from Fig. 1, the phenyl groups are oriented differently with respect to the

five-membered rings. The interplanar angles between TTF and the phenyl groups are $113.1(1)^\circ$ [for C(31) to C(36)] and $77.97(6)^\circ$ [for C(41) to C(46)]. The bond lengths and angles listed in Table 1 do not reveal any significant variations from the values observed in structures of planar and non-planar TTF derivatives.⁹

The thiabenzoyl groups differ with respect to planarity. The angle between the planes defined by the S(2)–C(3)–O(1) group and the phenyl group [C(31) to C(36)] is 23° . The equivalent angle in the other independent thiabenzoyl group is 3° . This difference could suggest that conjugation was more pronounced in the almost planar thiabenzoyl group and an inspection of Table 1 shows that this is the case. S(2)–C(3) is shorter, C(3)–O(1) and C(3)–C(31) are longer than the equivalent bond lengths in the more twisted thiabenzoyl group.

Intermolecular S–S interactions often play an important role in the crystal packing of TTF derivatives. The bulky thiabenzoyl groups are oriented so that S(2) and S(3) have interatomic distances of 3.612 and 3.627 Å, respectively, to S(4) from another molecule related by a glide plane.

The packing illustrated by the stereopair in Fig. 2 appears also to be influenced by interactions between the planar groups in the molecule. The phenyl groups [C(31) to C(36)] which are almost parallel to the *b*-axis mutually interact and the phenyl groups [C(41) to C(46)] are almost parallel to the TTF moiety of a molecule related by the symmetry of a glideplane.

Experimental

Preparation of TTF(SCOPh)₄ (2).—To a solution of **1** (10.0 g, 24.6 mmol) in 100 cm³ of dry benzene at 40°C under argon was added solid dicobalt octacarbonyl (3.52 g, 12.3 mmol). The solution immediately turned dark brown with evolution of CO and formation of a black precipitate. After refluxing for 3 h the solution was filtered to remove the black solid which was washed with a further portion of dry benzene. The combined benzene solutions were treated with charcoal, filtered, reduced to half volume and cooled to 5°C . Filtration gave 1.80 g, 20% of **2**. Column chromatography of the remaining solution (silica, benzene eluent) gave a further 0.45 g, 5% of **2** to a total of 25% of **2** as red crystals m.p. 195°C ; m/z (PDMS) 748 (M^+ , 100%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1691 s (C=O); δ_{H} (200 MHz; CDCl_3 ; TMS) 7.95 (2 H, dd), 7.6 (1 H, m) and 7.45 (2 H, m); δ_{C} (200 MHz; CDCl_3 ; TMS) 186.5, 135.3, 134.4, 129.0, 127.9, 126.8 and 111.3 (Found: C, 54.6; H, 2.7; S, 33.9. $\text{C}_{34}\text{H}_{20}\text{O}_4\text{S}_8$ requires: C, 54.54; H, 2.67; S, 34.22%).

Preparation of Charge Transfer Salts.—A solution of **2** (91 mmol) in acetonitrile (30 cm³) was added to a solution of TCNQ (2 mmol) or DDQ (1 mmol) in acetonitrile (30 cm³). The solution was heated to 50°C for 10 min. and allowed to cool whereupon black crystals of the charge-transfer salt separated.

Electro-oxidation of **2** in a 0.1 mol dm⁻³ solution of Bu_4NBF_4 in TCE at a constant current of 2.00 μA gave thick feathery crystals of $\text{2}_3^+(\text{BF}_4)_5$ on the anode after 3 days.

$\text{2}(\text{TCNQ})_2$ (Found: C, 60.1; H, 2.4; N, 9.7. $\text{C}_{58}\text{H}_{28}\text{N}_8\text{O}_4\text{S}_8$ requires C, 60.19; H, 2.44; N, 9.67%).

$\text{2}(\text{DDQ})$ (Found: C, 50.3; H, 1.9; N, 2.5. $\text{C}_{42}\text{H}_{22}\text{N}_2\text{O}_6$ requires C, 51.69; H, 2.05; N, 2.87%).

$\text{2}_3^+(\text{BF}_4)_5$ (Found: C, 45.8; H, 2.3. $\text{C}_{102}\text{H}_{60}\text{B}_5\text{F}_{20}\text{O}_{12}\text{S}_{24}$ requires C, 45.77; H, 2.24%).

X-Ray Crystallography of 2.—TTF(SCOPh)₄ prepared as described above forms red plate-like crystals. Crystal data: $\text{C}_{34}\text{H}_{20}\text{O}_4\text{S}_8$, $M = 749.05$; Monoclinic. Cell dimension at 110 K, $a = 26.459(7)$, $b = 8.297(2)$, $c = 15.978(6)$ Å and $\beta = 105.98(2)^\circ$, $V = 3372(3)$ Å³ from a least-squares refinement of setting angles of 22 reflections ($17.4^\circ < \theta < 21.8^\circ$),

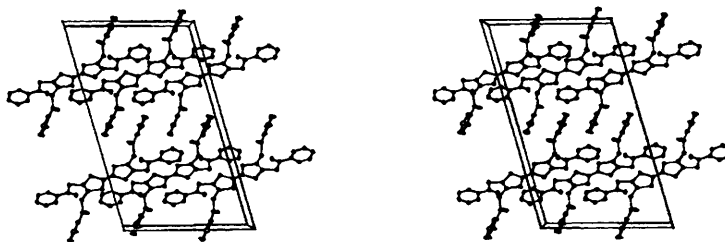


Fig. 2

Table 2 Positional parameters for the non-hydrogen atoms

Atom	x	y	z
C(1)	0.259 3(1)	0.724 7(3)	0.041 3(2)
S(1)	0.302 56(3)	0.560 17(8)	0.070 85(4)
C(2)	0.310 5(1)	0.580 9(3)	0.183 1(2)
S(2)	0.350 67(3)	0.437 44(8)	0.250 28(4)
C(3)	0.413 3(1)	0.536 1(4)	0.272 4(2)
O(1)	0.417 4(1)	0.673 3(3)	0.249 8(2)
C(4)	0.324 2(1)	0.908 2(3)	0.342 6(2)
O(2)	0.337 30(8)	0.981 4(2)	0.288 1(1)
S(3)	0.283 36(3)	0.728 32(8)	0.317 73(4)
C(5)	0.283 5(1)	0.698 0(3)	0.208 8(2)
S(4)	0.241 81(3)	0.816 64(8)	0.128 76(4)
C(31)	0.457 3(1)	0.437 3(4)	0.324 8(2)
C(32)	0.501 7(2)	0.514 8(4)	0.373 0(3)
C(33)	0.543 1(2)	0.429 5(5)	0.425 1(3)
C(34)	0.539 7(1)	0.262 4(5)	0.427 9(2)
C(35)	0.496 1(1)	0.184 0(4)	0.379 1(2)
C(36)	0.454 2(1)	0.270 1(4)	0.327 0(2)
C(41)	0.339 4(1)	0.950 4(3)	0.437 5(2)
C(42)	0.373 0(1)	1.081 3(3)	0.463 0(2)
C(43)	0.389 3(1)	1.123 8(3)	0.550 7(2)
C(44)	0.371 0(1)	1.039 9(3)	0.611 6(2)
C(45)	0.337 1(1)	0.911 6(3)	0.585 3(2)
C(46)	0.321 2(1)	0.866 1(3)	0.498 6(2)

$\lambda(\text{Mo-K}\alpha) = 0.710\ 73\ \text{\AA}$. Space group $C2/c$, $Z = 4$, $D_x = 1.475\ \text{g cm}^{-3}$, $\mu = 5.45\ \text{cm}^{-1}$.

Data Collection and Data Reduction.—CAD4 diffractometer, (Mo-K α) radiation obtained from a graphite monochromator, crystal, size $0.07 \times 0.3 \times 0.4\ \text{mm}$, cooled to $ca. 110 \pm 1\ \text{K}$ with an Enraf-Nonius gas-flow low-temperature device. $\omega/2\theta$ scan mode, $\Delta\omega = 1.5 + 0.35 \tan \theta$, ω -scan speed between 2.3 and 16.5 deg min^{-1} . 6174 ($hk \pm l$) reflections measured $1.0 < \theta / \text{deg} < 30$, 4922 unique, $R_{\text{int}} = 3.3\%$.

Structure Determination and Refinement.—Direct methods, MULTAN80,¹⁰ provided starting coordinates for the four sulfur atoms assuming the space group to be $C2/c$. Refinement by the full matrix least squares method minimizing $\Sigma w \times (|F_o| - |F_c|)^2$, $w^{-1} = (\sigma_{\text{cs}})^2(F) + 4 \times 10^{-4}|F|^2$; $\sigma_{\text{cs}}(F)$ calculated from counting statistics. 2502 reflections with $I > 2\sigma(I)$ were used in the refinement.

The hydrogen atoms were shown clearly in a difference electron density map and they were given a common isotropic temperature factor of $3.0\ \text{\AA}^2$. Final refinements included variation of their positional parameters. Maximum shifts after final cycle 0.34σ , $S = \Sigma w\Delta F^2/(n - m) = 1.11$, $R = 0.040$,

$R_w = 0.045$. Final difference electron density was featureless with peaks in the range -0.35 to $0.45\ \text{e \AA}^{-3}$. The final positional parameters for the non-hydrogen atoms are listed in Table 2.

The crystallographic computations were performed with the SDP-system.¹¹ The atomic scattering factors including corrections for anomalous dispersion were taken from *International Tables for X-Ray Crystallography*¹² and used as contained in the program. Anisotropic displacement parameters, thermal parameters and hydrogen atom coordinates have been deposited with the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC deposition scheme see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

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