Synthesis of Amphiphilic, Mono-functionalised Tetrathiafulvalenes; *X*-Ray Crystal Structure of 4-(6-Bromohexanoyl)tetrathiafulvalene

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Reaction of monolithiated-tetrathiafulvalene (TTF) has been used in the synthesis of amphiphilic TTF derivatives bearing long chains attached through carbon, silicon, sulphur, selenium, and tellurium atoms; the single crystal *X*-ray structure of the title compound is described.

The acidity of the vinylic protons of tetrathiafulvalene (TTF) and trapping of the resultant tetra-anion has been used extensively in the synthesis of substituted TTF derivatives bearing four thioalkyl, selenoalkyl, or telluroalkyl groups, including fused heterocyclic rings.[1] However, the synthetic potential of the TTF mono-anion (**1**) is largely unexplored and only a very limited number of mono-functionalised TTF derivatives have been studied.[2] Species (**1**) is known to disproportionate, even at very low temperatures, to afford the dilithio-derivative; consequently, trapping with electrophiles frequently yields mixtures of unreacted TTF and di- (and multi-) substituted TTFs which can be very difficult to separate from the desired mono-substituted product. To circumvent this problem, Bechgaard and co-workers have used trimethyl-TTF, where, clearly, only the mono-lithiated species can be formed.[3]

For our purposes, the presence of methyl substituents on the ring was undesirable and we now describe the synthesis from mono-lithiated TTF (**1**) of new mono-functionalised TTFs in which one hydrophobic side-chain is linked to the ring through carbon, silicon, sulphur, selenium, or tellurium atoms. The presence of the long chain substituent in these molecules greatly facilitates purification of the mono-substituted products. This work is motivated by current interest in electroactive Langmuir–Blodgett (LB) films of amphiphilic TTF systems.[2d,3,4] We have also determined the single crystal *X*-ray structure of compound (**5**) in order to gain insight into the packing of amphiphilic TTF derivatives in the solid state. This is a topic which is virtually unexplored.

Monolithio-TTF (**1**) was generated in ether at −78 °C using lithium di-isopropylamide (LDA) as base.† Anion (**1**) did not react with n-alkyl halides, but reaction with long chain acyl chlorides yielded acyl-TTF derivatives (**2**)—(**6**) (Scheme 1).‡ Reaction of species (**1**) with hexadecylchloroformate or hexadecylchlorothioformate similarly yielded ester- and thioester-TTF derivatives, (**7**) and (**8**), respectively. This direct, one-pot, method of forming TTF-esters was found to be far more efficient than proceeding *via* esterification of TTF-carboxylic acid (**11**).[2a] While alkylation of (**11**) proceeded cleanly with short-chain alcohols [*e.g.*, to yield ethyl-ester (**12**)], n-hexyl- and n-octyl-esters, (**13**) and (**14**), were obtained in only very low yields by this method. The use of acid chloride (**15**), in place of acid (**11**), also resulted in inefficient formation of esters (**13**) and (**14**).

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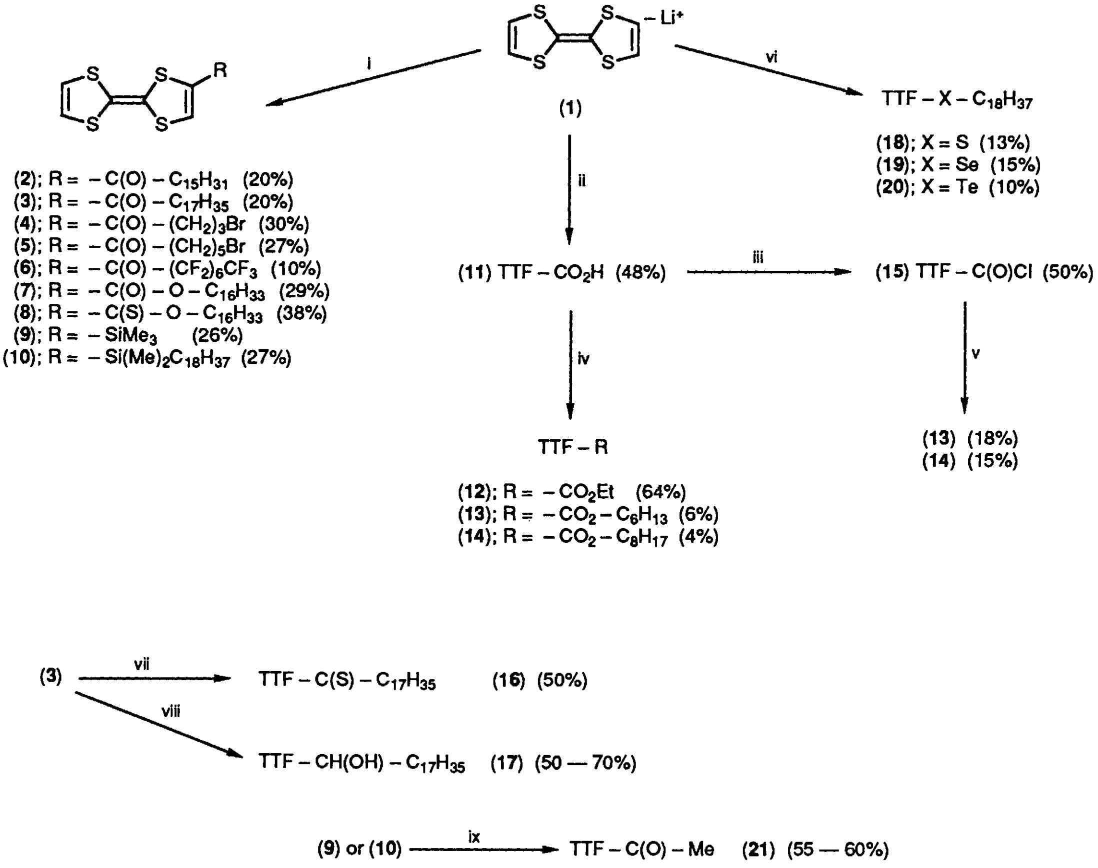
† Typical procedure: to a stirring suspension of TTF (500 mg, 2.4 mmol) in dry ether (40 ml) at −78 °C was added freshly-prepared LDA (1.1 equiv.). After 20 min at −78 °C, when a yellow precipitate of anion (**1**) had formed, the electrophile (3 equiv.) was added. The mixture was stirred at −78 °C for 2 h and then warmed to 20 °C overnight. Aqueous work-up, followed by column chromatography (silica, eluent hexane–toluene mixtures) afforded products (**2**)—(**10**).

‡ Compound (**2**) m.p. 81 °C; (**3**) m.p. 85 °C; (**4**) m.p. 205 °C (decomp.); (**5**) m.p. 114 °C; (**6**) m.p. 155—158 °C; (**7**) m.p. 71—72 °C; (**8**) m.p. 78—80 °C; (**9**) oil; (**10**) m.p. 39—42 °C; (**11**) ref. 2a; (**12**) m.p. 80—82 °C; (**13**) m.p. 61—64 °C; (**14**) m.p. 60—62 °C; (**15**) m.p. 122—125 °C (decomp.); (**16**) m.p. 71—76 °C; (**17**) m.p. 31—33 °C; (**18**) m.p. 55 °C; (**19**) m.p. 52 °C; (**20**) m.p. 50 °C.



Scheme 1. *Reagents and conditions:* i, R–Cl, ether, −78 °C; ii, solid carbon dioxide, ether, −78 °C (ref. 2a); iii, oxalyl chloride, dimethylformamide (catalytic), benzene–acetonitrile, 20 °C; iv, conc. sulphuric acid, ethanol, n-hexanol or n-octanol, reflux; v, appropriate alcohol, dichloromethane–pyridine, 0 → 20 °C; vi, elemental sulphur, selenium, or tellurium, ether, −78 °C, followed by n-octadecyl iodide at −78 °C; vii, Lawesson's reagent, toluene, reflux; viii, lithium aluminium hydride, ether, reflux; or zinc-mercury amalgam, conc. hydrochloric acid–water–toluene, reflux; ix, acetyl chloride, 20 °C.

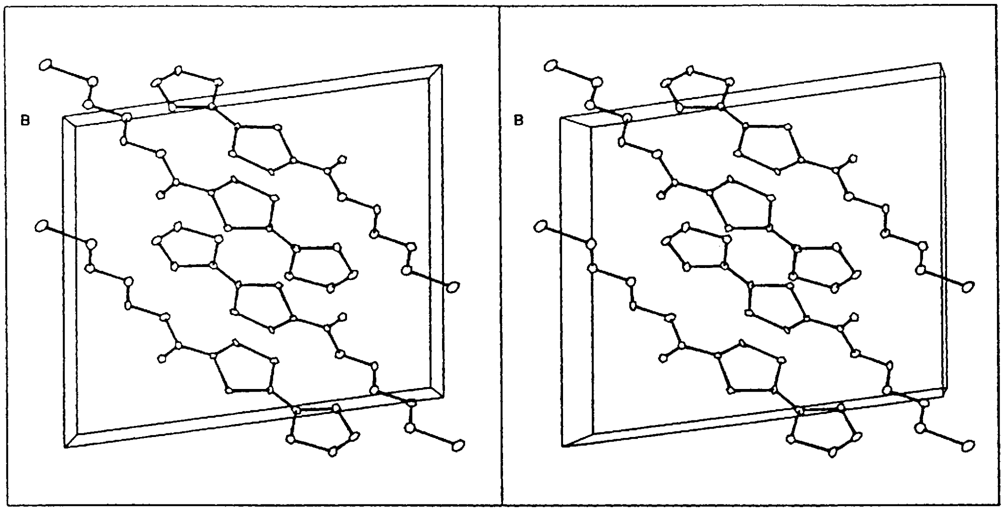


Figure 1. Single crystal *X*-ray structure of compound (**5**): stereo-view along the *b* axis.

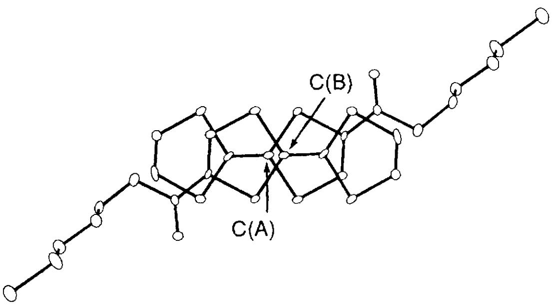


Figure 2. View of the dimerised pair, normal to the least squares molecular plane of the four sulphur atoms of molecule (**5**).

The ketone group in octadecanoyl-TTF (**3**) was readily thionated using Lawesson's reagent in toluene to afford thione (**16**), or reduced to yield the secondary alcohol (**17**) by reaction with either lithium aluminium hydride (70% yield)[4d] or zinc–mercury amalgam (50% yield). However, ketone (**3**) could not be transformed into the corresponding ketal derivative by reaction with 1,2-ethanediol and we have been unable to reduce ketone (**3**) to octadecyl-TTF.

Monolithio-TTF (**1**) underwent an insertion reaction on addition of one equivalent of either elemental sulphur, selenium, or tellurium; subsequent reaction of the chalcogenate anion with octadecyl iodide yielded the first mono(alkylchalcogeno)-TTF derivatives (**18**)—(**20**).§ The attachment of a tellurium-containing substituent to TTF by this straightforward method, albeit in low yield, is particularly noteworthy in view of the considerable problems often encountered in preparing tellurium-containing organic donors.[5]

Anion (**1**) has also been reacted with silicon reagents to yield the first mono-silylated TTF derivatives (**9**) and (**10**). The long-chain substituent on compound (**10**) again makes purification simple. We have established that both compounds (**9**) and (**10**) serve as efficient, shelf-stable, equivalents of TTF mono-anion (**1**). For example, reaction of either (**9**) or (**10**) with acetyl chloride neat at 20 °C, yielded acetyl-TTF (**21**)[2a] in 55—60% isolated yield, and (**9**) was similarly converted into (**4**) (40% yield). Reactions of compounds (**9**) and (**10**) with other electrophiles, to define the scope of this substitution reaction, are under active investigation.

The single crystal *X*-ray structure of compound (**5**) has been obtained¶ and a stereo-view is shown in Figure 1. The TTF units form dimerised pairs within which the molecules are linked by a centre of symmetry, and there is ring-over-bond overlap typical of many TTF systems[8] (Figure 2). The distance between the centres of the planes formed by the four sulphurs of the TTF rings is 3.85 Å. The shortest intermolecular distance is 3.42 Å, between C(A) and C(B) (Figure 2). The structure of 12-(tetrathiafulvalenyl)-11-dodecenoic acid is also composed of TTF dimers; this is the only other TTF derivative bearing one long chain to be characterised by *X*-ray analysis.[2d] It is significant that the carbonyl group of compound (**5**) lies in the same plane as the TTF ring; this configuration maximises the interaction of the carbonyl and TTF π-systems, which is consistent with the marked increase in ionisation potential that occurs when an acyl substituent is attached to the TTF ring. [*Cf.* TTF E_p = +0.34 and +0.78 V; compound (**2**) E_p = +0.52 and +0.90 V *vs.* Ag/AgCl in dichloromethane.]

In conclusion, a wide range of amphiphilic TTF derivatives has been prepared in a straightforward way from monolithio-TTF and the single crystal *X*-ray structure of one of these derivatives has been determined. The formation of high-quality, electroactive LB films of thioester (**8**) and an investigation into the structure of these layers will be described in a forthcoming publication.[9]

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§ On one occasion, when an excess of sulphur was added to anion (**1**), bis(octadecylthio)-TTF was isolated (m.p. 62 °C, 12% yield). We do not know which isomer this is.

¶ *Crystal data* for (**5**): $C_{12}H_{13}BrOS_4$, monoclinic space group $P2_1/c$, a = 14.654(4), b = 8.379(5), c = 12.490(4) Å, β = 97.61°, U = 1520 Å^3, Z = 4, $F(000)$ = 768, Mo-K_α radiation (graphite monochromator), λ = 0.7107 Å, μ = 31.29 cm^{-1}. The structure was solved by direct methods (SHELXS 86)[6] and refined by least squares[7] (anisotropic for non-hydrogens) to R = 0.086, R_w = 0.067 for 1052 observed ($F_o > 2\sigma F_o$) reflections from 2104 unique data collected using a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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