Chem. Mater. **1994,** *6,* 1419–1425 1419

Synthesis of Monofunctionalized Tetrathiafulvalene (TTF) Derivatives by Reactions of Tetrathiafulvalenyllithium with Electrophiles: X-ray Crystal Structures of Four TTF Derivatives Bearing Amide, Thioamide, and Thioester Substituents

Andrei S. Batsanov,[†,§] Martin R. Bryce,[*,†] Graeme Cooke,[†] Ajaib S. Dhindsa,[†,‡]
Julie N. Heaton,[†] Judith A. K. Howard,[*,†] Adrian J. Moore,[†] and Michael C. Petty[‡]

Department of Chemistry, University of Durham, Durham DH1 3LE, UK,
and Molecular Electronics Research Group, School of Engineering and Computing Science,
University of Durham, Durham DH1 3LE, UK.

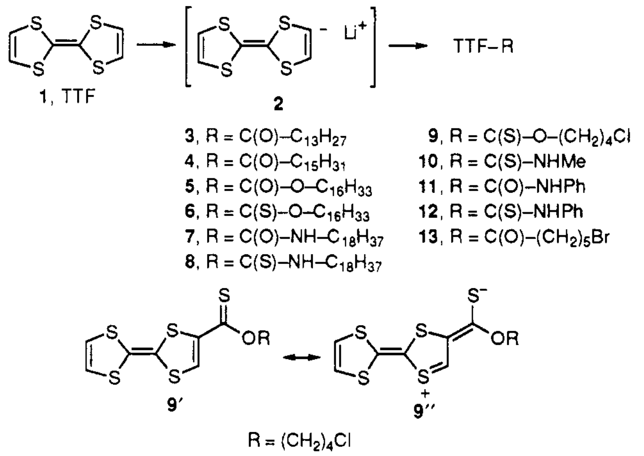
Received January 24, 1994. Revised Manuscript Received April 25, 1994[⊗]

The synthesis is described of a series of monofunctionalized tetrathiafulvalene (TTF) derivatives, by reactions of tetrathiafulvalenyllithium with a range of electrophiles: substituents are thereby attached to the TTF frame by carbonyl, ester, thioester, amide, and thioamide groups. The X-ray crystal structures of four TTF derivatives are described, three of them for the first time. These are 4-[*O*-(4-chlorobutyryl)thiocarboxyl]–TTF (**9**), 4-[*N*-methylthioamido]–TTF (**10**), 4-[*N*-phenylamido]–TTF (**11**), and 4-[*N*-phenylthioamido]–TTF (**12**). The electron-withdrawing ability of these substituents influences the geometry of the TTF ring. Within all four structures the shortest intermolecular S---S and S---C contacts are coplanar with, or slightly inclined to, the TTF planes. The structure of compound **10** provides the first example of κ-phase packing in a neutral TTF donor.

Introduction

Green first demonstrated that tetrathiafulvalene (TTF, **1**, Scheme 1) could be deprotonated by treatment with either butyllithium or lithium diisopropylamide (LDA) in ether at −78 °C and that the resultant monoanion **2** could be intercepted with electrophiles, e.g., CO_2, $ClCO_2Et$, MeC(O)Cl, Me_2SO_4, and $Et_3O^+PF_6^-$, to yield monosubstituted TTF derivatives in moderate yield.[1] The trapping reactions of anion **2** are, however, thwarted by the facile disproportionation of the anion which occurs at temperatures above −78 °C, to yield a complex mixture of unreacted TTF (**1**) and mono-, di-, and multisubstituted products, the purification of which can be very difficult. The synthetic potential of lithiated TTF species **2** has, therefore, been largely overlooked, and, consequently, there are only scattered reports in the literature on the synthesis and properties of monofunctionalized TTF derivatives.[2] These compounds are of considerable interest because (i) in the radical cation oxidation stage TTF forms organic metals,[3] the structural and electronic properties of which may be finely tuned by the presence of substituent groups, and (ii) the well-defined, two-stage, reversible redox behavior of the TTF system offers great scope in the construction of covalently bonded supramolecular electron relays.[4]

Scheme 1



3, R = C(O)–$C_{13}H_{27}$
4, R = C(O)–$C_{15}H_{31}$
5, R = C(O)–O–$C_{16}H_{33}$
6, R = C(S)–O–$C_{16}H_{33}$
7, R = C(O)–NH–$C_{18}H_{37}$
8, R = C(S)–NH–$C_{18}H_{37}$
9, R = C(S)–O–$(CH_2)_4Cl$
10, R = C(S)–NHMe
11, R = C(O)–NHPh
12, R = C(S)–NHPh
13, R = C(O)–$(CH_2)_5Br$

We now describe the synthesis from monolithiated TTF **2** of a wide range of new monofunctionalized TTFs.[5]

[†] Department of Chemistry.

[‡] Molecular Electronics Research Group.

[§] On leave from The Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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Notable features of this work are (i) the range of functional groups that react with TTF anion **2** is extended to include chlorothioformates, isocyanates, and isothiocyanates, yielding TTF thioester, amide, and thioamide derivatives, respectively; (ii) amphiphilic TTF derivatives suitable for the formation of highly conducting Langmuir–Blodgett films have been synthesized; (iii) the single-crystal X-ray structures of four monosubstituted TTF systems are described.

Results and Discussion

Synthesis of Monofunctionalized TTF Derivatives 3–12. We have recently reported the formation of LB films of a range of amphiphilic TTF systems and established that the presence of a carbonyl group, or a thiocarbonyl group, adjacent to the TTF ring results in improved quality of the LB films as-deposited, and increased in-plane conductivity of the films after iodine doping, in comparison with other functionalized TTF systems.[6] The present paper reports, in detail, the synthesis of amphiphilic TTF systems **3–8**, along with the related compounds **9–12** which were prepared analogously. TTF systems bearing side chains attached to the ring by thioester, amide, and thioamide functionality have not been synthesized previously.

Tetrathiafulvalenyllithium (**2**) was generated from TTF (**1**) using lithium diisopropylamide in dry ether at −78 °C, under carefully controlled conditions, by a modification of the literature route.[1] Amphiphilic TTF derivatives **3–8** were prepared by reactions of anion **2** as follows. Addition of tetradecanoyl chloride and hexadecanoyl chloride to an ethereal slurry of anion **2** afforded the long-chain acyl–TTF derivatives **3** and **4**, respectively, in 20–30% yields. Analogous reactions using hexadecylchloroformate and hexadecylchlorothioformate gave the ester and thioester derivatives **5** and **6**, respectively, in 29–38% yields. Reaction of anion **2** with octadecylisocyanate and octadecylisothiocyanate gave TTF–amide and –thioamide derivatives **7** and **8**, respectively, in 30–42% yields. Purification of the amphiphilic products **3–8** frequently required repeated column and/or preparative thin-layer chromatography followed by recrystallization. This inevitably resulted in some loss of product: therefore, the yields of purified products, quoted above, are generally lower than those of the analogous short-chain derivatives **9–12** described below, where purification was readily achieved by single-column chromatography followed by recrystallization.

Reaction of anion **2** with (4-chlorobutyryl)chlorothioformate, methylisothiocyanate, phenylisocyanate, and phenylisothiocyanate yielded compounds **9–12**, respectively. The formation of products **9–12** is directly analogous to the reactions of the long-chain reagents described above.

X-ray Crystal Structures of Compounds 9–12. Single crystals of compounds **9–12** were obtained (as a 1:1 toluene solvate for compound **11**), and their structures have been solved by X-ray diffraction. Although X-ray diffraction studies of TTF derivatives and derived complexes and salts are numerous,[3] the information on nonsymmetrically substituted, and especially on monosubstituted TTF derivatives, is almost nonexistent,[2b,c,g,5,7] while such compounds can provide novel types of crystal packing modes and intramolecular electronic effects.

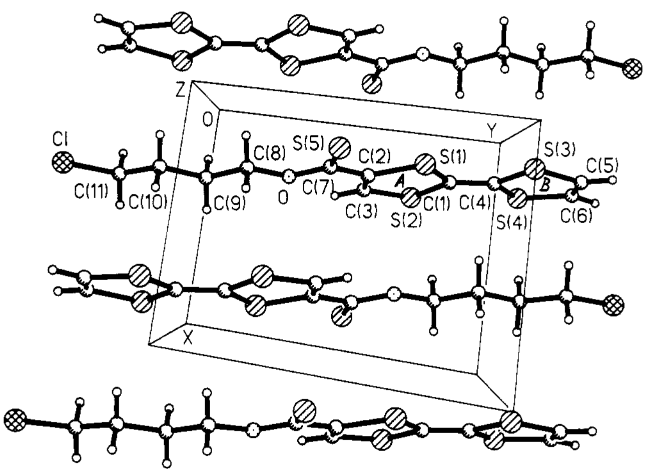

Figure 1. Crystal packing of **9** (projection down *y* axis).

Table 1. Selected Bond Distances (Å) and Angles (deg) in Compounds 9–12

	9	10	11	12
S(1)–C(1)	1.765(4)	1.757(4)	1.74(2)	1.79(4)
S(1)–C(2)	1.757(4)	1.762(4)	1.75(2)	1.79(3)
S(2)–C(1)	1.757(5)	1.753(4)	1.78(1)	1.77(3)
S(2)–C(3)	1.714(4)	1.719(4)	1.72(2)	1.68(4)
C(2)–C(3)	1.334(6)	1.344(5)	1.33(2)	1.37(5)
C(1)–C(4)	1.345(5)	1.337(6)	1.35(2)	1.26(5)
S(3)–C(4)	1.753(5)	1.758(4)	1.79(1)	1.77(4)
S(3)–C(5)	1.728(4)	1.737(5)	1.72(2)	1.73(4)
S(4)–C(4)	1.751(4)	1.753(4)	1.74(2)	1.79(4)
S(4)–C(6)	1.723(5)	1.736(5)	1.74(2)	1.76(4)
C(5)–C(6)	1.323(8)	1.312(7)	1.31(3)	1.35(5)
C(2)–C(7)	1.448(5)	1.454(5)	1.44(2)	1.41(5)
C(7)–S(5)	1.6335)	1.667(4)		1.70(4)
C(7)–O	1.334(5)		1.24(2)	
C(7)–N		1.327(5)	1.36(2)	1.36(4)
S(1)–C(2)–C(3)	116.8(2)	115.9(3)	116(1)	113(2)
S(2)–C(3)–C(2)	119.2(3)	118.7(3)	120(1)	122(2)
S(3)–C(5)–C(6)	117.8(4)	117.0(4)	119(1)	118(3)
S(4)–C(6)–C(5)	118.2(3)	119.0(4)	117(1)	117(3)

In molecule **9** (Figure 1) all non-hydrogen atoms are coplanar to within ±0.12 Å. Rings A and B exhibit only slight envelope-like folding (by 3.1 and 4.9°, respectively) along S···S lines, and the side chain adopts an entirely *trans*-planar conformation, with no torsion angle deviating from 180° by more than 4°. The thioester group of compound **9** is essentially coplanar with ring A of the TTF system and withdraws electrons from it, as indicated by the narrowing of the S(1)–C(2)–C(3) angle, and by shortening of the S(2)–C(3) bond (see Table 1) which can be best described by the resonance forms **9′** and **9″**. Inversion-related molecules form an infinite stack along the *x* direction in head-to-tail fashion with interplanar separations of ca. 3.7 Å. The intrastack overlap is not between TTF units but rather between ring A of TTF and the thioester group of an adjacent molecule, i.e., between

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(5) The synthesis and structure of compound **10** have been reported in a preliminary communication: Batsanov, A. S.; Bryce, M. R.; Cooke, G.; Heaton, J. N.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1701.

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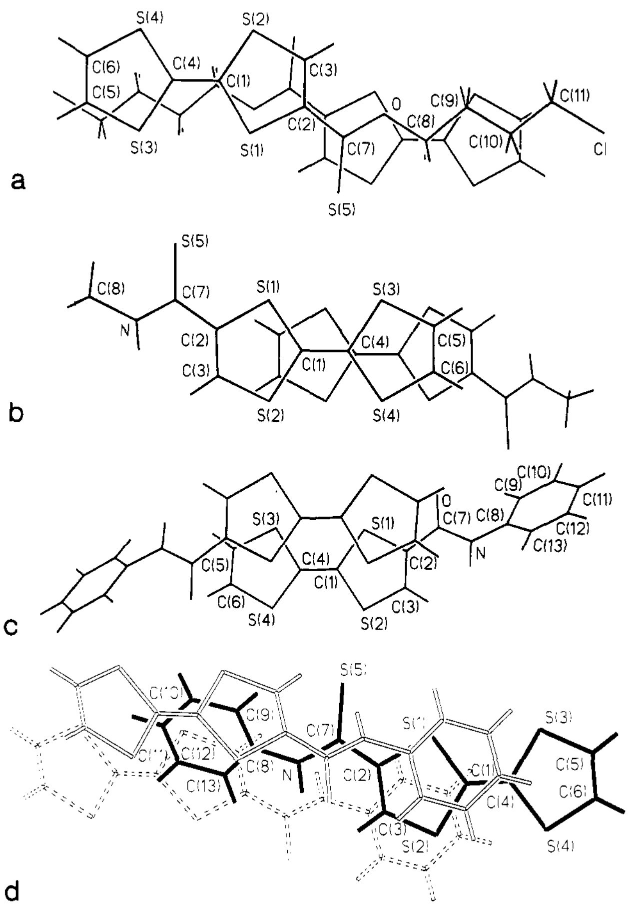

Figure 2. Molecular overlap in the structures of **9** (a), **10** (b), **11**·C_6H_5Me (c), and **12** (d); projections are onto the central C_2S_4 planes of the TTF moieties.

the most positively and negatively charged parts of the molecule, this being the most favourable orientation for charge transfer within the stack (Figure 2a). Thus structure **9** differs strikingly from compound **13** where the molecule is not planar but instead comprises two planar moieties, viz., TTF–$COCH_2$– and –$(CH_2)_4Br$, which are inclined by 73° to each other; molecules of **13** do not form stacks; instead they form dimers with TTF moieties in close contact.[2c]

It is possible that intermolecular charge-transfer interactions, similar to those observed in the crystal structure of compound **9**, occur within Langmuir–Blodgett films of the long-chain thioester system **6**, thereby increasing the ordering of the the TTF head groups. This could account for the significantly increased conductivity of the oxidized LB films of compound **6**, compared with values for acyl and ester derivatives **4** and **5**.[6]

In the structure of thioamide **10**, inversion-related molecules form a dimer (Figure 2) with ring-over-bond overlap of the TTF moieties (Figure 2b). The interplanar separation between their central C_2S_4 moieties is ca. 3.40 Å, while the rest of the molecule bends outward, with rings A and B folding along S···S lines by 22.8° and 13.9°, respectively (Figure 3). Dimers are packed in κ-fashion,[8] i.e., with the mean planes of contacting molecules being almost mutually perpendicular and their principle axes essentially parallel (Figure 4). This structure provides what we believe to be the first example of a κ-phase structure in a neutral TTF donor.

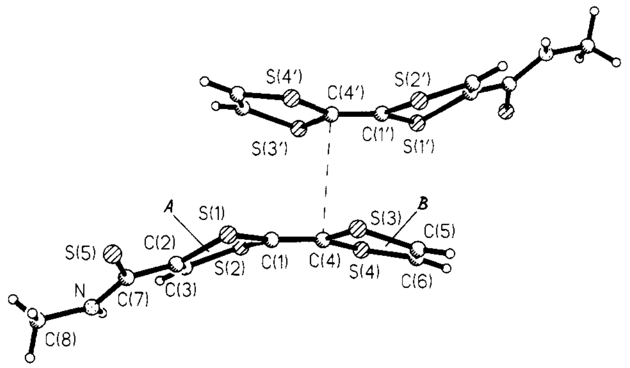

Figure 3. Molecular dimer in the structure of **10** (primed atoms are inversion related).

In molecule **11**, the TTF moiety is more planar than in molecule **10**, with rings A and B folding by only 9.3° and 1.2°, respectively. The inversion-related molecules of **11** form dimers with ring-over-ring overlap (together with a lateral shift of ca. 1.7 Å) of the TTF ring systems and interplanar separation of 3.75 Å (Figures 2c and 5a). These dimers are arranged alongside each other in the form of steps and are interleaved with solvent toluene molecules. Thus in **11**, like in **10**, no infinite molecular stacks exist. The N–H(1)---O hydrogen bonds in the structure of **11** are weak[9a] (N---O distance 3.44 Å).

The molecular structure of **12** is similar to that of **11** (Figure 5), although their crystal structures are very different, the former compound containing no solvent of crystallization. In **12**, heterocycles A and B are folded by 6° and 12°, respectively, and significant twist around the C(2)–C(7), C(7)–N, and N–C(8) bonds (by 11°, 8°, and 41°, respectively, versus 21°, 2°, and 37° in **11**) prevents π-electron conjugation between the phenyl and the TTF groups. Molecules of **12** stack in an unusual way along the crystallographic *y* direction (Figure 6). Adjacent molecules in the stack are related via the $21_1[{}^1/_2,y,{}^1/_2]$ screw axis, and they overlap in a head-to-tail (i.e., TTF-over-phenyl) fashion (Figure 2d). The stack can be regarded as a pair of substacks, each consisting of interleaved phenyl and TTF units, linked through the thioamido bridges. Within each of the substacks, contacting phenyl rings and A rings of TTF are parallel to within 6° and inclined to the other substack by ca. 36°. There are two symmetrically unrelated but essentially equal sets of interplanar separations of ca. 3.5 Å. Thioamido groups form an infinite chain of weak[9b] N–H---S(5) hydrogen bonds [N---S(5) 3.59 Å, H---S(5) 2.9 Å] within the stack.

The thioamido groups in both compounds **10** and **12** and the amido group in compound **11** are conjugated with ring A of the TTF system (the twist around the C(2)–C(7) bond being 12°, 21°, and 11°, respectively) and their electron-withdrawing ability influences the ring geometry much in the same way as in compound **9** (see **9′** and **9″**).

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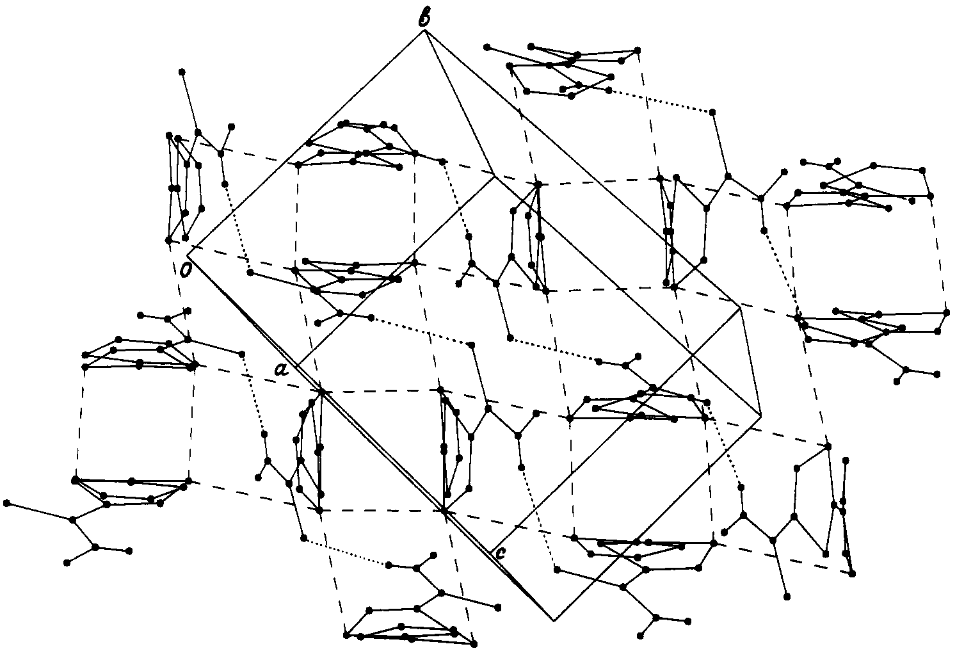

Figure 4. Crystal packing of **10**. Projection on (−201) plane, showing hydrogen bonds (dots) and shortest intermolecular contacts (dashes). Hydrogen atoms, except amide N–H, are omitted.

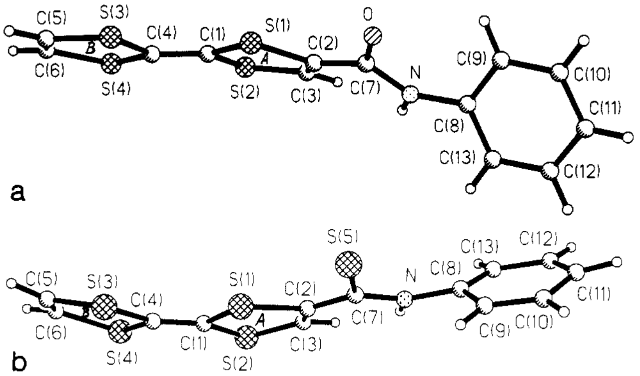

Figure 5. Molecular structures of **11** in a crystal of **11**·C_6H_5Me (a) and **12** (b).

These crystallographic results support our previous suggestion[6c] that resonance canonical forms of the type **9″** should contribute to the overall electronic structure of TTF derivatives of general formulas TTF–C(O)–R and TTF–C(S)–R, thereby serving to increase the polar nature of the TTF unit. Bond distances in **12** will not be discussed due to poor data from a twinned crystal.

It is noteworthy that in all four structures **9**–**12**, the shortest S---S contacts are those not within stacks or dimers but rather between molecules contacting edge-to-edge. Such packing is not uncommon for TTF derivatives, but the nature of S---S interactions remains a matter of controversy.[9a] The electronegativities of carbon and sulfur being close,[10] the net charge on the latter atoms in neutral TTF is negligible; the HOMOs (i.e., the lone pairs involved in π-conjugation) are almost perpendicular to the CSC plane, and σ^* LUMOs lie on the prolongations of these bonds. Thus in intermolecular secondary bonds sulfur can participate as either a nucleophile or an electrophile, depending upon the angle (θ) between the direction of the contact and the normal to the CSC plane (Figure 7). It is known[11] that intermolecular contacts of dicoordinate sulfur with nucleophilic atoms (F, Cl, Br, N, O, and I) usually have $\theta > 60°$, while those with electrophilic atoms (C, H, and I) including sulfur–metal donor–acceptor bonds[11b] have $\theta < 40°$. Therefore, S---S contacts with θ_1 = ca. 0° and θ_2 = ca. 90° (Figure 6a) may be regarded as weak donor–acceptor bonds. Row and Parthasarathy, in a study on structural correlations, concluded that dicoordinate sulfur atoms really prefer such kinds of contacts, without providing any quantitative estimation,[12] although the scattergram they present shows a fairly random distribution of θ_1 versus θ_2 (with a general tendency toward higher θ) and ca. 23% of S---S′ contacts have $\theta_1 = \theta_2$ and a few have θ_1 ca. = θ_2 without symmetrical restrictions. Furthermore, in some structures, the contacts of the latter type, with parallel CSC planes (Figure 6b) are responsible for electrical conduction in TTF-derived salts.[13] On the other hand, a purely physical interpretation of anisotropy of the intermolecular contacts, treating atoms as ellipsoids[14] or spheres excentric from the positions of atomic nuclei (the latter model first proposed by Pauling[10] and recently revived[15]) hitherto applied to monocoordinate atoms (including =S) may also prove valid for dicoordinate sulfur. Further study of this matter is necessary.

In the structures of compounds **9** and **11**, where all the TTF mean planes are crystallographically parallel, only the contacts of type *b* are possible. In the structure of **9** the inversionally related molecules form contacts S(1)---S(3) and S(1)---S(1) of 3.71 and 3.70 Å, respectively (with $\theta_1 = \theta_2$ = ca. 74°) which are shorter than the closest contact within the stack, S(4)---S(5) 3.83 Å. However, these interactions are isolated, the nearest contacts on the opposite side of the molecule (with another inversion partner) being much longer, viz., S(2)---S(2) 3.97 Å and

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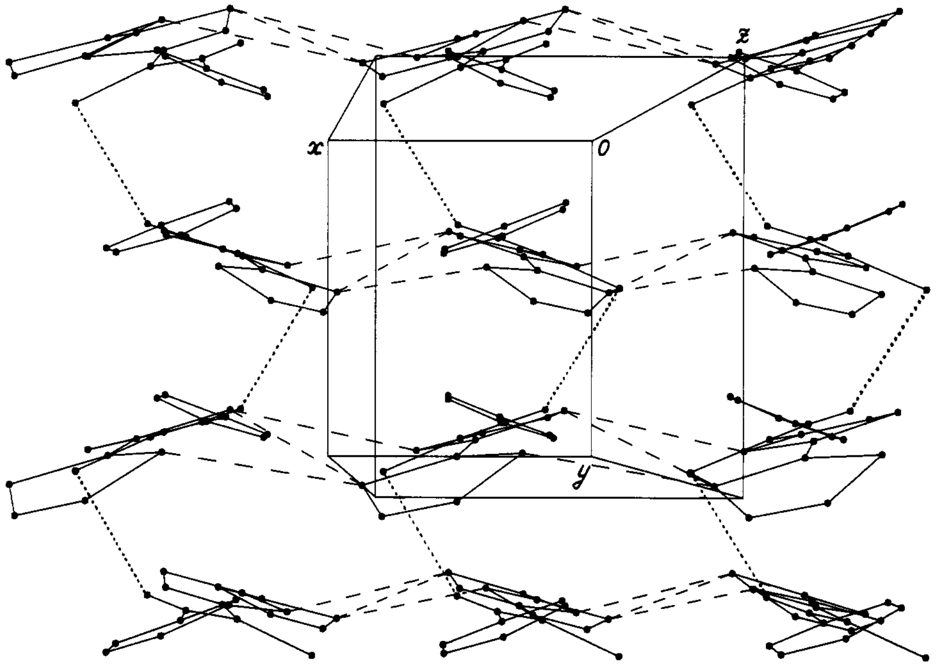

Figure 6. Crystal packing of **12**. Projection showing shortest S- - -S contacts (dashes) and hydrogen bonds (dots). Non-amide hydrogen atoms are omitted.

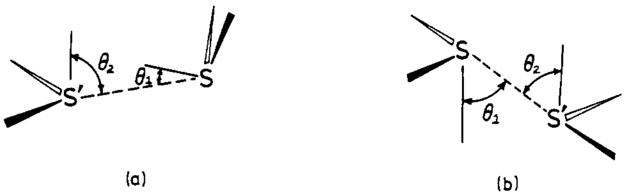

Figure 7. Types of S- - -S contacts (a) θ_1 = ca. 0° and θ_2 = ca. 90°; (b) $\theta_1 = \theta_2$, CSC planes parallel.

S(2)---S(4) 3.99 Å, with $\theta_1 = \theta_2$ = 35.5° and 37.6°, respectively. In the structure of **11** two inversionally related molecules form two, equivalent, S(1)---S(3) contacts and one S(3)---S(3) contact of 3.51 and 3.61 Å, respectively, with θ = 74–83°. The opposite edge of the TTF unit forms longer S---S contacts to *a* (3.80–3.89 Å) with θ = 25–40° to a translationally equivalent molecule. The shortest contact within the dimer is S(1)---S(3) 3.94 Å. Thus sheets of TTF units are not formed by either compound **9** or **11**. In the crystal of **12** such sheets are formed by the molecules symmetrically related via translation *x*, each TTF unit participating in three short S---S contacts on either side, all of approximately equal length (3.50–3.59 Å). Here, again, all S---S contacts are of type *b*, with similar, although symmetry-independent, θ_1 and θ_2 angles (54–61° and 65–74°, respectively).

On the contrary, the crystal packing of compound **10** exhibits short contacts of type *a*, namely, S(1)---S(4) = 3.85 Å and S(3)---S(2) = 3.57 Å, between the molecules related via the 2_1 axis $[{}^1/_2, y, {}^3/_4]$ and S(2)---S(3) = 3.65 Å, between those related via the $(x, {}^1/_4, z)$ glide plane (cf. the shortest contact within the dimer is S(2)---S(3′) = 3.66 Å). Within each contact, the CSC planes are nearly perpendicular, with dihedral angles of 104° for the S(1)---S(4) contact, and 94° for both the S(3)---S(2) and S(2)---S(3) contacts. Apparently, κ-packing of TTF units is especially favorable for the formation of type *a* contacts, which demand either crystal symmetry higher than triclinic and/or the presence of more than one independent TTF unit in the crystal. The shortest intermolecular S---S distances in structure **10** are essentially equal to double the isotropic radius of sulfur (1.80 Å)[16] and also to the sum of the short (along the bond direction) and long (perpendicular to the bond) axes in the ellipsoidal model (1.60 and 2.03 Å, respectively).[19] The S---S interactions form a two-dimensional network, linking the dimers into a layer parallel to the (100) plane (Figure 4) while the rather weak N–H---S(5) hydrogen bonds (N---S distance 3.56 Å, H---S distance 2.9 (Å) link molecules within the layer into an infinite chain parallel to the *z* axis.

It is worth commenting at this point that the potential role that hydrogen bonding might play in regulating crystal packing motifs in organic conductors is virtually unexplored, although H-bonding is widely recognized as an important design feature for crystal engineering in other solid state systems.[9] Hydrogen bonding involving $(\mathrm{O{-}H})_{\mathrm{water}}$---$\mathrm{X}_{\mathrm{anion}}$ has been observed in a few conducting and superconducting salts of TTF derivatives, e.g. (BEDT-TTF)$_3$Cl$_2$·2H$_2$O,[17] (BEDT-TTF)$_3$CuCl$_4$·H$_2$O[18] and (BEDO-TTF)$_2$ReO$_4$·H$_2$O,[19] and $(\mathrm{O{-}H})_{\mathrm{donor}}$---$\mathrm{X}_{\mathrm{anion}}$ interactions are present in κ-(EDT-TTFCH$_2$OH)$_2$X salts (X = ClO$_4$ and ReO$_4$).[20] It is also considered that $(\mathrm{C{-}H})_{\mathrm{donor}}$---anion interactions play an important part in determining the structure of BEDT-TTF cation radical salts.[21] Compound **10** provides the first example of donor---donor H-bonding

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Table 2. Crystal Data and X-ray Experimental Details for Compounds 9–12

	9	10	11	12
formula	$C_{11}H_{11}ClOS_5$	$C_8H_7NS_5$	$C_{13}H_9NOS_4{\cdot}C_7H_8$	$C_{13}H_9NS_5$
M	354.9	277.4	415.6	339.5
crystal system	triclinic	monoclinic	triclinic	monoclinic
a/Å	7.530(6)	11.720(3)	5.577(1)	6.093(2)
b/Å	10.033(6)	8.474(2)	13.233(2)	7.322(3)
c/Å	11.526(10)	11.231(2)	13.490(2)	15.524(7)
α/deg	65.51(8)	90	89.94(2)	90
β/deg	71.25(6)	92.88(2)	80.87(2)	97.12(3)
γ/deg	81.47(6)	90	85.24(2)	90
U/Å^3	750.2(9)	1114.0(4)	979.5(3)	687.2(5)
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 3)
Z	2	4	2	2
D_c/g cm^{-3}	1.57	1.65	1.41	1.64
F(000)	364	568	432	348
μ(Mo Kα)/cm^{-1}	9.3	10.0	4.9	8.3
color	black	dark red	red	black
crystal size/mm	0.12 × 0.25 × 0.69	0.01 × 0.24 × 0.50	0.05 × 0.15 × 0.55	0.03 × 0.20 × 0.50
cell refinement				
no. of reflections	16	23	24	20
2θ range/deg	25–27	9.5–22.6	20.2–27.8	9.5–22.5
diffractometer	Siemens R3m/V	Siemens R3m/V	Rigaku AFC6S	Rigaku AFC6S
scan mode	Wyckoff (limited ω)	$\theta/2\theta$	$\theta/2\theta$	ω
max 2θ/deg	50	53	50	50
no. of independent reflns	2027	2084	2028	1312
used reflns, $\lvert F\rvert > 4\sigma(F)$	1659	1264	1444	586
absorption correction	semiempirical[a]	numerical[b]	none	none
max	0.9132	0.9854		
min	0.7942	0.7902		
no. of variables	163	131	235	76
weight scheme ($w^{-1} = \sigma^2(R) + gF^2$, g)	0.0004	0.0002	unit weights	0.001
goodness-of-fit	1.76	1.19	2.78	2.34
R	0.035	0.033	0.096	0.125
$wR = R'$	0.049	0.034	0.119	0.133
max residual peak/e Å^{-3}	0.25	0.30	0.62	2.3[c]
max residual hole/e Å^{-3}	−0.21	−0.25	−0.79	−1.9[c]

[a] Based on 396 ψ-scans of 11 reflections. [b] Six faces were indexed. [c] In the vicinity of S atoms, refined in isotropic approximation.

in a TTF system to be revealed by X-ray analysis, and it is a tantalizing prospect that this may emerge as an important structural feature in the design of new κ-phase systems.

Conclusions

Reactions of tetrathiafulvalenyllithium (**2**) with electrophiles provide entry into new TTF derivatives bearing functionalized substituents. The accessibility of these materials raises new prospects for two burgeoning themes in the study of TTF materials, viz., conducting Langmuir–Blodgett films, and hydrogen-bonded interactions in solid-state structures. The X-ray crystal structures of compounds **9–12** have been obtained, and within all four structures the shortest intermolecular contacts are coplanar with, or slightly inclined to, the TTF planes. The discovery of a κ-phase dimer structure for compound **10** will add impetus to the study of new functionalized TTF derivatives and their derived cation radical salts.

Experimental Section

Synthesis. *Tetrathiafulvalenyllithium* (**2**) was prepared by a modification of the literature route,[1b] as follows: A solution of TTF (**1**, 0.25 g, 1.23 mmol) in dry ether (30 mL) was cooled, with stirring, to −78 °C. Freshly prepared LDA [from BuLi (1.6 M, 0.85 mL, 1.35 mmol) and diisopropylamine (0.2 mL, 1.35 mmol)] in dry ether (10 mL) was added dropwise over 1 min. The reaction mixture was maintained for 1 h at −78 °C, by which time a thick yellow precipitate of compound **2** had formed. The electrophile was then added dropwise over 1 min as a solution in ether or neat for *N*-phenylisothiocyanate.

General Procedure for Compounds 3–12. The electrophile (1.35 mmol, 1.1 equiv, relative to TTF (**1**)) was added to a stirring slurry of anion **2** and the reaction mixture maintained at −78 °C for 5 h; the temperature was then raised to 20 °C and stirring was continued overnight. The mixture was then poured into distilled water (100 mL); the aqueous layer was separated and extracted with dichloromethane. The ether and dichloromethane layers were combined, dried ($MgSO_4$), and evaporated, and the crude product was chromatographed. A silica column (eluent cyclohexane/toluene, 3:1 v/v) was used for compounds **3–9** and **11**, whereas a neutral alumina column (eluent toluene) was used for **10** and **12**. On some occasions repeated column chromatography was needed to obtain a pure product. There was obtained the following:

4-Tetradecanoyltetrathiafulvalene (**3**) from reaction of anion **2** and tetradecanoyl chloride, a red solid (130 mg, 25%); mp 80–81 °C. (Found: C, 57.8; H, 7.3. $C_{20}H_{30}OS_4$ requires: C, 58.0; H, 7.3%); m/z (EI) 414 (M^+); ν_{max}/cm^{-1} 1650 (C=O).

4-Hexadecanoyltetrathiafulvalene (**4**) from reaction of anion **2** and hexadecanoyl chloride, a red solid (110 mg, 20%); mp 81 °C (from ether/methanol). (Found: C, 59.4; H, 7.9. $C_{22}H_{34}OS_4$ requires: C, 59.7; H, 7.7%); m/z (EI) 442 (M^+); ν_{max}/cm^{-1} 1600 (C=O).

4-(Carbohexadecyloxy)tetrathiafulvalene (**5**) from reaction of anion **2** and hexadecylchloroformate, an orange solid (170 mg, 29%); mp 71–72 °C (from ether/methanol). (Found: C, 58.1; H, 7.3; S, 27.0. $C_{23}H_{36}O_2S_4$ requires: C, 58.4; H, 7.7; S, 27.1%); m/z (EI) 472 (M^+); ν_{max}/cm^{-1} 1720 (C=O).

4-(O-Hexadecylthiocarboxy)tetrathiafulvalene (**6**) from reaction of anion **2** and *O*-hexadecylchlorothioformate, a dark purple/black solid (228 mg, 38%); mp 78–80 °C. (Found: C, 56.5; H, 7.4; S, 32.8. $C_{23}H_{36}OS_5$ requires: C, 56.5; H, 7.4; S, 32.8%); m/z (EI) 488 (M^+); ν_{max}/cm^{-1} 1235 (C=S).

4-(N-Octadecylamido)tetrathifulvalene (**7**) from reaction of anion **2** and octadecylisocyanate, an orange solid (185 mg, 30%), mp 96–99 °C. (Found: C, 60.4; H, 8.4; N, 3.0. $C_{25}H_{41}NOS_4$ requires: C, 60.1; H, 8.2; N, 2.8%); m/z (DCI) 500 (M^+ + 1); ν_{max}/cm^{-1} (Nujol) 3320 (NH) and 1620 (C=O).

4-(N-Octadecylthioamido)tetrathiafulvalene (**8**) from reaction of anion **2** and octadecylisothiocyanate, a purple solid (260 mg, 42%), mp 107–111 °C. (Found: C, 58.2; H, 8.1; N, 2.6. $C_{25}H_{41}NS_5$ requires: C, 58.3; H, 8.0; N, 2.7%); *m/z* (EI) 515 (M^+); ν_{max}/cm^{-1} 3300 (NH).

4-[O-(4-Chlorobutyl)thiocarboxy]tetrathiafulvalene (**9**) from reaction of anion **2** and 4-(chlorobutyl)chlorothioformate, a purple solid (250 mg, 58%); mp 95–97 °C. (Found: C, 37.2; H, 3.2. $C_{11}H_{11}ClOS_5$ requires: C, 37.1; H, 3.1%); *m/z* (EI) 356 (M^+); δ_H ($CDCl_3$) 7.32 (1H, s), 6.29 (2H, s), 4.43 (2H, t), 3.53 (2H, t), 1.86 (2H, m), and 0.86 (2H, m); ν_{max}/cm^{-1} 1230 (C=S).

4-(N-Methylthioamido)tetrathiafulvalene (**10**) from reaction of anion **2** and methylisothiocyanate, a purple solid (200 mg, 58%); mp 188–190 °C. (Found: C, 35.0; H, 2.7; N, 4.9. $C_8H_7NS_5$ requires: C, 34.7; H, 2.5; N, 5.1%); *m/z* (DC1) 278 (M^+ + 1); ν_{max}/cm^{-1} (Nujol) 3300 (NH); δ_H [$(CD_3)_2C(O)$] 7.23 (1H, s), 6.63 (2H, s) and 3.13 (3H, d). Dark purple plates were obtained from dichloromethane/hexane.

4-(N-Phenylamido)tetrathiafulvalene (**11**) from reaction of anion **2** and phenylisocyanate, a red solid (200 mg, 50%); mp 147–150 °C. (Found: C, 48.3; H, 2.8; N, 4.2. $C_{13}H_9NOS_4$ requires: C, 48.3; H, 2.8; N, 4.3%); *m/z* (DC1) 324 (M^+ + 1); ν_{max}/cm^{-1} (Nujol) 3330 (NH) and 1720 (C=O); δ_H ($CDCl_3$) 7.41 (5H, m), 7.21 (1H, s), and 6.30 (1H, s). Red crystals of a 1:1 toluene solvate were obtained from toluene.

4-(N-Phenylthioamido)tetrathiafulvalene (**12**) from reaction of anion **2** and phenylisothiocyanate, brown crystals 130 mg, 30%; mp 169–172 °C from dichloromethane. (Found: C, 46.1; H, 2.7; N, 4.2. $C_{12}H_9NS_5$ requires: C, 46.0; H, 2.7; N, 4.1%); *m/z* (CI) 339 (M^+ + 1); δ_H ($CDCl_3$) 8.6 (1H, s), 7.4 (5H, m), 7.2 (1H, s), and 6.3 (2H, s).

X-ray Diffraction Analysis of Compounds 9–12. X-ray diffraction experiments were performed with four-circle computer-controlled diffractometer, at 293 K (**9**–**11**) and 150 K (**12**), using graphite monochromated Mo $K\alpha$ radiation. The crystals of **11**, being a 1:1 toluene solvate, decayed throughout the experiment due to loss of solvent; three check reflections lost 60% of their intensities in 70 h. The structures of compounds **9**–**12** were solved by direct methods and refined by full-matrix least-squares analysis using SHELXTPLUS programs. In compounds **9**–**11** all non-hydrogen atoms were refined with anisotropic displacement parameters, whereas for **12** in isotropic approximation. All hydrogen atoms were included in the refinement in riding model (except the amide hydrogen in compound **11**, refined in isotropic approximation). The absolute structure of **12** was not determined. Crystal data and experimental parameters are listed in Table 2; full lists of atomic coordinates, thermal parameters, and bond lengths and angles have been submitted as supplementary data.

Acknowledgment. We thank SERC for funding this work and the Royal Society and The Nuffield Foundation for financial support to A.S.B. and M.R.B., respectively.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, and bond lengths and angles (31 pages); tables of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.