JOURNAL OF
Materials
CHEMISTRY

(*N*-Methylthiocarbamoyl)tetrathiafulvalene derivatives and their radical cations: synthetic and X-ray structural studies

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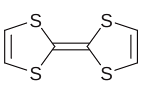
Lithiation of 4,5-bis(methylsulfanyl)-TTF **9**, 4,5-(ethylenedisulfanyl)-TTF **10**, 4,5-dimethyl-TTF **11** and 4,5,5′-trimethyl-TTF **12** (TTF = tetrathiafulvalene) followed by reaction with methyl isothiocyanate affords the corresponding (*N*-methylthiocarbamoyl)-TTF derivatives **14**–**17**, respectively, in 54–70% yields. These new TTF derivatives display a broad intramolecular charge-transfer band in their UV–VIS spectra arising from conjugation between the donor TTF ring and the acceptor *N*-methylthiocarbamoyl moiety. Steric hindrance between the adjacent *N*-methylthiocarbamoyl and methyl substituents in **17** causes a marked hyposchromic shift in this band (λ_{max} 395 nm) compared to compounds **14**–**16** (λ_{max} 435–467 nm). Consistent with the electron-withdrawing properties of the *N*-methylthiocarbamoyl substituent, its attachment to the TTF ring raises slightly the oxidation potential of the system. Charge transfer complexes of these donors and (*N*-methylthiocarbamoyl)-TTF **2** with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and salts with bromide anions are reported, some of which have high room temperature conductivity values. The X-ray crystal structures are presented for **16**, **17** and the salts **2**·Br, **14**·TCNQ and $(\mathbf{17})_2$·**20**. The structure of **16** comprises orthogonal dimers (*kappa* packing) while in the structure of **17** individual molecules are orthogonal to each other. There is weak intermolecular hydrogen bonding in both **16** and **17**. In the structure of **2**·Br, the radical cations $\mathbf{2}^{+\cdot}$ are almost planar and they form an infinite stair-like stack of dimers, with bromide anions situated between the stacks, and linked with the cation by a strong N–H···Br bond. The structure of **14**·TCNQ comprises mixed ···DDAADD··· stacks; the *N*-methylthiocarbamoyl group engages in an interstack N–H···N bond with a TCNQ anion. Analysis of the bond lengths in the structure suggests that there is partial charge transfer from **14** to TCNQ. In the structure of $(\mathbf{17})_2$·**20** molecules form mixed ···DDADDA··· stacks and analysis of bond lengths suggests that there is only a small degree of charge transfer from donor to acceptor. The geometries of compounds **2**, **14**, **16**, **17** were optimised using the PM3 semi-empirical method and the results compare favourably with the X-ray structural data.

It is well established that the structural features of tetrathiafulvalene (TTF, **1**) derivatives in the solid state are of crucial importance in obtaining high electrical conductivity (and superconductivity) from their charge-transfer complexes and radical ion salts. The control of molecular stacking by means of chemical modification of the TTF molecule remains a major challenge. In this context, the design of TTF-based donor molecules bearing substituents capable of effective intermolecular interactions, which may exert an orientating effect on the constituent molecules, is an emerging area. An increase in the dimensionality of the conduction process (most commonly achieved by close interstack chalcogen···chalcogen interactions) is known to stabilise the metallic state to low temperature, and in some cases gives rise to superconductivity.[1] A true one-dimensional metal is unstable to lattice instabilities, notably the Peierls distortion.[1e] From well established phenomena in solid-state chemistry, the use of I···X (X = CN or halogen)[2] and hydrogen-bonding[3] interactions are two areas currently being investigated as means of 'crystal engineering' in the field of organic conductors. A number of TTF derivatives bearing halogen substituents have been synthesised recently[4,5,6] and close I···X (X = CN[5,7] or halogen[6]) cation···anion interactions have been observed. Hydrogen-bonding cation···anion interactions have also been observed recently in a number of conducting and superconducting salts of TTF derivatives,[8] fuelling the preparation of TTF systems endowed with substituents capable of participating in intermolecular hydrogen-bonding (*e.g.* hydroxy, amido groups). Donor···donor hydrogen-bonding interactions have been revealed by X-ray analysis of a number of appropriately functionalised neutral TTF systems.[9,10] Notably, it was found that 4-(*N*-methylthiocarbamoyl)tetrathiafulvalene **2** was packed in a *kappa* fashion[10] (that is, the π-donor forms orthogonal dimers which are coupled through weak intermolecular forces); such an arrangement in a neutral TTF derivative is very rare.[9c,11] Currently, all the TTF-based superconductors with $T_c > 10$ K possess *kappa*-phase structures, *e.g.* κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[12] and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X = Br, Cl)[13] [BEDT-TTF **3** = bis(ethylenedithio)tetrathiafulvalene].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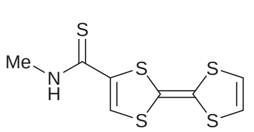
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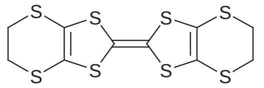
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The synthesis of functionalised TTF derivatives *via* lithiation and subsequent trapping of the intermediate mono-anion with electrophiles was first reported by Green[14] and this method

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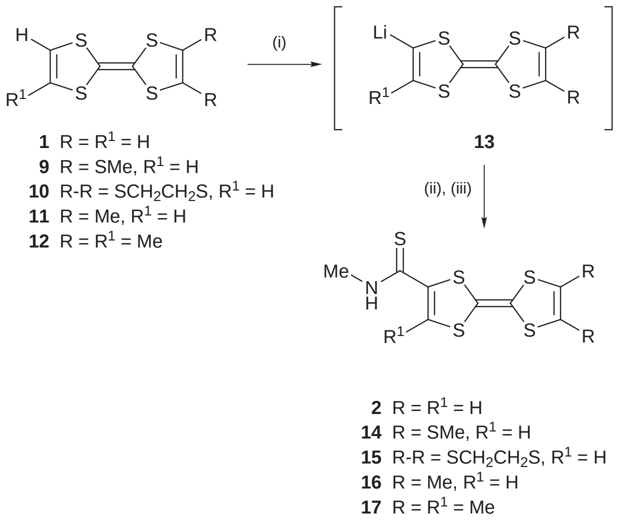
has subsequently been extended to afford a wide range of derivatives.[15] We employed this approach previously to prepare compound **2**[10] and have now utilised further this methodology to afford a number of new (*N*-methylthiocarbamoyl)-TTF derivatives designed to exhibit hydrogen-bonding in the neutral state, which may, potentially, be manifested in their charge-transfer complexes and radical ion salts.[16] Herein we describe (i) the syntheses of compounds **14**–**17**, (ii) single-crystal X-ray structures of neutral compounds **16** and **17**,[17] (iii) complexation studies on compounds **2** and **14**–**17** with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, **19**), and reactions with tetrabutylammonium tribromide which lead to bromide salts, and (iv) single-crystal X-ray structures of **2**·Br and **14**·TCNQ salts (both 1 : 1 stoichiometry) and complex $(\mathbf{17})_2\cdot\mathbf{20}$.

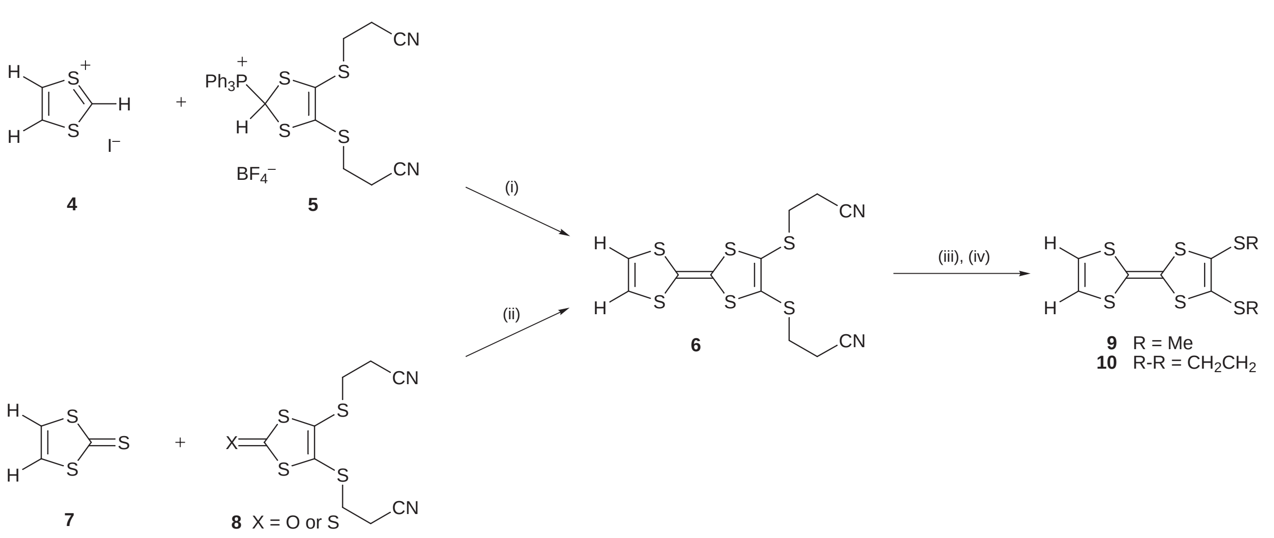
Results and Discussion

Compounds **9**,[18] **10**,[18] **11**[19] and **12**[19,20] were prepared according to literature procedures, utilising the coupling protocol pioneered by Lerstrup and co-workers, which selectively affords the unsymmetrical products.[19,21] As an alternative for the synthesis of compounds **9** and **10**, we have followed a sequence (Scheme 1) based upon a 'pseudo-Wittig' condensation[22] of 1,3-dithiolium salt **4**[23] and triphenylphosphonium tetrafluoroborate Wittig salt **5**[24] to afford compound **6**:[17] slow addition of triethylamine to a solution of compounds **4** and **5** proceeded cleanly affording a crude reaction mixture from which compound **6** could be easily isolated in 78% yield in *ca.* 5 g batches. Trimethyl phosphite and triethyl phosphite mediated 'cross-coupling'[25] of 1,3-dithiole-2-thione **7** and 4,5-bis(2′-cyanoethylthio)-1,3-dithiole-2-thione (or -one) **8**[26] also afforded compound **6** in moderate yields (20–35%); however, both coupling agents gave a complex mixture of products from which it proved exceptionally difficult and time-consuming to obtain a pure sample of compound **6**. Subsequent removal of the cyanoethyl groups in compound **6** occurred upon reaction with two equivalents of sodium ethoxide in ethanol–tetrahydrofuran, and alkylation of the derived dithiolate anions with either methyl iodide or 1,2-dibromoethane yielded the known products **9** and **10** (85 and 80% yields, respectively). In our hands there is little to choose between the route described herein to compounds **9** and **10** and that championed by Fourmigué *et al.*[18] in terms of laboratory time, yield and purity of the final products. One merit of Scheme 1 is that it proceeds *via* compound **6** which is especially versatile as a building block for analogous TTF systems, using the deprotection–dithiolate alkylation protocol of Becher and co-workers.[27]

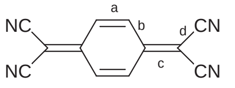
The reaction of compounds **9**–**12** with 1.1 equivalents of lithium diisopropylamide in diethyl ether (tetrahydrofuran for compound **10**[28]) at −78 °C afforded lithiated TTFs of general formula **13**, which were trapped with methyl isothiocyanate to give, after aqueous work-up, the desired products **14**–**17** (54–70% yields) (Scheme 2). These compounds were isolated as air-stable crystalline solids, which were notably darker in colour than most TTF derivatives (**14**–**16** are dark purple–black; **17** is very dark red) due to intramolecular charge-transfer from the donor TTF moiety to the acceptor *N*-methylthiocarbamoyl substituent, as observed previously for compound **2**.[10] Compared to TTF **1**, the electronic spectra of **2** and **14**–**17** in acetonitrile present a new, very broad absorption band centred at λ_{max} 435–467 nm (compounds **2**, and **14**–**16**) and λ_{max} 395 nm (compound **17**). The marked hypsochromic shift in this band for compound **17** reflects steric hindrance between the *N*-methylthiocarbamoyl moiety and the adjacent Me group, causing the former to twist significantly out of the plane of the TTF ring, thereby reducing the intramolecular conjugation (as confirmed by the X-ray structure, see below). The electrochemistry of compounds **14**–**17**, studied by cyclic voltammetry, shows two reversible one-electron oxidations typical of the TTF system at potentials consistent with their substitution patterns.



Scheme 2 *Reagents and conditions:* (i) LDA, Et_2O (THF for compound **10**[28]), −78 °C, 1.5 h; (ii) MeNCS, −78 to 20 °C over 12 h; (iii) H_2O



Scheme 1 *Reagents and conditions:* (i) Et_3N, MeCN, 20 °C, 2 h; (ii) $P(OR)_3$ (R = Me or Et), reflux, 4 h; (iii) NaOEt, EtOH–THF, 20 °C, 4 h; (iv) either MeI or $Br(CH_2)_2Br$, 20 °C, 16 h



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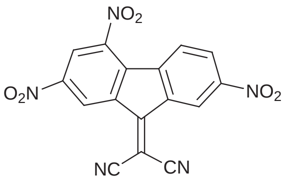

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Compounds **2** and **14–17** all form 1:1 complexes when mixed with equimolar amounts of TCNQ in hot acetonitrile (isolated as black powders in 35–65% yields). A 2:1 complex of compound **17** and 2,4,7-trinitro-9-(dicyanomethylene)fluorene **20**[29] was isolated from chlorobenzene solution. Similarly, metathesis reactions of compounds **2** and **14–17** with tetrabutylammonium tribromide in hot acetonitrile afforded 1:1 bromide salts (isolated as black powders in 62–75% yields). The conductivity of the complexes, (**2** and **14–17**)·TCNQ, $(\mathbf{17})_2$·**20** and (**2** and **14–17**)·Br, are in the range $\sigma_{rt}=5\times10^{-8}-1.2\ \mathrm{S\ cm^{-1}}$ (2-probe, compressed pellet measurements, 20 °C). The value of 1.2 S cm^{-1} for **2**·TCNQ is a remarkably high value.

X-Ray crystal structures

The molecular structures of **16**, **17** and the **2**·Br and **14**·TCNQ salts are shown in Fig. 1–3. The structure of $(\mathbf{17})_2$·**20** is shown in Fig. 8. The molecular geometry of the TTF unit (Table 1) can be compared with that of neutral **2**, studied earlier at ambient[10a] and low (150 K)[10c] temperatures. The central C_2S_4 system of the TTF moiety remains approximately planar in all cases; thus, molecular conformations can be described by angles of folding of the dithiole rings along the S···S vectors (θ_1 for the thiocarbamoyl-substituted ring and θ_2 for the unfunctionalised ring) and the S(1)–C(2)–C(7)–S(5) torsion angle τ, defining the orientation of the planar thiocarbamoyl group.

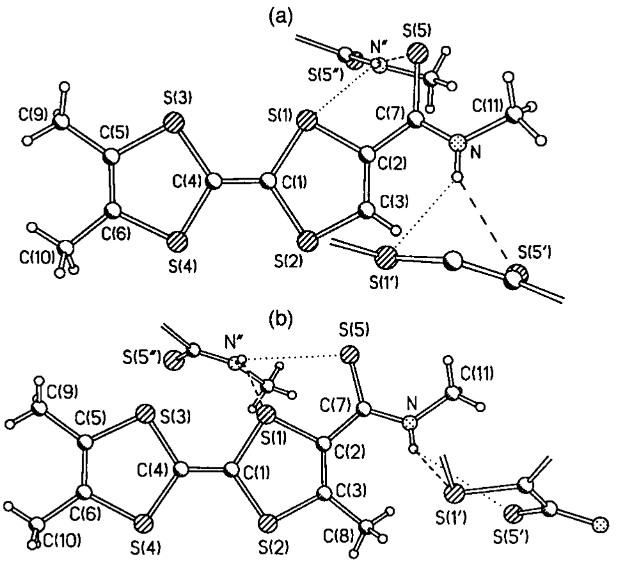


Fig. 1 Molecular structures of **16** (a) and **17** (b), showing 'strong' (dashes) and 'weak' (dots) intermolecular hydrogen bonds

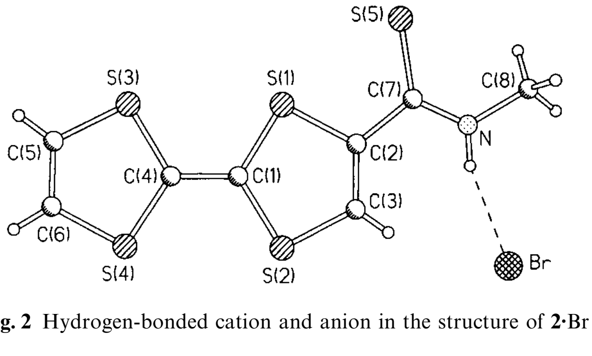


Fig. 2 Hydrogen-bonded cation and anion in the structure of **2**·Br

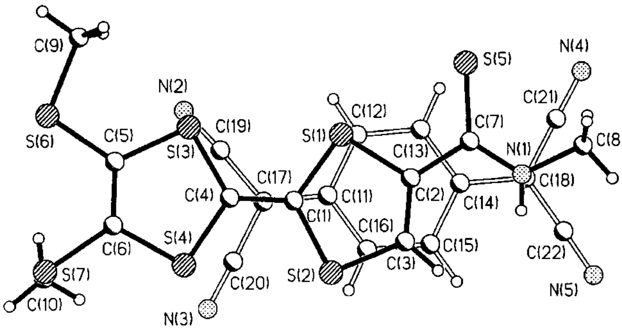


Fig. 3 Donor and acceptor in the structure of **14**·TCNQ

The S(2)–C(3) bond in neutral species **16** and **17** is significantly shorter than other chemically equivalent C–S bonds, by 0.036 Å in **16** and 0.013 Å in **17** (*cf.* 0.03 Å in **2**); this is in agreement with our previous suggestion[10a,30] that the mesomeric effect of the C=S group in structure **18** gives rise to a significant contribution from the canonical form **18′**, thereby increasing the polarity of the TTF moiety (Scheme 3). The S(2)–C(3) bond contraction is smaller [and the C(2)–C(7) bond marginally longer] in **17**, wherein the methyl substituent at C(3) forces an increase of τ, interfering with the conjugation. Charge transfer from the TTF moiety in **2**·Br and **14**·TCNQ has the usual effect upon bond distances.[31] As the HOMO has nodes in the C–S bonds but not in C=C, the latter lengthen (especially the central C=C bond, by 0.04–0.05 Å) and the former contract (by 0.02–0.04 Å), with the exception of the S(2)–C(3) bond which shortens insignificantly in $\mathbf{14}^{+\cdot}$ and not at all in $\mathbf{2}^{+\cdot}$. Thus, the non-equivalence of C–S bonds diminishes but persists; this effect can be easily understood when considering the resonance form **18′**. It is obvious that electron density is withdrawn only from the TTF moiety while the thiocarbamoyl group is practically unaffected.

In a TCNQ moiety **19**, *a* and *c* bonds tend to lengthen and *b* and *d* bonds tend to contract with increasing negative charge on the acceptor, *b*–*c* and *d*–*c* values changing practically linearly[32] from 0.069 and 0.062 Å, respectively, in neutral TCNQ[33] to (average) 0.037 and 0.030 Å in a series of A·$(\mathrm{TCNQ})_2$ salts (A = cation with a tetraalkylammonium centre)[34] and to zero in a TCNQ radical anion.[35] In **14**·TCNQ, the average bond lengths are: $a=1.367(3)$, $b=1.433(7)$, $c=1.411(6)$ and $d=1.428(4)$ Å (see Table 2) suggesting that the charge transfer (ρ) is *ca.* 0.7 electrons per molecule; this is slightly higher than in the parent TTF-TCNQ salt which has segregated stacks of donor and acceptor moieties,[36] where similar geometrical estimates give $\rho=0.6$ and neutron diffusion methods[37a] give $\rho=0.59$. Similar ρ values were estimated from IR spectroscopic data.[37b] The charge ρ^+ on the TTF moiety can be calculated using linear dependence

$$f=1.757-0.0385(\rho^+),$$[31b]

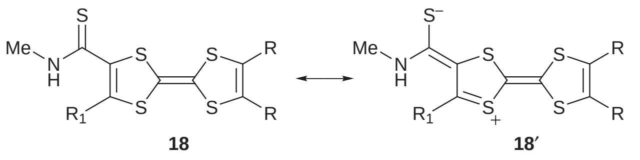
where f is the average length of the inner C–S bonds. For **14**·TCNQ this gives $\rho^+\cong0.5$; the discrepancy with the TCNQ charge may be due to the substituents at the TTF moiety (the equation was derived for *un*substituted TTF). The central C=C bond, slightly shorter than in **2**·Br, also suggests partial oxidation of **14**.

The crystal of **16** is broadly isostructural with that of **2**, comprising dimers of molecules (contacting face-to-face) arranged in a *kappa* mode, *i.e.* in chessboard fashion with the molecular planes of contacting dimers mutually perpendicular and their long axes parallel [Fig. 4(a)]. However, molecules

Table 1 Experimental and calculated selected bond distances (Å) and dihedral angles (°) in **2**, **14**, **16** and **17**, and their radical cations

	X-ray		PM3		X-ray	PM3		X-ray	PM3		X-ray		PM3	
	2	**2**·Br	**2**	$\mathbf{2}^{+\cdot}$	**14**·TCNQ	**14**	$\mathbf{14}^{+\cdot}$	**16**	**16**	$\mathbf{16}^{+\cdot}$	**17**	$(\mathbf{17})_2$·**20**[a]	**17**	$\mathbf{17}^{+\cdot}$
S(1)–C(1)	1.763(3)	1.727(3)	1.762	1.755	1.743(2)	1.763	1.752	1.765(3)	1.763	1.756	1.760(2)	1.758(4)	1.761	1.756
S(2)–C(1)	1.758(3)	1.738(3)	1.764	1.731	1.728(2)	1.764	1.732	1.762(3)	1.764	1.732	1.754(2)	1.748(4)	1.760	1.727
S(1)–C(2)	1.769(2)	1.745(3)	1.771	1.775	1.754(2)	1.771	1.774	1.767(3)	1.771	1.776	1.766(2)	1.777(4)	1.764	1.782
S(2)–C(3)	1.726(3)	1.725(3)	1.726	1.724	1.717(2)	1.726	1.723	1.728(3)	1.726	1.725	1.749(2)	1.736(4)	1.757	1.752
C(2)–C(3)	1.343(3)	1.352(4)	1.352	1.349	1.354(3)	1.352	1.349	1.342(5)	1.352	1.348	1.350(3)	1.357(6)	1.354	1.353
C(1)–C(4)	1.348(3)	1.396(5)	1.351	1.392	1.386(3)	1.350	1.393	1.346(4)	1.351	1.392	1.344(3)	1.351(5)	1.351	1.392
S(3)–C(4)	1.760(3)	1.718(3)	1.765	1.730	1.743(2)	1.758	1.721	1.749(3)	1.760	1.725	1.760(2)	1.760(4)	1.760	1.725
S(4)–C(4)	1.761(3)	1.728(3)	1.764	1.733	1.735(2)	1.758	1.724	1.759(3)	1.760	1.728	1.759(2)	1.759(4)	1.760	1.729
S(3)–C(5)	1.753(3)	1.718(4)	1.741	1.713	1.754(2)	1.754	1.736	1.762(3)	1.758	1.728	1.760(2)	1.756(4)	1.757	1.728
S(4)–C(6)	1.749(3)	1.727(4)	1.741	1.713	1.741(2)	1.754	1.736	1.764(3)	1.757	1.729	1.760(2)	1.755(4)	1.757	1.729
C(5)–C(6)	1.317(5)	1.341(5)	1.342	1.356	1.361(3)	1.357	1.370	1.335(5)	1.352	1.369	1.333(3)	1.353(6)	1.352	1.369
C(2)–C(7)	1.467(3)	1.490(4)	1.476	1.462	1.483(2)	1.476	1.462	1.465(4)	1.476	1.462	1.477(3)	1.475(6)	1.480	1.463
C(7)–S(5)	1.680(3)	1.680(3)	1.634	1.671	1.667(2)	1.634	1.669	1.678(3)	1.634	1.670	1.675(2)	1.674(5)	1.627	1.675
C(7)–N	1.321(3)	1.312(4)	1.382	1.356	1.328(3)	1.382	1.357	1.322(4)	1.382	1.356	1.326(3)	1.325(6)	1.382	1.354
θ_1	23.6(1)	3.4(3)			4.8(2)			17.5(2)			4.1(1)	0		
θ_2	14.5(1)	1.8(3)			6.9(2)			4.9(2)			3.9(1)	0		
τ	12.4(3)	9.6(5)	143.0	0.0	1.1(3)	143.2	0.0	18.1(3)	143.0	0.0	27.7(3)	3.9(6)	101.6	1.2

[a] For $(\mathbf{17})_2$·**20**, carbon atom numbers are C(1*n*) instead of C(*n*), N(1) for N.



Scheme 3

Table 2 Bond distances (Å) in the TCNQ radical anion of **14**·TCNQ

C(11)–C(12)	1.444(3)	C(11)–C(16)	1.427(3)
C(13)–C(14)	1.427(3)	C(14)–C(15)	1.436(3)
C(12)–C(13)	1.366(3)	C(15)–C(16)	1.367(3)
C(11)–C(17)	1.404(3)	C(14)–C(18)	1.417(3)
C(17)–C(19)	1.433(3)	C(17)–C(20)	1.428(3)
C(18)–C(21)	1.426(3)	C(18)–C(22)	1.423(3)
C(19)–N(2)	1.148(3)	C(20)–N(3)	1.153(3)
C(21)–N(4)	1.153(3)	C(22)–N(5)	1.154(3)

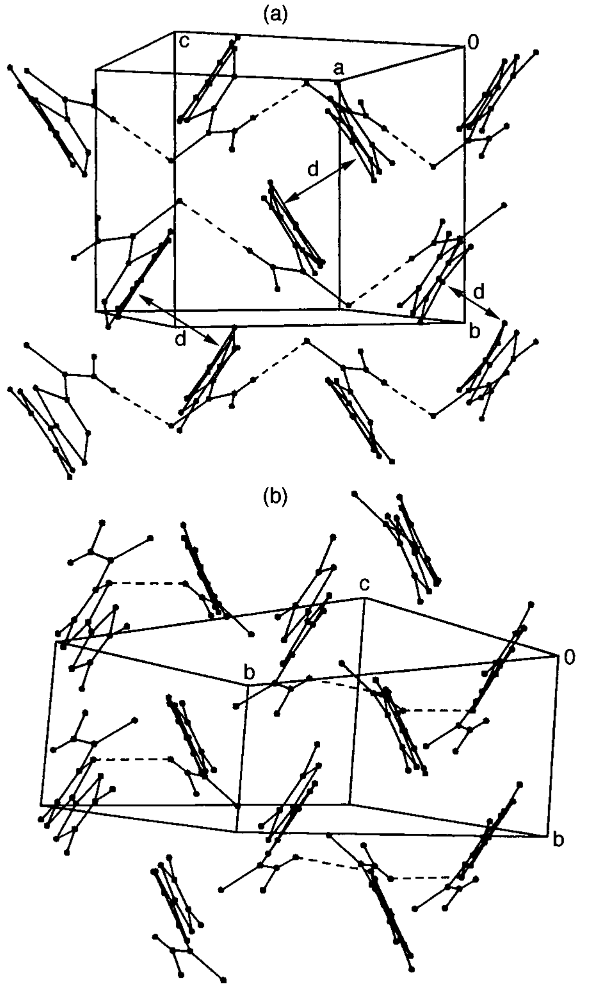


Fig. 4 *kappa*-Packing of dimers in **16** (a) showing interplanar separations in the dimers, $d = 3.40$ Å, and of molecules in **17** (b)

within a dimer overlap differently in **2** and **16**. This overlap can be described by relative shifts (slips) of the molecules from a perfectly eclipsed position: longitudinal (δ) parallel to the central C=C bond and lateral (ε) perpendicular to it. In **2**, $\delta = 1.6$ and $\varepsilon = 0.2$ Å which corresponds to the most common type of overlap observed in structural studies of TTF salts, in which the central C=C bond of one molecule lies over a dithiole ring of the other. In **16** the shifts are much larger, $\delta = 3.4$ and $\varepsilon = 1.6$ Å, the S(4) atom lying over the centre of a dithiole ring (Fig. 5). The interplanar separation (*d*) between central TTF planes (C_2S_4) in **16** (3.40 Å) is larger than in **2** (3.32 Å) and the shortest intradimer S···S contacts in the former (3.70–3.74 Å) are slightly longer than twice the van der Waals radius of sulfur (1.81 Å).[38] Interdimer contacts between the TTF sulfur atoms are even longer (3.88–4.00 Å). A short S(5)···S(5′) distance (3.34 Å) between thiocarbonyl groups contacting in a nearly linear fashion (C–S···S 172.4°) is in good agreement with the supposed 'ellipsoidal' shape of monocoordinate sulfur atoms (with the van der Waals 'radii' of 1.60 and 2.03 Å for the C–S···S angles of 180 and 90°, respectively)[39] although this model leaves entirely open the question of the physical nature of this asphericity. The NH group in **16** forms a bifurcated contact with the S(1) and S(5) atoms of a molecule belonging to a perpendicularly oriented dimer and symmetry related with the first one *via* glide plane *c*. The N···S distances of 3.783(3) and 3.425(3) Å and H···S of 2.97 and 2.51 Å (henceforth all hydrogen bond distances are normalised for N–H bond length of 1.03 Å, obtained from neutron diffraction[40]), respectively, indicate that the hydrogen bonding is principally with S(5).

The structure of **17** can be seen as the orthogonal packing of individual molecules rather than dimers [Fig. 4(b)]. Here, the molecule is much closer to a planar conformation. The intermolecular contacts between TTF sulfur atoms (3.95–4.02 Å) and the short S(5)···S(5′) contact of 3.59 Å are

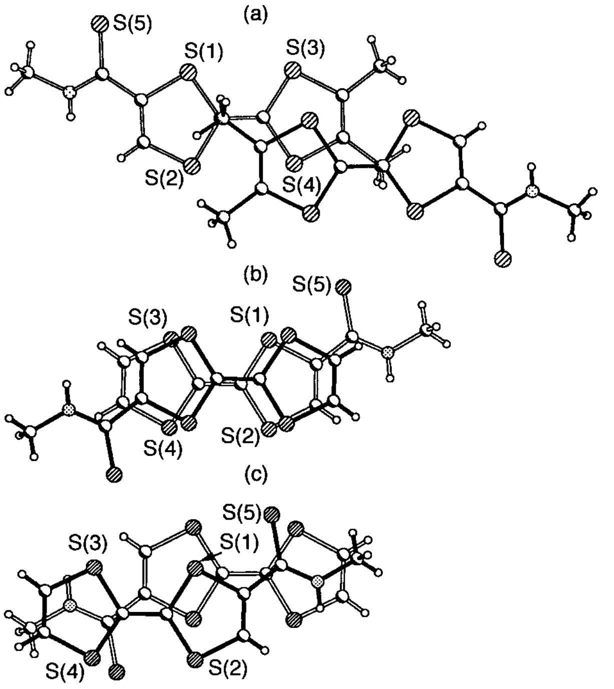


Fig. 5 Molecular overlap in the structures of **16** (a) and **2**·Br (b, c)

similar to those observed in the structure of **16**. The NH group also forms a bifurcated contact with the S(1) and S(5) atoms of a 'perpendicular' molecule, but in this case the former atom is more strongly bonded [N···S(1) 3.456(2), N···S(5) 3.697(2), H···S(1) 2.64, H···S(5) 3.06 Å, respectively]. The shorter H···S distances thus fall within the normal range for NH···S hydrogen bonding, 2.28–2.72 Å (average 2.46 Å) from neutron diffraction.[40]

The motif of **2**·Br is entirely different to that of neutral **2**. Here, $\mathbf{2}^{+\cdot}$ radical cations have almost planar TTF moieties and form an infinite stair-like stack of dimers, running parallel to the *y* direction. Adjacent cations in a stack are inversion-related. Within a dimer, TTF moieties are nearly eclipsed ($\delta = 0.6$, $\varepsilon = 0.1$ Å), with the interplanar separation $d = 3.34$ Å and S···S contacts 3.35–3.39 Å. Between these dimers, $d = 3.46$ Å (shortest S···S distances 3.77–3.94 Å) and the overlap of TTF moieties is only partial ($\delta = 3.1$, $\varepsilon = 1.4$ Å). However, this arrangement corresponds to the best possible overlap of the *entire* cations of **2** (*i.e.* including the *N*-methylthiocarbamoyl substituent).

All TTF planes within a single stack of **2**·Br are parallel but inclined by 46° to those of adjacent stacks. The interstack contacts S(1)···S(2′) 3.88, S(5)···S(3″) 3.47, S(5)···S(2′) 3.54 Å and their symmetrical equivalents (Fig. 6) form infinite chains parallel to the *z* axis. The anion is situated between stacks and is linked with the cation by a unique strong N–H···Br hydrogen bond [H···Br 2.22 Å] into an ionic pair. Even the N···Br distance of 3.210(2) is shorter than the sum of their van der Waals radii (3.51 Å). The contacts Br···S(4) of 3.38 and Br···S(3) of 3.57 Å with other cations are shorter than the sum of their van der Waals radii (3.68 Å).[38] This effect can be explained in terms of specific polar (electrostatic) interactions.[2a]

The structure of **14**·TCNQ comprises mixed stacks of a ···DDAADD··· type (Fig. 7) with interplanar separations of TTF···TTF *ca.* 3.5, TTF···TCNQ *ca.* 3.2, and TCNQ···TCNQ *ca.* 3.25 Å. The TTF moiety shows only insignificant folding of dithiole rings and a small (3.8°) twist around the central C(1)=C(4) bond. The TCNQ radical anion is planar to within ±0.04 Å (with a slight boat-like distortion). The TTF moieties are laterally slipped ($\delta = 0.4$, $\varepsilon = 1.1$ Å) and the overlap of TCNQ moieties is of a common ring over C=C bond type. The NH group is engaged in an N(1)–H···N(5) interstack hydrogen bond with an anion [H···N 2.00 Å], supported by a short C(3)–H···N(5) contact [H···N 2.34 Å] with the same anion.

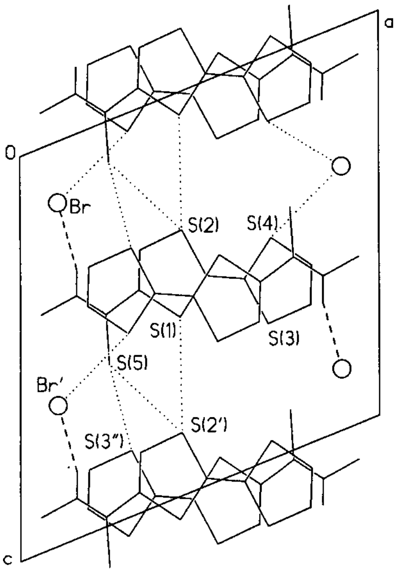


Fig. 6 Interstack packing in the structure of **2**·Br

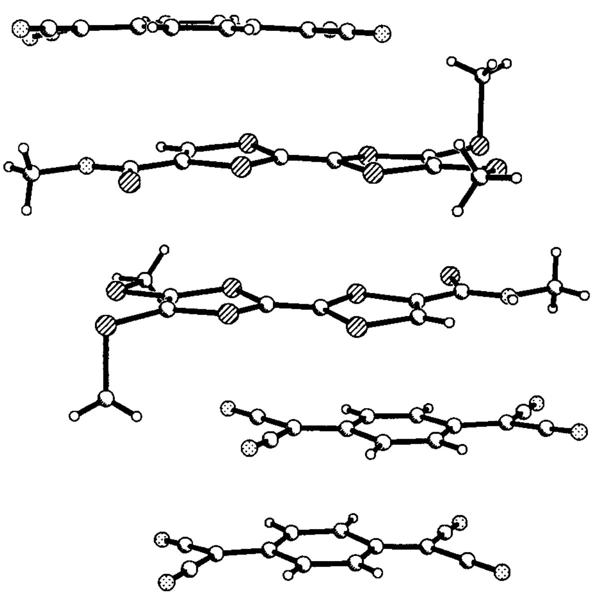


Fig. 7 Mixed stack in the structure of **14**·TCNQ

In the structure of $(\mathbf{17})_2\cdot\mathbf{20}$, molecule **17** is in a general position, while that of 2,4,7-trinitro-9-(dicyanomethylene)fluorene (**20**) is situated on a crystallographic two-fold axis, passing through the atoms C(7), C(8) and the midpoint of the C(5)–C(5′) bond (Fig. 8). One nitro group in **20** is thus disordered between two positions (4 and 5, in chemical notation) with equal occupancies. The same kind of disorder (with the same crystallographic symmetry) was displayed by pristine **20**;[29b] the consequent low precision of the molecular geometry makes comparison with the present structure difficult. Very elongated thermal ellipsoids of its oxygen atoms, O(41) and O(42), indicate further rotational disorder, probably of a continuous character, since our attempts to refine these atoms in 'split' positions gave no improvement. The intermolecular distance O(41)···C(18″) 2.83 Å is much shorter than the mean van der Waals contact of 3.24 Å, but the shortening is probably spurious, due to the disorder of the nitro group and probably also of C(18), which has large displacement parameters.

The conformation of **20** contrasts with those of 2,4,5,7-

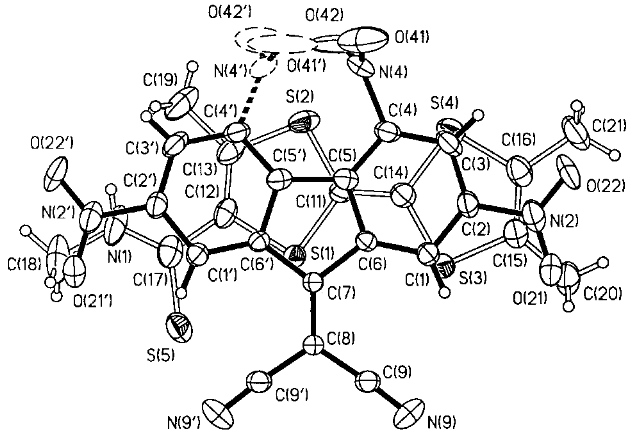


Fig. 8 Donor and acceptor molecules in the structure of $(\mathbf{17})_2{\cdot}\mathbf{20}$. Primed atoms are symmetrically related *via* twofold axis.

tetranitro analogues.[41] In the latter, the fused tricyclic system adopts a boat-like conformation with the dihedral angle of 8–12° between the benzene rings. The nitro groups in positions 4 and 5 are bent out of the mean molecular plane in opposite directions and form dihedral angles of 27–42° with this plane. In **20**, the fused system is essentially planar, the nitro group at C(4) is inclined to its plane (A) by 77°, but its nitrogen atom does not deviate from plane A. Thus the steric strain is completely relieved. The nitro group at C(2) and the $C(CN)_2$ moiety are inclined to plane A insignificantly, by 5 and 2°. Molecule **17** in this structure is almost flat. Both dithiole rings are rigorously planar, twist angles around the C(11)–C(14) and C(12)–C(17) bonds are *ca.* 4°.

Molecules in the crystal form a mixed ···DDADDA··· stack (Fig. 9), with mean interplanar separations D···A 3.35 and D···D 3.58 Å. However, bond lengths in the **17** moiety show only minor and somewhat irregular changes from the neutral species (Table 1), *i.e.* the overall charge transfer is rather small. The overlap between donor and acceptor molecules is shown in Fig. 8, the overlap between adjacent molecules of **17** resembles that in **2**·Br (see above). The distance between the amido group and the cyano nitrogen atom N(9″) (H···N 2.45 Å) is characteristic of a weak dipole–dipole interaction rather than a real hydrogen bond.

The overlap between TTF moieties in various structures can be rationalised as a compromise between two tendencies: to minimise the core (steric) repulsion and to maximise the overlap between the HOMOs.[42] The main contributors to the repulsion are sulfur atoms, which are substantially bigger than the carbon atoms. On the other hand, the HOMO is localised mainly on the central C_2S_4 moiety of the TTF, and especially on the sulfur atoms. Boat-like bending of a TTF system can only increase this localisation.[42d] Thus the most sterically favourable stacking, one with sulfur atoms over gaps, corresponds to the minimum of orbital overlap and *vice versa*, the fully eclipsed stacking is least favourable sterically but most favourable in the sense of HOMO overlap. The former arrangement is observed for neutral TTF derivatives, where HOMOs are fully occupied and their overlap can give no significant bonding contribution. When the TTF system is oxidised to +1, the overlap of these orbitals (now SOMOs) produces the maximum energy gain—hence, the nearly-eclipsed overlap in **2**·Br [Fig. 5(b)]. On the other hand, oxidation makes dithiole rings more aromatic in character and simultaneously reduces the repulsion between non-bonding electrons of the sulfur atoms, which causes the boat-like folding of TTF[43] (observed, remarkably, in the gas phase[44]). Therefore, positively charged TTF moieties are invariably planar, while neutral ones adopt both planar and folded conformations (by various degrees).[45]

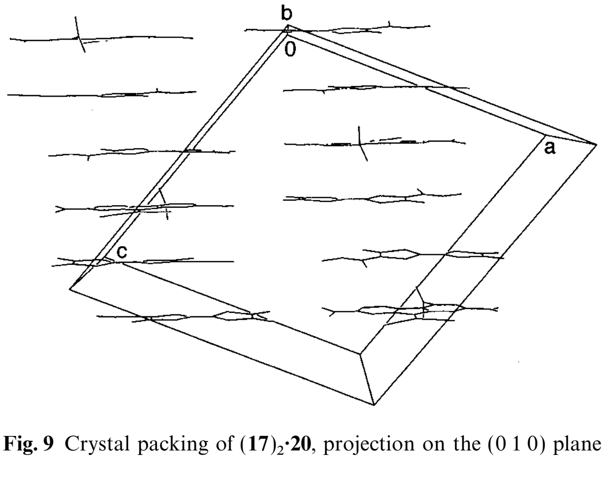


Fig. 9 Crystal packing of $(\mathbf{17})_2{\cdot}\mathbf{20}$, projection on the (0 1 0) plane

Molecular orbital calculations

To gain a better understanding of bonding in thiocarbamoyl TTF derivatives, we performed molecular orbital quantum-chemical calculations at the Hartree–Fock SCF level of approximation, for neutral molecules **2**, **14**, **16** and **17** and their radical cations. The molecular geometries, fully optimised using the PM3 semi-empirical method[46] (Table 1), show an average discrepancy with the experimental (X-ray) bond distances (for neutral molecules) of 0.006 Å in the TTF moiety and 0.012 Å overall. Particularly, the observed shortening of the S(2)–C(3) bond as compared to chemically equivalent C–S bonds (see above) is well reproduced by the calculations. The biggest discrepancies are observed for the side-chain bonds, C(7)=S(5) (underestimated by 0.044–0.048 Å) and C(7)–N (overestimated by 0.056–0.060 Å). Similar discrepancies were obtained earlier[9c] for (*N,N*-dimethylcarbamoyl)-TTF and manifest a general shortcoming of the PM3 method in calculating the structures of various nitrogen-containing compounds.[47]

Calculated changes in bond lengths upon oxidation of neutral molecules to radical cations do not fully agree with the experimental data for **2**→**2**·Br. In the latter, oxidation causes lengthening of all C=C bonds and contraction of all S–C bonds [except the already short S(2)–C(3) bond] in the TTF moiety. The calculated bond lengths behave mostly in the same way, but the S(1)–C(1), S(1)–C(2) and C(2)–C(3) bonds remain practically unaltered. Calculations for all other molecule–cation-radical pairs studied herein reproduce the same pattern.

The HOMO and LUMO energies for molecules **2**, **14**, **16**, **17** and their cation radicals were calculated. Although the PM3 method is rather poor at predicting *absolute* HOMO energies (*e.g.* giving −7.99 eV for **1**, against the experimental ionisation potential in the gas phase of 6.70 eV[48]), the calculated *relative* stabilities of the HOMOs, **14** (−8.27 eV) < **2** (−8.23 eV) < **16** (−8.14 eV) < **17** (−8.05 eV), are in good agreement with the succession of $E_1^{1/2}$ oxidation potentials for these compounds (0.52, 0.43,[9c] 0.41, and 0.38 V, respectively).

The Mulliken atomic charges in neutral molecules are strongly negative [−(0.19–0.33) e] on carbon atoms and positive (0.25–0.30 e) on sulfur atoms, similar to related TTF derivatives reported earlier.[9c] The positive charge in the radical cations is delocalised less on the dithiole ring (A) linked to the thiocarbamoyl group (0.2–0.3 e) than on the other ring (*ca.* 0.5 e).

The calculated minimum-energy conformation of neutral molecules is characterised by a planar TTF moiety and a substantial twist around the C(2)–C(7) bond. The torsion angle τ (see above) is *ca.* 143° in **2**, **14** and **16**; in **17** the 5-methyl substituent induces a stronger twist, $\tau = 101.6°$. These conformations are quite different from those observed in the crystal structures. However, the rotation barriers around the

C(2)–C(7) bonds are very low. Those calculated in rigid-rotor approximation [*i.e.* without a relaxation of all other molecular coordinates during the rotation around the C(2)–C(7) bond], which always gives an overestimate of the barrier energy, do not exceed 2.6 kcal mol^{-1}. Indeed, calculation of **14** as a completely optimised rotor gives even smaller barriers of 1.15 kcal mol^{-1} at $\tau = 4.6°$ (*cis*-planar conformation) and 0.19 kcal mol^{-1} at $\tau = 179.4°$ (*trans*-planar conformation). Therefore, τ can easily change under the influence of crystal packing and hydrogen bonds. In **17** the adjacent methyl group introduces a much higher barrier to rotation at $\tau = 0$ or 180°, comparable with that in the cation radical; however, further from $\tau = 0$ or 180° the rotation is practically free. For radical cations **2**$^{+\cdot}$, **14**$^{+\cdot}$, **16**$^{+\cdot}$ and **17**$^{+\cdot}$ the favourable conformation is *cis*-planar with τ close to 0° and the rotation barriers (now defined by electron conjugation) an order of magnitude higher than in neutral **2**, **14** and **16**. This agrees well with the X-ray structures of **2**·Br, **14**·TCNQ, and (**17**)$_2$·**20**, exhibiting only minor twists.

Whether the favourable conformation of the TTF moiety in neutral molecules is planar is open to discussion. These results seem to be extremely basis-sensitive,[43] while electron diffraction data are indicative of a non-planar conformation in the gas phase.[44] The *ab initio* calculations (6–31G* level) show that in any case the potential well is extremely flat-bottomed: folding of both dithiole rings by $\theta = 10$ and 20° needs only 0.1 and 1.0 kcal mol^{-1}, respectively.[9c] The former energy is hardly of any real significance, and even the latter may be easily furnished by intermolecular interactions.

Conclusions

The present study illustrates the fact that recent advances in synthetic TTF chemistry provide access to a far wider range of TTF derivatives than was hitherto available, including highly-functionalised systems which possess interesting solid state properties. Following our earlier work on (*N*-methylthiocarbamoyl)-TTF **2**,[10] we have efficiently synthesised compounds **14**–**17**, which were designed to explore the effects of the *N*-methylthiocarbamoyl substituent on the properties of the TTF system. Solution UV–VIS spectroscopic and cyclic voltammetric studies establish that there is intramolecular charge-transfer between the donor TTF and the acceptor *N*-methylthiocarbamoyl moieties. Within this series of TTF derivatives, X-ray crystal structures reveal unusual packing motifs in both the neutral and radical cation species, with intermolecular interactions arising from hydrogen bonding and/or electrostatic interactions of the *N*-methylthiocarbamoyl group. The observation of distorted *kappa* packing modes in the structure of **16** is notable. Crystal structures have been obtained for two 1:1 salts, *viz.* **2**·Br and **14**·TCNQ and for the complex (**17**)$_2$·**20**: to date, single crystals of segregated-stack, mixed-valence salts of donors **2** and **14**–**17** have not been obtained. The synthesis of new TTF systems bearing substituents which can engage in intermolecular interactions, and the radical cation salts of these donors, is presently under investigation, with a view to the 'supramolecular engineering' of new materials in which intermolecular interactions regulate the structural and transport properties in a controllable manner.[49]

Experimental

General methods

^{1}H NMR Spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz. ^{13}C NMR Spectra were obtained on a Varian 400 spectrometer operating at 100.581 MHz. Coupling constants J are given in Hz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. IR Spectra were recorded on a Perkin-Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600. UV Spectra were obtained on a Kontron Uvicon 930 spectrophotometer using quartz cells. Extinction coefficients (ε) are all quoted in M^{-1} cm^{-1}. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. Cyclic voltammetric data were obtained on a BAS 50W electrochemical analyser (1×10^{-5} M solution of donor in acetonitrile under argon, 1×10^{-1} M tetrabutylammonium perchlorate supporting electrolyte, platinum working and counter electrodes, Ag/AgCl reference electrode, 20 °C). All reagents were of commercial quality and used as supplied unless otherwise stated; solvents were dried where necessary using standard procedures and distilled for chromatographic use.

4,5-Bis(2-cyanoethylsulfanyl)tetrathiafulvalene 6

To a stirred solution of salt **4**[23] (10.0 g, 16.08 mmol) and phosphonium salt **5**[24] (3.70 g, 16.08 mmol) under argon at 20 °C was dropwise added triethylamine (10 cm^3, excess) over 0.5 h and the mixture stirred overnight. After evaporation, the residue was chromatographed (silica, 200–400 mesh) eluting with dichloromethane to afford compound **6** as orange needles (4.69 g, 78%), mp 77 °C (from MeCN) (Analysis found: C, 38.4; H, 2.9; N, 7.5; $C_{12}H_{10}N_2S_6$ requires: C, 38.5; H, 2.7; N, 7.5%); *m/z* (DCI) 375 (M$^+$ + 1, 100%); δ_H (CDCl$_3$) 6.37 (2H, s), 3.09 (4H, t, J 7.1), 2.74 (4H, t, J 7.1); λ_{max} (MeCN) (ε) 390 (1.3×10^3), 310 (5.1×10^3), 294 (4.8×10^3), 195 (7.2×10^3) nm; CV (MeCN) $E_1^{1/2}$ 0.41, $E_2^{1/2}$ 0.79 V.

4,5-Bis(methylsulfanyl)tetrathiafulvalene 9

To a stirred solution of compound **6** (2.00 g, 5.35 mmol) in dry ethanol–tetrahydrofuran (1:1 v/v, 150 cm^3) under argon at 20 °C was added sodium ethoxide [from sodium (245 mg, 10.70 mmol) in ethanol (25 cm^3)] and the mixture was stirred for 4 h (during this time the solution colour changed from orange to deep red). Methyl iodide (2 cm^3, excess) was added and the mixture stirred at 20 °C for a further 12 h. The mixture was diluted with dichloromethane (250 cm^3), washed with water (3×100 cm^3), the organic phase dried (MgSO$_4$) and the solvent was evaporated *in vacuo*. Chromatography (silica, 200–400 mesh) of the residue eluting with hexane–dichloromethane (1:1 v/v) afforded compound **9** (1.44 g, 91%) as a red solid, mp 65 °C (lit.,[18] mp 63–65 °C); δ_H (CDCl$_3$) 6.33 (s, 2H), 2.42 (s, 6H).

4,5-(Ethylenedisulfanyl)tetrathiafulvalene 10

To a stirred solution of compound **6** (1.00 g, 2.67 mmol) in dry ethanol–tetrahydrofuran (1:1 v/v, 150 cm^3) under argon at 20 °C was added sodium ethoxide [from sodium (123 mg, 5.35 mmol) in ethanol (25 cm^3)] and the mixture was stirred for 4 h. 1,2-Dibromoethane (0.5 cm^3, excess) was added and the mixture stirred at 20 °C for a further 12 h. The mixture was concentrated to *ca.* 30 cm^3 and the precipitated solid collected by filtration and washed with ethanol (25 cm^3). Chromatography (silica, 200–400 mesh) of the residue eluting with dichloromethane afforded compound **10** (637 mg, 81%) as an orange solid, mp 204–206 °C (lit.,[18] mp 206–207 °C); δ_H (CDCl$_3$) 6.32 (s, 2H), 3.29 (s, 4H).

General procedure for compounds 14–17

To a stirred solution of compound **9**–**12** (3.0 mmol) in dry diethyl ether (tetrahydrofuran for compound **10**[28]) (100 cm^3) under argon at −78 °C was added lithium diisopropylamide–tetrahydrofuran complex (2.06 cm^3, 3.1 mmol of a 1.5 M solution in cyclohexane) and stirring continued for 2 h. Methyl isothiocyanate (330 mg, 4.5 mmol) was added and the mixture allowed to warm to 20 °C over 12 h. Water (100 cm^3) was added and the mixture stirred for 2 h (during this time the organic phase became burgundy red in colour). The mixture was extracted with toluene (3×100 cm^3), the organic extracts were combined, washed with water (100 cm^3), dried ($MgSO_4$) and evaporated *in vacuo*. Chromatography (silica 200–400 mesh for compounds **14** and **15**; alumina 70–230 mesh for compounds **16** and **17**) of the residue eluting initially with hexane–toluene (1 : 1 v/v) afforded unreacted compounds **9**–**12**; subsequent elution with toluene afforded the products. There were thus obtained:

4-(*N*-Methylthiocarbamoyl)-4′,5′-bis(methylsulfanyl)tetrathiafulvalene 14. Black needles (697 mg, 63%), mp 134–135 °C (from MeCN) (Analysis found: C, 32.3; H, 3.2; N, 3.8; $C_{10}H_{11}NS_7$ requires: C, 32.5; H, 3.0; N, 3.8%); *m*/*z* (EI) 369 (M^+, 70%), (CI) 370 (M^++1, 65); δ_H ($CDCl_3$) 7.25–7.20 (1H, br s), 7.11 (1H, s), 3.24 (3H, d, *J* 4.9), 2.42 (6H, s); ν_{max} (KBr) 3400–3200 (br, NH), 1532, 1516, 1362 (C=S), 1205, 1044, 788 cm^{-1}; λ_{max} (MeCN) (ε) 435 (2.8×10^3), 325 (sh, 2.1×10^4), 290 (2.8×10^4), 198 (2.9×10^4) nm; CV (MeCN) $E_1^{1/2}$ 0.52, $E_2^{1/2}$ 0.83 V.

4-(*N*-Methylthiocarbamoyl)-4′,5′-(ethylenedisulfanyl)tetrathiafulvalene 15. Black needles (595 mg, 54%), mp 185–186 °C (from CS_2) (Analysis found: C, 32.6; H, 2.6; N, 3.9; $C_{10}H_9NS_7$ requires: C, 32.7; H, 2.5; N, 3.8%); *m*/*z* (EI) 367 (M^+, 45%); (CI) 368 (M^++1, 35); δ_H ($CDCl_3$) 7.30–7.20 (1H, br s), 7.11 (1H, s), 3.30 (4H, s), 3.23 (3H, d, *J* 4.8); ν_{max} (KBr) 3350–3150 (br, NH), 1524, 1518, 1358 (C=S), 1205, 1045, 791 cm^{-1}; λ_{max} (MeCN) (ε) 450 (1.2×10^3), 326 (sh, 1.0×10^4), 309 (1.3×10^4), 231 (1.1×10^4), 208 (1.3×10^4) nm; CV (MeCN) $E_1^{1/2}$ 0.53, $E_2^{1/2}$ 0.86 V.

4-(*N*-Methylthiocarbamoyl)-4′,5′-dimethyltetrathiafulvalene 16. Black plates (604 mg, 66%), mp 171–172 °C (from toluene) (Analysis found: C, 39.5; H, 3.8; N, 4.4; $C_{10}H_{11}NS_5$ requires: C, 39.3; H, 3.6; N, 4.6%); *m*/*z* (EI) 305 (M^+, 45%), (CI) 306 (M^++1, 65); δ_H ($CDCl_3$) 7.30–7.20 (1H, br s), 7.19 (1H, s), 3.23 (3H, d, *J* 4.8), 1.95 (6H, s); δ_C ($CDCl_3$) 188.5, 133.7, 129.4, 123.0, 122.7, 116.2, 105.2, 32.8, 16.2, 13.7; ν_{max} (KBr) 3400–3250 (br, NH), 1542, 1520, 1346 (C=S), 1216, 1048, 773 cm^{-1}; λ_{max} (MeCN) (ε) 467 (1.8×10^3), 323 (sh, 1.9×10^4), 297 (2.2×10^4), 205 (1.7×10^4) nm; CV (MeCN) $E_1^{1/2}$ 0.41, $E_2^{1/2}$ 0.79 V.

4-(*N*-Methylthiocarbamoyl)-4′,5,5′-trimethyltetrathiafulvalene 17. Dark red needles (670 mg, 70%), mp 174–175 °C (from toluene) (Analysis found: C, 41.3; H, 4.2; N, 4.3; $C_{11}H_{13}NS_5$ requires: C, 41.4; H, 4.1; N, 4.4%); *m*/*z* (EI) 319 (M^+, 85%), (CI) 320 (M^++1, 100); δ_H ($CDCl_3$) 7.40–7.30 (1H, br s), 3.21 (3H, d, *J* 4.8), 2.25 (3H, s), 1.94 (6H, s); δ_C ($CDCl_3$) 186.6, 137.4, 125.3, 123.0, 122.7, 113.2, 105.4, 33.2, 13.7; ν_{max} (KBr) 3400–3250 (br, NH), 1572, 1524, 1347 (C=S), 1218, 1052, 733 cm^{-1}; λ_{max} (MeCN) (ε) 395 (2.2×10^3), 328 (sh, 1.4×10^4), 297 (2.2×10^4), 213 (sh, 1.9×10^4), 205 (2.2×10^4) nm; CV (MeCN) $E_1^{1/2}$ 0.38, $E_2^{1/2}$ 0.76 V.

General procedure for compounds 2 and 14–17: TCNQ and bromide salts

A solution of compound **2** and **14**–**17** (0.1 mmol) in hot, dry acetonitrile (10 cm^3) and a solution of (i) 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (20 mg, 0.1 mmol), or (ii) tetrabutylammonium tribromide (48 mg, 0.1 mmol) in hot, dry acetonitrile (10 cm^3) were mixed and refluxed for 10 min under argon. After cooling, the product precipitated (for **2d**·TCNQ slow evaporation of the solvent was necessary before precipitation occurred); the black solid was collected by filtration and washed with ethanol. There were thus obtained:

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 2: TCNQ salt. 24 mg, 50% [Analysis found: C, 50.0; H, 2.5; N, 14.3; $C_{20}H_{11}N_5S_5$ (1 : 1 stoichiometric complex) requires: C, 49.9; H, 2.3; N, 14.5%]; ν_{max} (KBr) 2200 cm^{-1} (C≡N); σ_{rt} (2-probe, compressed pellet) 1.2 S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 14: TCNQ salt. 29 mg, 50% [Analysis found: C, 45.9; H, 2.6; N, 12.4; $C_{22}H_{15}N_5S_7$ (1 : 1 stoichiometric complex) requires: C, 46.0; H, 2.6; N, 12.2%]; ν_{max} (KBr) 2188 cm^{-1} (C≡N); σ_{rt} (2-probe, compressed pellet) 5×10^{-6} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 15: TCNQ salt. 20 mg, 35% [Analysis found: C, 46.5; H, 2.2; N, 12.1; $C_{22}H_{13}N_5S_7$ (1 : 1 stoichiometric complex) requires: C, 46.2; H, 2.3; N, 12.3%]; ν_{max} (KBr) 2212, 2198 cm^{-1} (C≡N); σ_{rt} (2-probe, compressed pellet) 3×10^{-6} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 16: TCNQ salt. 33 mg, 65% [Analysis found: C, 51.4; H, 3.0; N, 14.3; $C_{22}H_{15}N_5S_5$ (1 : 1 stoichiometric complex) requires: C, 51.8; H, 3.0; N, 13.7%]; ν_{max} (KBr) 2204 cm^{-1} (C≡N); σ_{rt} (2-probe, compressed pellet) 9×10^{-2} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 17: TCNQ salt. 32 mg, 61% [Analysis found: C, 52.2; H, 3.2; N, 13.4; $C_{23}H_{17}N_5S_5$ (1 : 1 stoichiometric complex) requires: C, 52.8; H, 3.3; N, 13.4%]; ν_{max} (KBr) 2200 cm^{-1} (C≡N); σ_{rt} (2-probe, compressed pellet) 7×10^{-2} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 2: bromide salt. 27 mg, 75% [Analysis found: C, 26.8; H, 2.1; N, 4.0; $C_8H_7BrNS_5$ (1 : 1 stoichiometric complex) requires: C, 26.9; H, 2.0; N, 3.9%]; σ_{rt} (2-probe, compressed pellet) 5×10^{-5} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 14: bromide salt. 28 mg, 62% [Analysis found: C, 26.9; H, 2.7; N, 3.2; $C_{10}H_{11}BrNS_7$ (1 : 1 stoichiometric complex) requires: C, 26.7; H, 2.5; N, 3.1%]; σ_{rt} (2-probe, compressed pellet) 1×10^{-8} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 15: bromide salt. 31 mg, 70% [Analysis found: C, 26.6; H, 2.1; N, 2.8; $C_{10}H_9BrNS_7$ (1 : 1 stoichiometric complex) requires: C, 26.8; H, 2.0; N, 3.1%]; σ_{rt} (2-probe, compressed pellet) 3×10^{-8} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 16: bromide salt. 25 mg, 65% [Analysis found: C, 31.3; H, 2.9; N, 3.8; $C_{10}H_{11}BrNS_5$ (1 : 1 stoichiometric complex) requires: C, 31.2; H, 2.9; N, 3.6%]; σ_{rt} (2-probe, compressed pellet) 3×10^{-6} Scm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 17: bromide salt. 29 mg, 74% [Analysis found: C, 33.2; H, 3.2; N, 3.5; $C_{11}H_{13}BrNS_5$ (1 : 1 stoichiometric complex) requires: C, 33.1; H, 3.3; N, 3.5%]; σ_{rt} (2-probe, compressed pellet) 1×10^{-6} S cm^{-1}.

4-(*N*-Methylthiocarbamoyl)tetrathiafulvalene 17: 2,4,7-trinitro-9-(dicyanomethylene)fluorene 20 complex: (17)$_2$·20. Compound **20**[29a] (3.1 mg, 0.85 mmol) was dissolved in hot chlorobenzene (1 cm^3). The solution was cooled to 35–40 °C, then compound **17** was added. After a week at room temperature black crystals (6.2 mg, 73%) suitable for X-ray analysis were isolated by filtration; σ_{rt} (2-probe, compressed pellet) 5×10^{-4} S cm^{-1}.

X-Ray crystallography

All single-crystal X-ray diffraction experiments were carried out at *T*=150 K (using Cryostream open-flow N_2 gas cooling devices), on a Rigaku AFC6S 4-circle diffractometer (for **2**·Br,

Table 3 Crystal data

Compound	**2**·Br	**14**·TCNQ	**16**	**17**	(**17**)$_2$·**20**
Formula	$C_8H_7NS_5{}^+Br^-$	$C_{10}H_{11}NS_7 \cdot C_{12}H_4N_4$	$C_{10}H_{11}NS_5$	$C_{11}H_{13}NS_5$	$2C_{11}H_{13}NS_5 \cdot C_{16}H_5N_5O_6$
M	357.36	573.81	305.50	319.52	1002.30
Symmetry	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
a/Å	13.126(4)	7.982(1)	13.199(1)	19.055(1)	18.060(1)
b/Å	7.392(2)	12.876(1)	9.534(1)	6.603(1)	13.566(1)
c/Å	13.570(4)	13.465(1)	10.509(1)	11.544(1)	18.697(1)
α (°)	90	108.99(1)	90	90	90
β (°)	111.72(2)	104.44(1)	94.98(1)	102.85(1)	109.25(1)
γ (°)	90	95.81(1)	90	90	90
U/Å^3	1223.2(7)	1241.7(2)	1317.4(2)	1416.1(2)	4324.7(5)
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$C2/c$
Z	4	2	4	4	4
μ/cm^{-1}	41.8	6.6	8.5	8.0	5.7
D_x/g cm^{-3}	1.94	1.54	1.54	1.50	1.54
Crystal size/mm	0.44 × 0.09 × 0.05	0.4 × 0.09 × 0.06	0.38 × 0.3 × 0.1	0.4 × 0.28 × 0.14	0.52 × 0.04 × 0.04
$2\theta_{max}$ (°)	55	54	50.5	51.3	50
Data total	2927	8847	5302	6102	12792
Data unique	2803	5299	2138	2423	3719
Data obs., $I > 2\sigma(I)$	2110	4408	2006	2225	2792
R_{int}	0.067/0.025[a]	0.061/0.035[a]	0.037	0.079	0.072
Abs. correction	empirical[b]	integration	semiempirical[c]	—	—
$T_{min,\ max}$	0.47 : 1.00	0.80 : 0.97	0.76 : 0.93	—	—
No. of variables	164	368	166	207	350
$wR(F^2)$, all data	0.075	0.095	0.091	0.090	0.125
Goodness of fit	1.07	1.09	1.28	1.11	1.15
$R(F)$, obs. data	0.031	0.039	0.038	0.032	0.054
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.63, −0.44	0.32, −0.30	0.27, −0.23	0.32, −0.26	0.31, −0.37

[a] Before and after the absorption correction. [b] On 108 ψ-scans of 3 reflections, TEXSAN software.[51] [c] On Laue equivalents, SHELXTL software. [d] $w^{-1} = \sigma^2(F^2) + (AP)^2 + BP$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

$2\theta/\omega$ scan mode) or a Siemens 3-circle SMART diffractometer with a CCD area detector (ω scan mode in frames of 0.3°). Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) was used. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[50] All non-H atoms were refined with anisotropic displacement parameters, all H atoms in isotropic approximation (methyl groups in **16** as rigid bodies). For (**17**)$_2$·**20**, solution in the space group $C2/c$ implies the crystallographic symmetry (axis 2) and thus the disorder of **20** and gives some unreasonably short intermolecular contacts; therefore, we attempted also the refinement in space groups Cc and $P2_1/n$ (making use of some extremely weak reflections with odd $h + k$, due more likely to $\lambda/2$ contamination), wherein axis 2 is absent. Neither model led to a consistent refinement. Attempts to rationalise the rotational disorder of the nitro group O(41)N(4)O(42) in terms of 'split' positons of the oxygen atoms were also unsuccessful.

Crystal data and experimental details are listed in Table 3; full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre, 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 1145/99.

MO Computational procedure

The geometries of molecules and cation radicals of **2**, **14**, **16** and **17** were optimized using the PM3 semiempirical method as implemented in the HyperChem 4.5 program.[52] The Polak–Ribiere algorithm was used for the optimization; the gradient norm achieved in all the calculations was less than 0.01 kcal mol^{-1} Å^{-1}. Restricted Hartree–Fock (RHF) formalism was used for neutral molecules whereas spin-unrestricted Hartree–Fock (UHF) formalism was used for radical cations.[53] Tables of calculated (PM3) parameters for compounds **2**, **14**, **16** and **17** and their cation radicals are available as supplementary data (**SUP 57385**; 2 pp.) deposited with the British Library. Details are available from the editorial office.

We thank EPSRC for funding the work in Durham and Bangor, the Leverhulme Trust for a Visiting Fellowship at Durham University (A.S.B.), the Royal Society for a Leverhulme Senior Research Fellowship (J.A.K.H.) and an Exchange Fellowship (I.F.P.).

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Paper 8/02037J; *Received* 13*th March*, 1998