JOURNAL OF
Materials
CHEMISTRY

New bi(tetrathiafulvalenyl) derivatives and their radical cations: synthetic and X-ray structural studies

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Received 28th January 2000, Accepted 15th March 2000
Published on the Web 25th April 2000

A series of bi(tetrathiafulvalenyl) derivatives has been prepared from iodo-TTF precursors by Ullmann coupling (copper in refluxing *N,N*-dimethylformamide) or by reaction with copper(I) thiophene-2-carboxylate (CuTC) in 1-methylpyrrolidin-2-one at 20 °C. Solution electrochemical and UV-VIS spectroscopic studies suggest that there is no significant through-bond interaction between the two TTF units in these systems. The X-ray crystal structures are reported for 4,5,5′,5″,4‴,5‴-hexakis(methylsulfanyl)-4′,4″-bitetrathiafulvalene **9** and a semiconducting 1 : 1 perchlorate salt of 4,5:4‴,5‴-bis(ethylenedithio)-5′,5″-dimethyl-4′,4″-bitetrathiafulvalene $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO_4}^-$. The torsion angle around the central bond is 89° in **9** and 77° in $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO_4}^-$. The crystal packing of $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO_4}^-$ is characterised by puckered layers, parallel to the (001) plane, of cations contacting *via* their sulfur atoms; the anions occupy infinite channels, parallel to the *z*-axis and running through the cation motif.

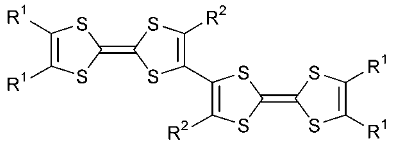
New derivatives of tetrathiafulvalene (TTF)[1] continue to be of paramount importance for the study of crystalline charge-transfer complexes and radical ion salts which are relevant to the development of molecular organic metals[2] and other areas of materials chemistry.[3] The control of molecular stacking (the supramolecular architecture) by means of chemical modification of the TTF molecule remains a major challenge.[4] In this context, dimeric TTF systems[5] afford a means of controlling the juxtaposition of neighbouring TTF molecules in the solid state (and, perhaps, ultimately the band filling of one- and two-dimensional organic conductors[6]) by varying the structure of the linking group. The solution electrochemical properties of bi(TTFs) provide information on the extent of any interaction between the various redox states of two TTF units. A large number of bi(TTF) derivatives are now known[5] in which the two TTF groups are separated by a variety of bridges, *e.g.* single atoms (chalcogens or phosphorus),[7] alkene and alkyne units,[8] aryl groups,[6a,9] trisulfide groups[10] and (most commonly) alkyl chains.[6c,11] It is notable that while many elaborate bi- and tri-TTF cyclophane and cage structures are known,[5b,5c,12] there are remarkably few reports of the simplest TTF dimers comprising the direct linkage of two TTF units, *i.e.* the bitetrathiafulvalene series.

The parent system **1** was first reported in a conference abstract in 1982 with no physical or experimental data.[13] Following contradictory reports on its properties (as collated elsewhere)[14] compound **1** was unequivocally synthesised by Becker *et al. via* a low-yielding (22%) Ullmann coupling of 4-iodo-TTF at 130–140 °C, which gave a mixture of products: the structure of **1** was confirmed (X-ray structural analysis) but its study was hampered by insolubility in organic solvents.[14] Prior to our work, multi-step, low-yielding syntheses of the more soluble derivatives **2**–**4**[15] and **5**[16] had been reported. The synthesis of new analogues, and the development of more efficient synthetic routes, were needed for more detailed studies on this under-explored family of bi(TTF) derivatives. We recently reported the synthesis of analogue **6** in 75% yield from 4-iodo-4′,5,5′-trimethyl-TTF.[17] Herein we extend this work to embrace a series of bi(TTF)s; we discuss their solution electrochemistry and report the crystal structures of **9** and the salt $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO_4}^-$.

Results and discussion

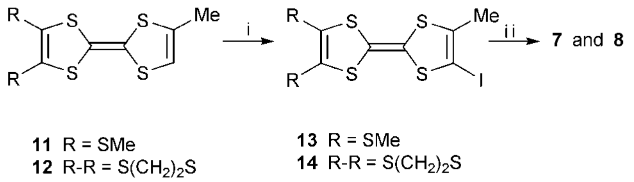
Synthesis

We initially explored the coupling of iodo-TTF derivatives as a route to new bi(TTF) systems. Lithiation of TTF derivatives **11**[18] and **12**[18] using lithium diisopropylamide (LDA) followed by iodination with perfluorohexyl iodide[19] afforded **13** and **14** in 65 and 45% yield, respectively (Scheme 1). Conversion of **13** and **14** into bi(TTF) derivatives **7** and **8** was acheived by the Ullmann coupling (copper in refluxing *N,N*-dimethylformamide) (60 and 62% yields, respectively) and for **13**, preferably, by reaction with copper(I) thiophene-2-carboxylate (CuTC) in 1-methylpyrrolidin-2-one at 20 °C[20] (80% yield). Insolubility of **14** prevented the analogous CuTC reaction. For the synthesis of the hexakis(methylsulfanyl)TTF derivative **9** we required the hitherto uncharacterised tris(methylsulfanyl)TTF **20**.[21] The stable thiol **15**,[22] which has been alkylated previously by Becher *et al.*[23] and Cava *et al.*[24] was readily converted into **16** which was "cross-coupled" with **17**[25] under standard conditions[26] in the presence of triethyl phosphite to afford TTF derivative **18** (59% yield, Scheme 2). Removal of the cyanoethyl protecting groups of **18**, using sodium methoxide, and methylation of the

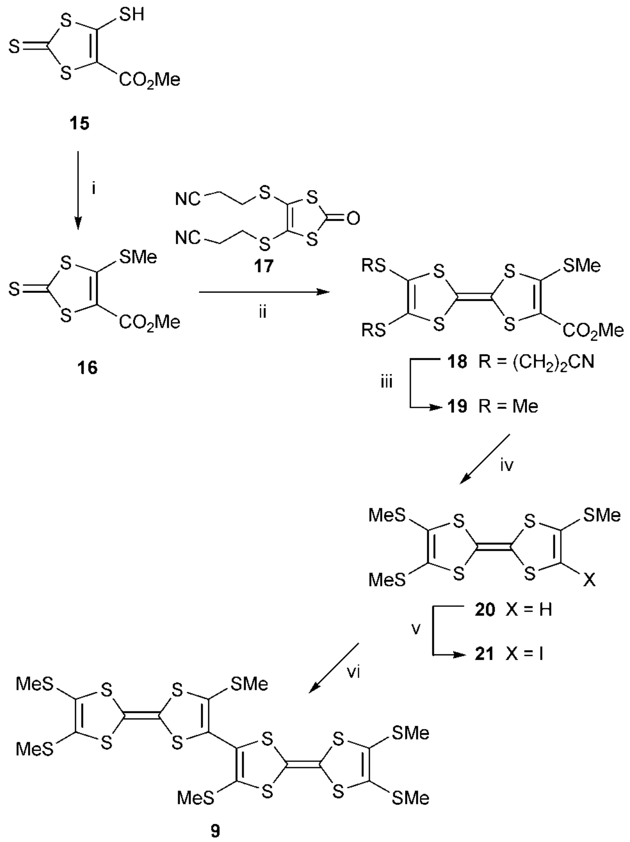


1 $R^1 = R^2 = H$
2 $R^1 = SMe$; $R^2 = H$
3 $R^1 = SBu$; $R^2 = H$
4 $R^1 = SHex$; $R^2 = H$
5 $R^1 = Me$; $R^2 = H$
6 $R^1 = R^2 = Me$
7 $R^1 = SMe$; $R^2 = Me$
8 $R^1\text{-}R^1 = S(CH_2)_2S$; $R^2 = Me$
9 $R^1 = R^2 = SMe$
10 $R^1\text{-}R^1 = O(CH_2)_2O$; $R^2 = H$

DOI: 10.1039/b000790k



Scheme 1 *Reagents and conditions*: i, LDA, Et_2O (for **11**) or THF (for **12**), −78 °C, then $CF_3(CF_2)_5I$; ii, Cu, DMF, reflux, or (for **13**) CuTC, NMP, 20 °C.



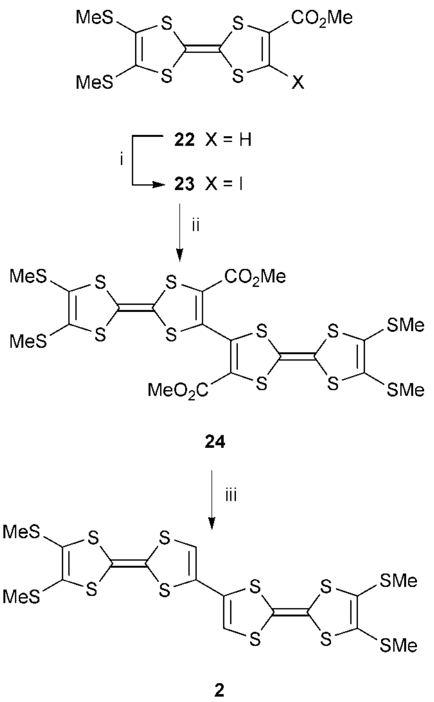
Scheme 2 *Reagents and conditions*: i, NaOMe, MeOH, then MeI, 20 °C; ii, $P(OMe)_3$, PhMe, reflux; iii, NaOMe, MeOH, THF, then MeI, 20 °C; iv, LiBr, DMF, 140 °C; v, LDA, Et_2O, −78 °C, then $CF_3(CF_2)_5I$; vi, CuTC, NMP, 20 °C.

transient dithiolate species with methyl iodide gave the tris(methylsulfanyl) derivative **19** (81% yield). Deesterification was readily achieved with lithium bromide in DMF at 140 °C[27] to give **20** (95% yield); lithiation–iodination of **20** gave **21** (91% yield) which underwent CuTC-mediated coupling to give the target bi(TTF) derivative **9** (72% yield).

These new bi(TTF) derivatives **7**–**9** all possess substituents at the carbon atoms adjacent to the linkage site, which, by analogy with **6**,[17] will prevent coplanarity of the two TTF systems. For comparison we wanted a derivative which was unsubstituted at these carbons. The literature routes to derivatives **1**–**5**[14–16] are inefficient (and **1** is known to be extremely insoluble[14]) so we explored alternative routes to **2** and **5**. Attempted coupling of 4-iodo-4′,5′-bis(methylsulfanyl)TTF or 4-iodo-4,5-dimethylTTF (both of which were synthesised by lithiation–iodination of the precursor TTF derivatives, by analogy with compound **13**)[28] using Ullmann conditions or the CuTC-mediated route gave complex product mixtures containing only small amounts of the desired bi(TTF) derivatives **2** and **5**, respectively. It appears, therefore, from our work herein and Becker's earlier synthesis of **1**,[14] that in the TTF series these coupling methodologies are practical (in terms of clean reactions and reasonable yield) only when there is a substituent adjacent to the iodo group. Accordingly, the readily-available compound **22**[29] was subjected to the lithiation–iodination protocol to afford **23**, albeit in only 24% yield (Scheme 3). This low yield (which contrasts with the efficient formation of **13**, **14** and **21**, above) is probably due to steric hindrance between the ester group and the electrophile in the lithiated intermediate, rather than to inefficient lithiation.[30] Compound **23** coupled to yield **24** (65% yield) which was deesterified to afford the target compound **2** (59% yield). This sequence represents an alternative synthesis of **2** to that reported by Tatemitsu *et al.*[15a] Recently, Iyoda *et al.* have reported a different synthesis of **10**, from the corresponding trimethylstannyl-TTF derivative.[31]

Solution electrochemical and UV-VIS spectroscopic data

An interesting aspect of bi(TTF) systems is the extent to which the two TTF units interact in solution in their neutral and charged states. We, therefore, studied the solution electrochemical and UV-VIS spectroscopic data for the new bi(TTF) systems **7**–**9**. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) data were consistent with those reported previously for analogous compounds, in that the first oxidation wave is split into two, single-electron waves ($E_2^{ox}-E_1^{ox}=ca.$ 70 mV) representing the sequential formation of the radical cation and diradical dication species, and the first oxidation is slightly positively shifted compared with the corresponding monomeric TTF. On scanning to more positive potentials a broadened two-electron wave is seen in the CV. For compound **6**[17] (but not for **7**–**9**) this third wave is resolved in the DPV into two, closely overlapping waves (with $E_4^{ox}-E_3^{ox}=30$ mV). The DPV of **7** is shown in Fig. 1, and values of the oxidation potentials for **6**[17] and **7**–**9** as measured by DPV are collated in Table 1. For the parent system **1** (in acetonitrile at 70 °C!) Becker *et al.* reported four distinct one-electron waves in the CV,[14] although Iyoda *et al.* have subsequently reported two, two-electron waves (in benzonitrile at 20 °C).[32] Both Becker *et al.*[14] and Tatemitsu *et al.*[15] assume coplanarity of the two TTF units of **1**[14] and **2**–**4**[15] and the formation of stable cation radicals which are delocalised over the whole molecule. However, this splitting of the first wave seen for all bitetrathiafulvalenes could occur regardless of any through-



Scheme 3 *Reagents and conditions*: i, LDA, THF, −78 °C, then $CF_3(CF_2)_5I$, 20 °C; ii, CuTC, NMP, 20 °C; iii, LiBr, DMF, 140 °C.

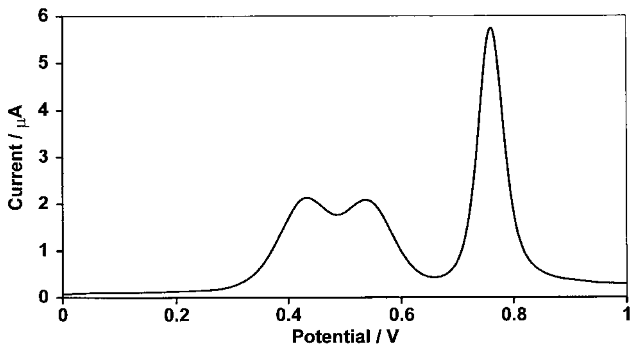


Fig. 1 DPV of compound **7** (for conditions see Experimental section).

bond interactions, because of a through-space coulombic repulsion.

If the two TTF units in the dimers are interacting intramolecularly then a red shift in the UV-VIS spectra might be expected. Table 2 collates these data for a series of bi(TTF)s and the model compounds TTFMe$_3$,[33] TTFSMe$_4$ and TTF.[34] A general trend is that dimers **2**, **4** and **6**–**8** do display a small red shift of one or more of their absorptions with the largest shifts being in the longer wavelength absorption (typically 20–30 nm). These results imply that the dimers possess a more delocalised π-system but this is not reflected in a lower first oxidation potential compared to their monomeric counterparts; rather, as noted above, the dimers are slightly harder to oxidise. To achieve such extended π-systems across the two TTF moieties would require their coplanarity, as seen in the crystal structure of compound **1**.[14] Any such orbital delocalisation will be disrupted in **6**–**9** by the substituents α to the ring junction. It is significant, therefore, that compound **2** (with no α substituent to hinder coplanarity) and compound **9** [with bulky SMe α substituents, and presumably a twisted structure in solution, as observed in the solid state (see below)] display very similar UV-VIS spectra. This would suggest that there is no significant through-bond interaction between the two TTF moieties in this series of compounds. This conclusion from our experimental data is consistent with theoretical calculations that the coefficients of the HOMO on the peripheral carbons of TTF are small,[6c,35] so through-bond interactions in bi(TTF)s should be negligible.[6c] These systems are, therefore, distinct from extended and vinylogous TTFs[36] and bis-fused derivatives,[2b] which possess extensive conjugation.

X-Ray crystal structures of 8 and $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO}_4^-$

The molecule of **9** (Fig. 2) possesses no crystallographic symmetry. The methylsulfanyl substituent S(5)C(8)H$_3$ is disordered over two positions A and B with occupancies of 62 and 38%, respectively. The conformations of the two TTF moieties are significantly different: one adopts a boat conformation, folding along the S(11)···S(12) and S(13)···S(14) vectors by 21° and 25°, respectively; the other is folded only along the S(3)···S(4) vector, by 9°. The torsion angle around the central C(2)–C(12) bond is 89° (*cf.* 54° in **6**[17]) due to the bulky methylsulfanyl substituents, all of which adopt out-of-planar conformations, with torsion angles in the range 100–164°.

Crystals of $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO}_4^-$ suitable for X-ray analysis were obtained by electrocrystallisation under constant current conditions. To our knowledge the only other crystal structure of a cation radical salt of a bitetrathiafulvalene derivative is $\mathbf{10}^{+\cdot}\cdot\mathrm{ClO}_4^-$.[31] In the structure of $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO}_4^-$ the cation radical (Fig. 3) is located on a twofold axis, passing through the midpoint of the C(2)–C(2′) bond. The twist around this bond is 77° (*cf.* coplanarity of the two TTF moieties in $\mathbf{10}^{+\cdot}\cdot\mathrm{ClO}_4^-$).[31] Both TTF moieties in $\mathbf{8}^{+\cdot}$ adopt a slight boat-like folding by *ca.* 9° along the S(1)···S(2) and S(3)···S(4) vectors. The peripheral ethylenedithio bridges adopt an envelope conformation, folding by 57° along the S(5)···C(9) vector. In the anion (Fig. 3) the O(1) atom lies on a twofold axis, while every other atom is disordered over two positions, related by this axis. The precision of the structure is insufficient to discuss bond distances. Atomic displacement parameters and large residual electron density may be indicative of some disorder in the cation as well. The crystal packing of $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO}_4^-$ (Fig. 4) is characterised by puckered layers, parallel to the (001) plane, of cations contacting *via* their sulfur atoms; these S···S distances (3.57–3.66 Å) are close to standard van der Waals contacts (3.60–3.68 Å).[37] The anions occupy infinite channels, parallel to the *z*-axis and running through the cation motif. The salt is a semiconductor: the conductivity, measured by a standard two-probe compressed pellet method,[38]was $\sigma_{\mathrm{rt}} = 1.6 \times 10^{-3}$ S cm^{-1}.

Other crystalline semiconducting charge-transfer complexes and salts which were isolated are given in the Experimental section, but none was suitable for X-ray analysis.

Conclusions

A range of bi(TTF) derivatives comprising directly-linked TTF units has been synthesised. The solution electrochemical and UV-VIS spectroscopic data suggest that there is very little intramolecular interaction between the two TTF moieties, in accord with previous theoretical calculations on bi(TTF)s.[6c] The salt $\mathbf{8}^{+\cdot}\cdot\mathrm{ClO}_4^-$ represents a very rare example of a crystalline cation radical salt in this series. It is notable that a 1 : 1 stoichiometry has been observed for perchlorate salts of both the twisted bi(TTF) **8** and for the planar analogue **10**.[31] This stoichiometry (*i.e.* 2 TTF moieties : 1 anion) provides a band which is 3/4 filled, and is especially favourable for the formation of organic superconductors (*e.g.* the famous TMTSF and BEDT-TTF series).[39] These results should encourage further studies directed towards stoichiometry control in conducting radical ion salts of bi(TTF) systems.

Experimental

General

All reactions were carried out under a blanket of argon which was dried by passage through a column of phosphorus pentoxide. All reaction solvents were dried and distilled immediately before use using standard procedures. Anhydrous dimethylformamide and 1-methylpyrrolidin-2-one were obtained directly from Aldrich. ^{1}H and ^{13}C NMR spectra were obtained on Varian Unity 300, Oxford 200 and Varian VXR 400 spectrometers; chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS) as an internal reference (0 ppm). Mass spectra were recorded on a Micromass Autospec

Table 1 DPV of TTF derivatives. For details of conditions see the Experimental section.

Compound	E_1^{ox}/mV	E_2^{ox}	E_3^{ox}	E_4^{ox}	$E_2^{ox}-E_1^{ox}$	$E_4^{ox}-E_3^{ox}$
6	380	456	750	780	76	30
7	466	540	770 (2e)	—	74	—
8	544	631	917 (2e)	—	87	—
9	529	596	770 (2e)	—	67	—

Table 2 UV-VIS spectroscopic data for bi(TTF) derivatives and model TTFs.

Compound	λ/nm (log ε)	λ/nm (log ε)	λ/nm (log ε)	λ/nm (log ε)	λ/nm (log ε)
1[a,b,14]	—	320	—	412	—
2[c]	264 (4.26)	312 (4.29)	328 (4.28)	412 (3.99)	—
4[d,15b,c]	—	316 (4.45)	330 (4.47)	415 (4.00)	—
6[e]	230 (4.41)	326 (4.80)	334 (4.65)	390 (4.08)	473 (3.38)
7[c]	250 (5.14)	314 (5.24)	336 (5.26)	392 (4.70)	494 (3.47)
8[f]	—	316 (4.99)	340 (4.90)	386 (4.30)	—
9[c]	264 (5.34)	312 (5.35)	334 (5.32)	412 (4.71)	—
11[c]	272 (5.14)	302 (5.21)	324 (5.21)	378 (4.60)	450 (3.90)
12[c]	—	312 (5.14)	334 (5.04)	368 (4.47)	—
TTF[e,33]	308 (4.08)	316 (4.09)	357 (sh)	446 (2.42)	—
$TTFMe_3$[e,32]	222 (3.88)	297 (4.25)	307 (4.23)	322 (4.20)	467 (3.25)
$TTFSMe_4$[c]	260 (5.36)	312 (5.33)	334 (5.33)	380 (4.75)	

[a]In toluene. [b]No value for ε given. [c]In DCM. [d]In chloroform. [e]In MeCN. [f]In 1,1,2-trichloroethane.

spectrometer operating at 70 eV with the ionisation mode as indicated. Melting points were recorded on a Reichert-Kofler hot-stage microscope and are uncorrected. Electronic absorption spectra were obtained on a Unicam UV-2 instrument operating with 1 cm quartz cells. Elemental analyses were obtained on a Carlo-Erba Strumentazione instrument. Column chromatography was carried out using Prolabo silica (70–230 mesh). Solvents were distilled prior to use for chromatography, with the exception of dichloromethane which was used as supplied. CV and DPV data were measured using a BAS CV50 electrochemical analyser with internal resistance compensation. Experiments were performed in a one-compartment cell with platinum working and counter electrodes and aqueous Ag/AgCl as reference, using 5 cm^3 of *ca.* 10^{-4} M solution of the donor in an anhydrous and degassed 0.1 M solution of tetrabutylammonium hexafluorophosphate (Fluka, puriss.) as the supporting electrolyte in the solvent system specified. For CV experiments the scan rate was 100 mV s^{-1}; for DPV the sample width was 8 ms, pulse amplitude 50 mV, pulse width 20 ms, pulse period 200 ms. Potentials have been corrected *vs.* the decamethylferrocene redox couple.[40]

4-Iodo-5-methyl-4′,5′-bis(methylsulfanyl)tetrathiafulvalene 13

Compound **11**[18] (600 mg, 1.93 mmol) was dissolved in diethyl ether (75 cm^3). The solution was cooled to −78 °C and lithium diisopropylamide (LDA) (1.5 M in cyclohexane) (1.4 cm^3, 2.15 mmol) was added dropwise over 2 min. The reaction was stirred at −78 °C for 3 h then perfluorohexyl iodide (0.83 cm^3, 3.8 mmol) was added and the reaction was allowed to reach 20 °C overnight. The mixture was concentrated *in vacuo* and the residue was dissolved in toluene (100 cm^3); the extract was washed with water (3 × 100 cm^3) and dried ($MgSO_4$). Purification by column chromatography on silica gel (eluent: hexane–toluene 5 : 1, v/v) followed by recrystallisation from dichloromethane–hexane gave **13** (550 mg, 65%) as red crystals; mp 89–90 °C (Analysis found: C, 24.95, H, 1.95%; $C_9H_9IS_6$ requires: C, 24.76, H, 1.95%); *m*/*z* (CI) 437 (MH^+, 100%), 312 (60), 195 (12); δ_H ($CDCl_3$) 2.41 (6 H, s), 2.07 (3 H, s); ν_{max} (KBr) 1284, 918, 880, 771, 713 cm^{-1}; CV (MeCN): $E_1^{1/2}$ 0.46, $E_2^{1/2}$ 0.72 V.

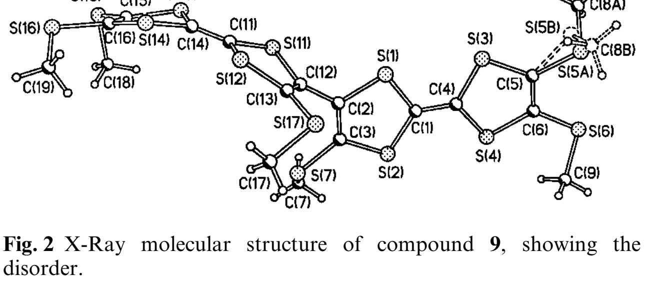


Fig. 2 X-Ray molecular structure of compound **9**, showing the disorder.

4-Iodo-5-methyl-4′,5′-ethylenedithiotetrathiafulvalene 14

By analogy with the preparation of **13**, compound **12**[18] (600 mg, 1.95 mmol) dissolved in tetrahydrofuran (60 cm^3) reacted with LDA (1.5 M in cyclohexane) (1.43 cm^3, 2.15 mmol) and perfluorohexyl iodide (0.86 cm^3, 4.0 mmol). Workup as described for **13**, followed by column chromatography on silica gel (eluent: hexane–toluene 3 : 1, v/v) and then recrystallisation from benzonitrile gave **14** (380 mg, 45%) as dark red crystals; mp 143 °C (decomp.) (Analysis found: C, 25.09, H, 1.58%; $C_9H_7IS_6$ requires: C, 24.88, H, 1.62%); *m*/*z* (EI) 434 (M^+, 100%); δ_H (DMSO-d_6) 3.37 (3 H, s), 2.04 (4 H, s); ν_{max} (KBr) 1284, 918, 880, 771, 713 cm^{-1}; CV (PhCN): $E_1^{1/2}$ 0.44, $E_2^{1/2}$ 0.78 V.

4,5,4‴,5‴-Tetrakis(methylsulfanyl)-5′,5″-dimethyl-4′,4″-bitetrathiafulvalene 7

Compound **13** (200 mg, 0.46 mmol) was dissolved in 1-methylpyrrolidin-2-one (5 cm^3). Copper(I) thiophene-2-carboxylate[20] (263 mg, 1.3 mmol) was added and the mixture was stirred for 1 h at 20 °C, then diluted with ethyl acetate (100 cm^3). A solution of 15% aqueous ammonia was added until a clear blue aqueous layer had formed. This layer was extracted with ethyl acetate (50 cm^3). The organic extracts were combined and washed sequentially with water (2 × 100 cm^3), brine (1 × 100 cm^3), dried ($MgSO_4$) and the solvent removed *in vacuo*. Recrystallisation from dichloromethane–hexane afforded **7** as yellow crystals (115 mg, 80%) mp 109–111 °C (Analysis found: C, 34.63, H, 2.82%; $C_{18}H_{18}S_{12}$ requires: C, 34.92, H, 2.93%; *m*/*z* (EI) 618 (M^+, 100%), 380 (92), 230 (85), 198 (73); δ_H ($CDCl_3$) 2.41 (12 H, s), 1.97 (6 H, s); δ_C ($CDCl_3$) 132.3, 127.8, 127.2, 118.0, 112.3, 107.6; ν_{max} (KBr) 1577, 1422, 1143, 961, 888, 777 cm^{-1}; DPV (CH_2Cl_2) E^{ox} 0.466, 0.540, 0.770 (2e) V.

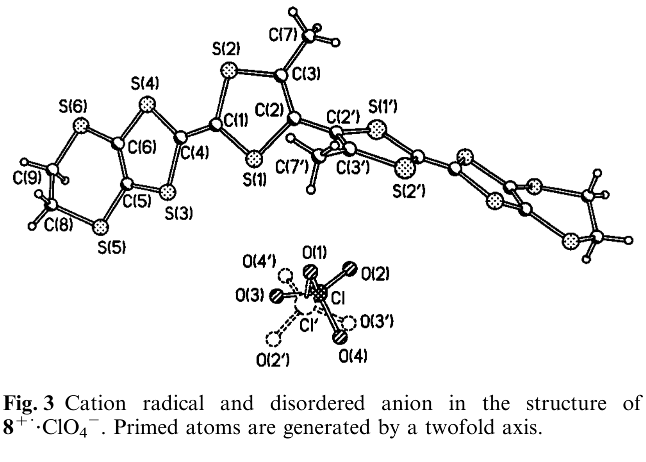


Fig. 3 Cation radical and disordered anion in the structure of $8^{+\cdot}\cdot ClO_4^-$. Primed atoms are generated by a twofold axis.

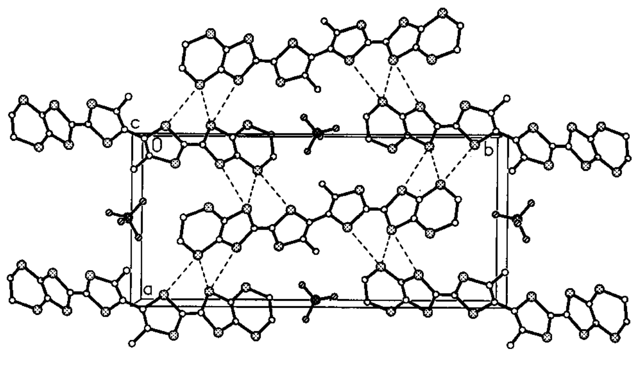


Fig. 4 Crystal packing of **8**$^{+\bullet}$·ClO$_4^-$, showing inter-cation S···S contacts of 3.57–3.61 Å. The anion disorder is omitted.

4,5:4‴,5‴-Bis(ethylenedithio)-5′,5″-dimethyl-4′,4″-bitetrathiafulvalene 8

Copper powder (290 mg, 4.6 mmol) was added to a solution of compound **14** (200 mg, 0.46 mmol) in DMF (15 cm^3). The mixture was refluxed for 3 h, then diluted with toluene (100 cm^3) and filtered through a bed of Celite with washings of hot toluene. The filtrate was washed with water (3 × 200 cm^3), the organic layer was separated and dried (MgSO$_4$), and evaporated *in vacuo*. Recrystallisation from toluene afforded **8** as orange crystals (87 mg, 62%); mp 220 °C (decomp.) (Analysis found: C, 35.17, H, 2.30%; $C_{18}H_{14}S_{12}$ requires: C, 35.15, H, 2.29%); *m/z* (EI) 618 (M$^+$, 100%); δ_H (CDCl$_3$) 2.41 (8 H, s), 1.97 (6 H, s); δ_C (CDCl$_3$) 132.3, 127.8, 127.2, 118.0, 112.3, 107.6; ν_{max} (KBr) 1579, 1145, 775 cm^{-1}. DPV (CH$_2$Cl$_2$) E^{ox} 0.544, 0.631, 0.917 (2e) V.

4-Methoxycarbonyl-5-methylsulfanyl-4′,5′-bis(2-cyanoethylsulfanyl)tetrathiafulvalene 18

4,5-Bis(2′-cyanoethylsulfanyl)-1,3-dithiole-2-thione **17**[25] (1.21 g, 4.2 mmol) and compound **16**[23,24] (1.0 g, 4.2 mmol) were suspended in toluene (30 cm^3). Triethyl phosphite (15 cm^3) was added and the mixture was refluxed for 90 min. The toluene was removed *in vacuo* and methanol (200 cm^3) was added to the residue. The precipitated solid was filtered and washed with methanol (3 × 50 cm^3). The crude product was purified by column chromatography on silica gel eluting initially with dichloromethane and then with dichloromethane–ethyl acetate (98 : 2, v/v). The second orange fraction was isolated and recrystallised from chloroform–methanol to give **18** (1.2 g, 59%) as an orange powder; mp 124–125 °C (Analysis found: C, 37.48, H, 2.86, N, 5.77%; $C_{15}H_{14}N_2O_2S_7$ requires: C, 37.63, H, 2.94, N, 5.85%); *m/z* (EI) 478 (M$^+$, 66%), 250 (66), 130 (80), 88 (100); δ_H (CDCl$_3$) 3.79 (3 H, s), 3.08 (4 H, t, $J = 7$ Hz), 2.73 (4 H, t, $J = 7$ Hz), 2.59 (s, 3 H); δ_C (CDCl$_3$) 160.3, 148.2, 128.5, 127.5, 117.4, 117.3, 113.1, 112.6, 107.9, 52.4, 31.3, 31.2, 18.9, 18.8, 18.2; ν_{max} (KBr) 2949, 1685, 1493, 1427, 1254, 1084 cm^{-1}.

4-Methoxycarbonyl-4′,5,5′-tris(methylsulfanyl)tetrathiafulvalene 19

Sodium methoxide (305 mg, 5.65 mmol) was added to a mixture of anhydrous methanol–THF (1 : 3, v/v, 50 cm^3) at 20 °C. Compound **18** (900 mg, 1.88 mmol) was added and the reaction was stirred for 30 min at 20 °C until a deep red colour had developed. Methyl iodide (0.47 cm^3, 7.52 mmol) was then added, after which the reaction was stirred for a further 15 min. The solvents were removed *in vacuo* and the residue was dissolved in dichloromethane (100 cm^3). The extract was washed with water (3 × 100 cm^3) and dried (MgSO$_4$), and the solvent removed *in vacuo*. Purification by column chromatography on silica gel (eluent: dichloromethane) followed by recrystallisation from chloroform–methanol gave **19** (610 mg, 81%) as a pink powder; mp 86–88 °C (Analysis found: C, 32.74, H, 2.96%; $C_{11}H_{12}O_2S_7$ requires: C, 32.97, H, 3.01%); *m/z* (EI) 400 (M$^+$, 21%), 385 (5), 57 (100); δ_H (CDCl$_3$) 3.72 (3 H, s), 2.53 (3 H, s), 2.35 (6 H, s); ν_{max} (KBr) 1695, 1492, 1427, 1248, 1083 cm^{-1}.

4′,5,5′-Tris(methylsulfanyl)tetrathiafulvalene 20

Compound **19** (250 mg, 0.63 mmol) was dissolved in *N,N*-dimethylformamide (10 cm^3). Lithium bromide (1.08 g, 0.0125 mol) was added and the mixture was heated at 140 °C for 90 min. After cooling, the reaction was diluted with brine (100 cm^3), and extracted with dichloromethane (2 × 50 cm^3). The organic extracts were combined and washed with brine (3 × 100 cm^3) and dried (MgSO$_4$). Removal of the solvent *in vacuo* gave **20** (200 mg, 95%) as a deep red oil; *m/z* (EI) 342 (M$^+$, 100%), 327 (43), 192 (58); δ_H (CDCl$_3$) 6.27 (1 H, s), 2.40 (9 H, s); δ_C (CDCl$_3$) 128.7, 127.3, 119.2, 114.7, 108.4, 19.4, 19.1; CV (MeCN): $E_1^{1/2}$ 0.45, $E_2^{1/2}$ 0.73 V.

4-Iodo-4′,5,5′-tris(methylsulfanyl)tetrathiafulvalene 21

To a suspension of compound **20** (935 mg, 2.73 mmol) in diethyl ether (100 cm^3) at −78 °C, LDA (1.5 M in cyclohexane) (2.0 cm^3, 3 mmol) was added dropwise over 3 min to form a thick yellow precipitate. The reaction was stirred at −78 °C for 3 h then perfluorohexyl iodide (1.18 cm^3, 5.46 mmol) was added and the reaction was allowed to reach 20 °C overnight. The reaction was diluted with water (100 cm^3) and extracted with toluene (3 × 50 cm^3). The organic extracts were combined and washed sequentially with water (2 × 100 cm^3), brine (1 × 100 cm^3) and dried (MgSO$_4$). Removal of the solvents *in vacuo* and recrystallisation from dichloromethane–hexane gave **21** (1.16 g, 91%) as an orange powder; mp 60–61 °C (Analysis found: C, 23.00, H, 1.93%; $C_9H_9IS_7$ requires: C, 23.07, H, 1.93%); *m/z* (EI) 468 (M$^+$, 98%), 254 (77), 128 (100); δ_H (CDCl$_3$) 2.42 (9 H, s); δ_C (CDCl$_3$) 130.5, 127.5, 127.4, 114.5, 111.1, 71.6, 19.24, 19.23, 19.21; ν_{max} (KBr) 1416, 1307, 974, 897, 766 cm^{-1}; CV (MeCN): $E_1^{1/2}$ 0.50, $E_2^{1/2}$ 0.73 V.

4,5,5′,5″,4‴,5‴-Hexakis(methylsulfanyl)-4′,4″-bitetrathiafulvalene 9

By analogy with the preparation of **7**, compound **21** (200 mg, 0.43 mmol), NMP (5 cm^3) and CuTC (244 mg, 1.28 mmol) gave a crude product which was dissolved in a small amount of CH$_2$Cl$_2$, filtered through a plug of silica and recrystallised from dichloromethane–hexane to give **9** (106 mg, 72%) as an orange powder; mp 160–161 °C (Analysis found: C, 31.38, H, 2.65%; $C_{18}H_{18}S_{14}$ requires: C, 31.64, H, 2.65%); *m/z* (EI) 682 (M$^+$, 77%), 444 (100), 207 (49); δ_H (CDCl$_3$) 2.42 (18 H, s); δ_C (CDCl$_3$) 131.2, 127.7, 127.2, 122.8, 110.8, 110.7, 19.6, 19.2; ν_{max} (KBr) 1420, 954, 885, 771 cm^{-1}. DPV (CH$_2$Cl$_2$) E^{ox} 0.529, 0.596, 0.770 (2e) V.

4-Methoxycarbonyl-5-iodo-4′,5′-bis(methylsulfanyl)tetrathiafulvalene 23

By analogy with the preparation of **14**, compound **22**[29] (a red solid, mp 72 °C; lit. mp[29] not given) (1.0 g, 2.8 mmol) in THF (100 cm^3), LDA (1.5 M in cyclohexane) (2.07 cm^3, 3.1 mmol) and perfluorohexyl iodide (1.25 cm^3, 5.6 mmol) gave a crude product which was dissolved in dichloromethane (100 cm^3) washed with water (3 × 100 cm^3) and dried (MgSO$_4$), and the solvent removed *in vacuo*. Purification by column chromatography on silica gel (eluent: hexane–dichloromethane (2 : 1, v/v) followed by recrystallisation from dichloromethane–hexane gave **23** (330 mg, 24%) as red crystals; mp 89–90 °C (Analysis found: C, 25.07, H, 1.90%; $C_{10}H_9IO_2S_6$ requires: C, 25.00, H, 1.88%); *m/z* (EI) 480 (M$^+$, 63%), 330 (17), 44 (100); δ_H (CDCl$_3$)

3.82 (3 H, s), 2.41 (6 H, s); $\nu_{\max}$ (KBr) 1722, 1712, 1518, 1282, 1236, 1065 cm^{-1}; CV (MeCN): $E_1^{1/2} = 0.57$, $E_2^{1/2} = 0.82$ V.

5′,5″-Bis(methoxycarbonyl)-4,5,4‴,5‴-tetrakis(methylsulfanyl)-4′,4″-bitetrathiafulvalene 24

As described for the preparation of **7**, compound **23** (140 mg, 0.29 mmol), NMP (5 cm^3) and CuTC (167 mg, 0.87 mmol) gave a crude product which was purified by column chromatography on silica gel (eluent: hexane–dichloromethane 2 : 1, v/v) followed by recrystallisation from CH_2Cl_2–MeOH to give **24** (67 mg, 65%); mp 168–170 °C (Analysis found: C, 33.97, H, 2.56%; $C_{20}H_{18}O_4S_{12}$ requires: C, 33.90, H, 2.56%); *m/z* (CI) 708 (MH$^+$, 100%); δ_H ($CDCl_3$) 3.77 (6 H, s), 2.42 (12 H, s); δ_C ($CDCl_3$) 131.2, 127.8, 127.3, 122.9, 110.9, 110.8, 19.6, 19.2; $\nu_{\max}$ (KBr) 1716, 1703 cm^{-1}.

4,5,4‴,5‴-Tetrakis(methylsulfanyl)-4′,4″-bitetrathiafulvalene 2

To a solution of compound **24** (40 mg, 5.6×10^{-5} mol) in DMF (10 cm^3) lithium bromide (430 mg, 5 mmol) was added and the mixture was heated at 140 °C for 90 min. After cooling, the reaction was diluted with brine (100 cm^3), and extracted with dichloromethane (2×50 cm^3). The organic extracts were combined and washed with brine (3×100 cm^3) and dried ($MgSO_4$). The solution was then filtered through a plug of silica (eluent: dichloromethane). Removal of the solvent *in vacuo* gave **2** (20 mg, 95%) as a tan solid; mp 172 °C (lit.[15a] 172–173 °C); δ_H ($CDCl_3$) 6.22 (2 H, s), 2.42 (12 H, s).

Salt $\mathbf{8}^{+\cdot}\cdot ClO_4^-$

In a two compartment cell with platinum wire cathode and anode, a solution of **8** (1.4×10^{-4} mol l^{-1}) in anhydrous 1,1,2-trichloroethane containing Bu_4NClO_4 (1×10^{-1} mol l^{-1}) was electrolysed at a constant current of 2.5 mA at 20 °C. After 4 days, black shiny crystals of $\mathbf{8}^{+\cdot}\cdot ClO_4^-$ suitable for X-ray analysis were harvested from the anode; σ_{rt} (2-probe, compressed pellet) $= 1.6 \times 10^{-3}$ S cm^{-1}.

The following charge-transfer complexes (all 1 : 1 stoichiometry) were isolated by cooling hot acetonitrile solutions of the donor and acceptor moieties mixed in a 1 : 2 stoichiometric ratio. **6** : TCNQ ($\sigma_{rt} = 1.2 \times 10^{-2}$ S cm^{-1}); **6** : 2,5-Br_2TCNQ ($\sigma_{rt} = 9.0 \times 10^{-3}$ S cm^{-1}); **6** : F_4TCNQ ($\sigma_{rt} = 1.4 \times 10^{-3}$ S cm^{-1}); **8** : 2,5-Br_2TCNQ ($\sigma_{rt} = 8.7 \times 10^{-4}$ S cm^{-1}). The salt $\mathbf{6}^{+\cdot}\cdot ClO_4^-$ (stoichiometry unknown; $\sigma_{rt} = 3.2 \times 10^{-6}$ S cm^{-1}) was also isolated.

X-Ray crystallography†. X-Ray diffraction was carried out for **9** with a SMART 1K CCD area detector mounted on a 3-circle diffractometer (graphite-monochromated Mo-Kα radiation). Full sphere of reciprocal space was nominally covered by 5 sets of ω scans, each set at different ϕ and/or 2θ angles. Reflection intensities were integrated by the SAINT program.[41] A semi-empirical absorption correction[42] was based on intensities of Laue equivalents. For very poorly diffracting $\mathbf{8}^{+\cdot}\cdot ClO_4^-$ the experiment was performed on a Rigaku AFC6S 4-circle diffractometer (graphite-monochromated Cu-Kα radiation, $2\theta/\omega$ scan mode). The intensities were integrated and corrected for absorption (empirical method, on 72 ψ-scans of two reflections) using TEXSAN software.[43] The crystals were cooled using Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostats. Both structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[44] A conventional refinement of **9** converged with $R_1[F^2 \geqslant 2\sigma(F^2)] = 0.072$ and $\Delta\rho_{\max} = 1.03$ e Å^{-3}, showing indications of twinning with the twin law $h' = h, k' = -k, l' = -l - 2h/3$, *i.e.* almost perfect overlap of reflections with $|h| = 3n$. The twin refinement[45] gave the component contributions of 86.1 and 13.9(1)% and reduced R_1 by 3%. The crystal data and experimental details are listed in Table 3.

Table 3 Crystal data

Compound	**9**	$\mathbf{8}^{+\cdot}\cdot ClO_4^-$
Formula	$C_{18}H_{18}S_{14}$	$C_{18}H_{14}S_{12}ClO_4$
Formula weight	683.16	714.46
T/K	120	150
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (# 14)	$P2_12_12$ (# 18)
a/Å	8.374(3)	11.074(3)
b/Å	12.684(2)	24.139(7)
c/Å	26.295(3)	4.876(2)
β/°	96.20(1)	90
V/Å^3	2776.6(6)	1303.4(7)
Z	4	2
μ/mm^{-1}	1.10 (Mo-Kα)	10.5 (Cu-Kα)
Reflections measured	21201	1429
Unique reflections	5026	1277
R_{int}	0.032	0.061
R/data $I \geqslant 2\sigma(I)$	0.042/4639	0.128/893
$R(F^2)$, all data	0.119	0.407

Acknowledgements

We thank EPSRC for funding this work.

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