Dithiaheterocycle-annelated tetrathiafulvalene π-donors: a structure–property correlation study

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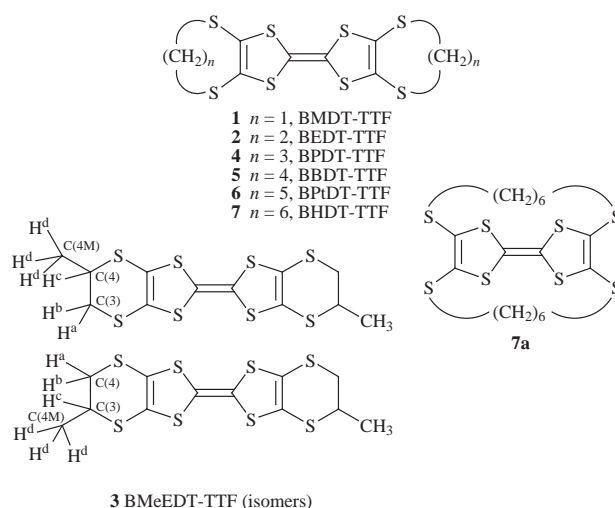[d] Department of Chemistry, Howard University, Washington, DC 20059, USA

Single-crystal X-ray structures of BEDT-TTF analogues 3, 6, 7 and 7a along with the preparation of a range of new cation-radical salts derived from these π-electron donors are reported. Physical properties (*i.e.* colour, cyclic voltammetry data and solid-state conductivities of the derived cation-radical salts) of the donors are discussed in terms of their crystal and molecular structures. The synthesis of compound 7 has been re-investigated. An efficient synthesis of both isomers 7 and 7a along with the other related TTF derivatives is presented. The crystal structure of the precursor thione 10 is also described.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **2** and related donors have yielded several superconducting cation-radical salts.[1] The study of structure–property correlations in these salts has established, among many other subtle factors, the importance of the conformation of the C_6S_8 core. In this context, several modifications have been made around the central C_6S_8 core. When the peripheral -$(CH_2)_2$- bridge in structure **2** is replaced with -(CH_2)- or -$(CH_2)_3$-, the resultant TTFs **1**[2] and **4**,[3] respectively, do not yield superconducting salts. Recently, we reported the synthesis and structure of compound **5** incorporating the bulkier -$(CH_2)_4$- bridge.[4] The unique feature of the structure was the very high planarity of the C_6S_8 core, which is non-planar in structure **2**. Shibaeva *et al.*[5] have shown that the TTF **5** yields cation-radical salt [(BBDT-TTF)$_2$Cl$_2$·H$_5$O$_2$], which is metallic up to 80 K.

In continuation of our studies, we recently reported the synthesis of TTFs **6** and **7** containing the -$(CH_2)_5$- and -$(CH_2)_6$- bridges, respectively, along with a modified synthesis of compound **3**.[6] Preliminary studies on these donors indicated compounds **3** and **6** to be quite similar to the TTF **2** in donor abilities, whereas compound **7** exhibited quite different colour, cyclic voltammogram and donor behaviour as compared with π-donors **1–6**. The unexpected physical and chemical properties of compound **7** could easily be interpreted in terms of its 'phane'-like isomer **7a**. However, based on the limited data available, a definite structure for the -$(CH_2)_6$-bridge product could not be assigned. Later on, a theoretical study of these systems revealed that, for a -$(CH_2)_6$- bridge, a 'phane'-like structure **7a** can be formed, though it would be less stable than structure **7** with 'D_{2h}' symmetry by ~10 kcal mol^{-1}.‡[,7]

In view of the interesting theoretical results, we thought it worthwhile to probe the structure of product **7** in more detail. However, in our hands the original preparation of compound **7** did not seem to proceed exactly as reported. Hence, it seemed sensible to probe the preparation more deeply and also to investigate further the possibility of preparing compound **7** by the tetrathiolate route.[8] In this paper the preparation and characterisation of both isomers **7** and **7a** along with related TTF derivatives are described. In addition this paper reports the crystal and molecular structures of compounds **3**, **6**, **7**, **7a** and **10**. The synthesis and characterisation of a range of cation-

1 n = 1, BMDT-TTF
2 n = 2, BEDT-TTF
4 n = 3, BPDT-TTF
5 n = 4, BBDT-TTF
6 n = 5, BPtDT-TTF
7 n = 6, BHDT-TTF

7a

3 BMeEDT-TTF (isomers)

radical salts derived from TTFs **3**, **5**, **6** and **7a** are also reported. A portion of this work has already appeared.[9]

Results and discussions

π-Donors **3**, **5** and **6** were prepared by following the procedures reported earlier.[4,6] A 300 MHz ^{1}H NMR spectrum of compound **3** showed it to be a mixture of isomers (*vide infra*). Two sets of resonances were observed for different protons in the ratio ~60:40. However, the coupling constants [^2J (H^a,H^b) 13.04 Hz, ^2J (H^a,H^c) 7.4 Hz, ^2J (H^b,H^c) 3.05 Hz, ^2J (H^c,Me) 6.75] for the sets were almost identical. The presence of the isomers was further confirmed by selective decoupling of H^a, H^b, H^c and Me protons. The chemical-shift-correlation (COSY) NMR spectrum revealed the magnetic inequality of protons H^a and H^b and the following connectivities: (i) H^c with H^a, H^b and H^d, (ii) H^a with H^b and H^c, (iii) H^b with H^a and H^c, (iv) H^d with H^c protons.

The preparation of compound **7** requires further comment. The synthesis of precursor thione **10** was carried out as reported previously *via* the coupling of 1,6-dibromohexane with the dithiolate synthon **9**[6] (Scheme 1). The reaction proceeded as reported to afford thione **10**, except that the melting point of the thione was 128 °C instead of the reported 158 °C. The structure of product **10** was unambiguously estab-
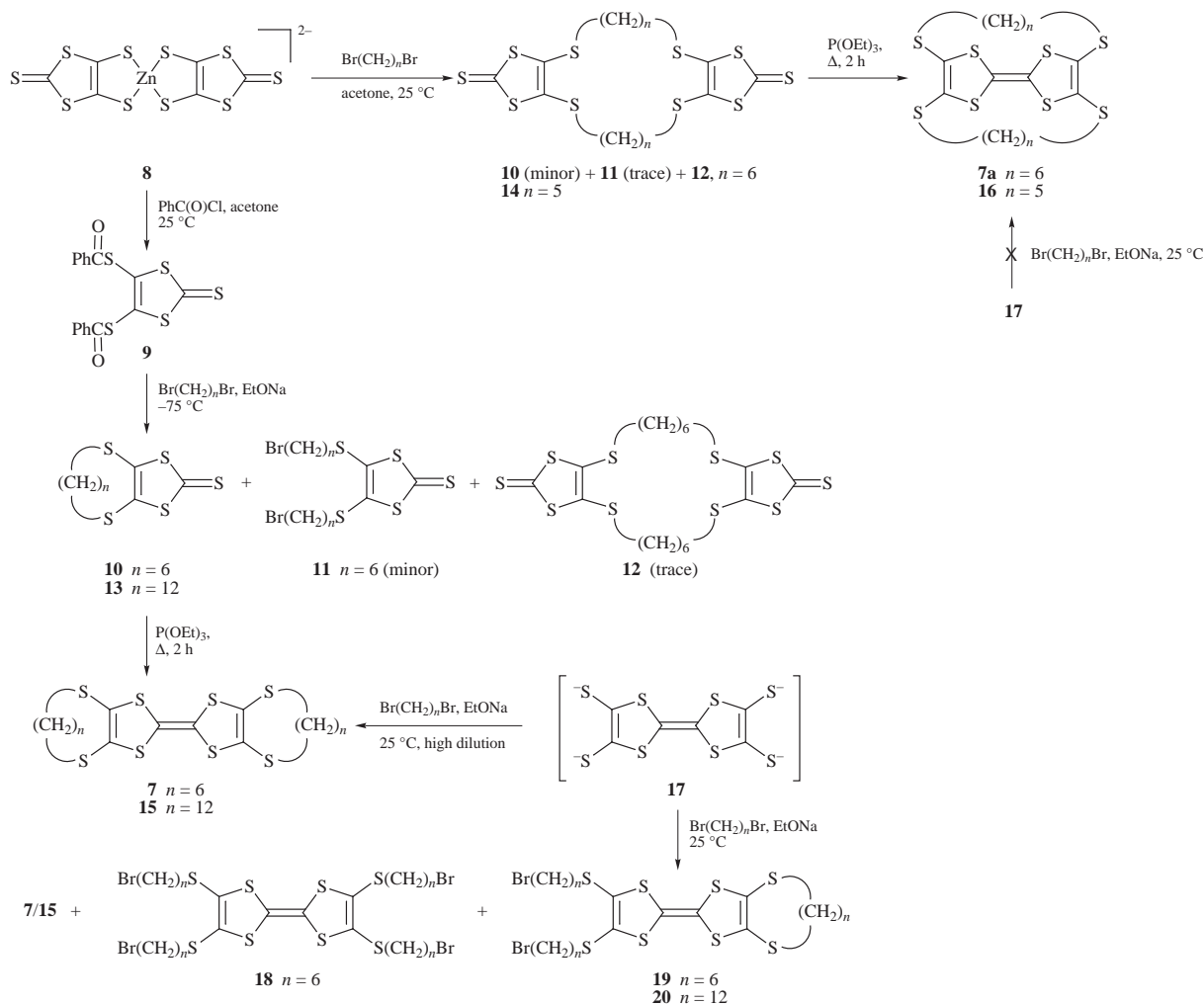
Scheme 1

lished by a single-crystal X-ray study (*vide infra*). The crude compound **10** was dissolved in chloroform by heating and was then column chromatographed on silica gel with hexane as an eluent to yield the thione **10** as the major product followed by the uncyclised thione **11** in minor amounts. Later on, by increasing the polarity of the eluting solvent system [hexane–ethyl acetate (90 : 10)] the dimeric thione **12** could be obtained in trace amounts. Similarly, 1,12-dibromododecane was treated with the dithiolate synthon **9** to give the thione **13**. No dimeric thione was isolated in this reaction.

All attempts to isolate the dimeric thione **12** in better yields by reaction of the dithiolate synthon **9** with 1,6-dibromohexane under high-dilution conditions afforded mainly compound **10** and negligible quantities of dimer **12**. However, a much better yield (30%) of the sparingly soluble dimeric thione **12** could be obtained by coupling of the 'zincate' synthon, [Zn(dmit)$_2$]$^{2-}$ **8**, with 1,6-dibromohexane. The reaction also gave the monomeric thione **10** in 7% yield along with the uncyclised thione **11** in 5% yield. Thiones **10** and **11** could easily be removed from dithione **12** by washing of the crude product with chloroform in which these are highly soluble. Thiones **10** and **11** were separated by column chromatography. In order to check the generality of the 'zincate' synthon route for the synthesis of dimeric thiones, 1,5-dibromopentane was allowed to react with [Zn(dmit)$_2$]$^{2-}$ **8** to afford the desired dimeric thione **14**.

The coupling reaction of thione **10** with triethyl phosphite afforded **7**. The identity of orange coloured product **7** was confirmed by ^{1}H NMR spectroscopy, which showed a multiplet at δ 2.84 corresponding to eight SCH$_2$ protons. The structure of compound **7** was unambiguously established by single-crystal X-ray determination (*vide infra*). Similarly thione **13** upon

reaction with neat triethyl phosphite yielded the corresponding TTF **15**. Coupling of the dimeric thione **12** with triethyl phosphite afforded the 'phane'-like TTF **7a**. The structure of compound **7a** was unambiguously established by single-crystal X-ray determination (*vide infra*). Similarly coupling of the dimeric thione **14** yielded the 'phane'-like TTF **16**. Recently, Otsubo and co-workers[10] have reported synthesis of the related quadruple-bridged 'TTF belt' with [CH$_2$C(Me$_2$)CH$_2$] spacer *via* dimeric coupling of the corresponding dimeric ketone. However, we have observed that for higher analogues, *i.e.* -(CH$_2$)$_5$- and -(CH$_2$)$_6$-, coupling of the precursor dimeric thiones **12** and **14** yielded the corresponding 'TTF-cage' compounds **7a** and **16**.

Attempts to prepare compound **7** by the tetrathiolate route,[8] *i.e.* by the reaction of tetrathiolate anion **17** with 1,6-dibromohexane, afforded the uncyclised TTF **18** and partially cyclised TTF **19** as the major products and the desired TTF **7** in only trace amounts. However, using high-dilution techniques, compound **7** could be obtained as the major product. TTF **15** could also be synthesised by high-dilution methods using the tetrathiolate anion synthon **17**. Normal dilution afforded the partially cyclised TTF **20** as the major product and the TTF **15** as minor product.
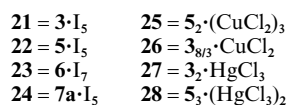
The cyclic voltammograms of TTFs **7**, **15**, **18** and **19** showed two single-electron, reversible redox waves while compounds **7a** and **16** showed only the second irreversible redox wave (Table 1). The cyclic voltammetry behaviour of compounds **7a** and **16** was similar to those reported by Mullen and co-workers[11] and Robert and co-workers[12] for related 'phane'-like TTFs. Kilburn *et al.*[13] have reported the observation of two reversible one-electron oxidation waves for some non-planar 'phane'-like TTFs.

Compound	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	$\Delta E^{1/2}$ (V)
BEDT-TTF **2**	0.455	0.875	0.420
7[b]	0.570	1.024	0.454
7a[b]		1.20	
15[b]	0.506	0.861	0.355
16[b]		1.19	
18[a]	0.490	0.935	0.445
19[a]	0.497	0.905	0.408

[a] Recorded *vs.* SCE, Pt electrode, scan rate 100 mV s^{-1}, 5×10^{-4} mol dm^{-3} compound, 0.1 mol dm^{-3} Bu$_4$N$^+$PF$_6^-$ in CH$_2$Cl$_2$. [b] Recorded *vs.* Ag/AgCl.

The cation-radical salts (**21–28**) of TTFs **3**, **5**, **6** and **7a** were obtained by chemical oxidation of the donors with CuCl$_2$, HgCl$_2$ and I$_2$. The obtained complexes are grey-black or black, crystalline and insoluble in non-polar solvents. The salts exhibited a broad electronic absorption extending to the IR region, indicating a partially oxidised state of the donors. For all the salts, the ESR spectra showed a symmetric singlet. The observed *g*-values are nearly equal to the free-electron value, suggesting that the signal was due to unpaired electrons. The ion-radical salts of **6** and **7a** with I$_2$, *i.e.* [(BPtDT-TTF)·I$_7$ **23**, (**7a**)·I$_5$ **24**] exhibited room temperature conductivities in the range of 10^{-6} S cm^{-1} and can be classified as insulators. The salts of donors with CuCl$_2$, *i.e.* [(BBDT-TTF)$_2$·(CuCl$_2$)$_3$ **25** and (BMeEDT-TTF)$_{8/3}$·(CuCl$_2$) **26**] did not show any signal due to Cu^{2+} ion, thus indicating the diamagnetic state of Cu. The room-temperature (rt) conductivities of these ion-radical salts were observed in the range 10^{-2}–10^{-7} S cm^{-1}. The TTF **7a** did not react with CuCl$_2$.

$$21 = 3 \cdot I_5 \qquad 25 = 5_2 \cdot (CuCl_2)_3$$
$$22 = 5 \cdot I_5 \qquad 26 = 3_{8/3} \cdot CuCl_2$$
$$23 = 6 \cdot I_7 \qquad 27 = 3_2 \cdot HgCl_3$$
$$24 = 7a \cdot I_5 \qquad 28 = 5_3 \cdot (HgCl_3)_2$$

The cation-radical salts of compound **3** with CuCl$_2$ and HgCl$_2$ [(BMeEDT-TTF)$_{8/3}$·(CuCl$_2$) **26**, (BMeEDT-TTF)$_2$·(HgCl$_3$) **27**] exhibited two-probe rt conductivities of 10^{-2} and 10^{-3} S cm^{-1}, respectively, which prompted us to study their conductivity behaviour as a function of temperature. The complexes showed different trends in conductivity upon lowering the temperature. Salt [(BMeEDT-TTF)$_{8/3}$·(CuCl$_2$) **26**] remains conducting down to ~100 K; below this temperature there is a phase change and the salt becomes semiconducting (Fig. 1). On the other hand, salt [(BMeEDT-TTF)$_2$·(HgCl$_3$) **27**] exhibited semiconducting behaviour down to ~130 K. On further cooling, it exhibited a transition to a metallic phase and remained metallic down to ~10 K (Fig. 2).

Crystal and molecular structure of compound 3
The structure of compound **3** has been reported earlier[9] and only a brief comparative description will be given here. The crystal and molecular structure of compound **3** is quite similar to that of analogue **2**[14] except for the expected disorder near the C(3)–C(4) region (see structure **3**). Occupancies of the C(3M) and C(4M) methyl atoms are 0.596(3) and 0.404(3) respectively. Molecule **3** is non-planar. Interestingly, the shortest S···S intermolecular distance [3.434(3) Å] is slightly shorter than that found in compound **2** [3.482(2) Å]. Some relevant parameters of compound **3** are compared with the related TTFs (Table 2).

Crystal and molecular structure of compound 6
The molecular structure of compound **6** is shown in Fig. 3. Details of the crystal data are given in Table 3. The molecular and crystal structure of compound **6** is quite similar to that of analogue **5**.[4c] Like structure **5**, molecule **6** is centrosymmetric and the asymmetric units consist of half a molecule which is attached to the remaining half by a centre of inversion. In the
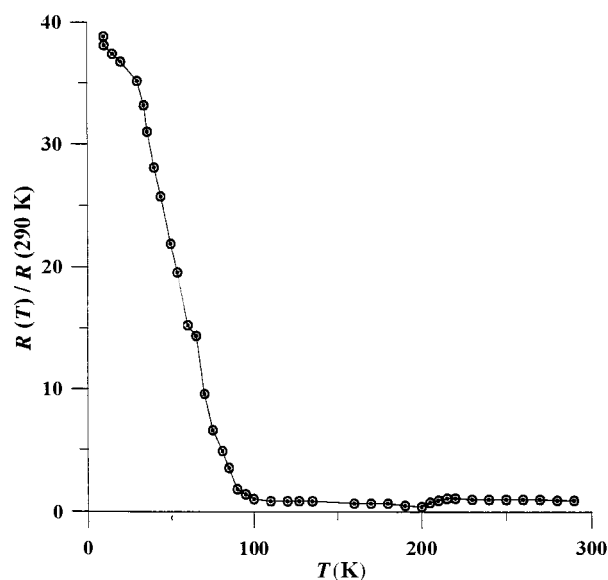
Fig. 1 Normalised resistance *vs.* temperature plot for compound **26**
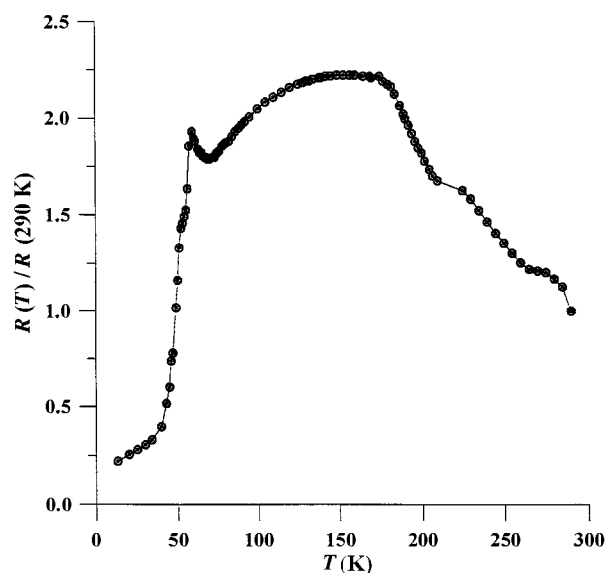
Fig. 2 Normalised resistance *vs.* temperature plot for compound **27**
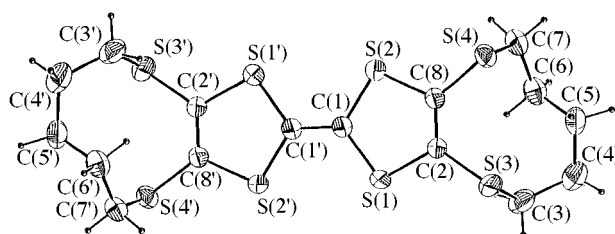
Fig. 3 Molecular structure of compound **6**

molecule, the C$_6$S$_8$ core is highly planar, S(1) deviating maximally by 0.0307 Å. However, in the nine-membered exterior ring, the atoms S(3), S(4), C(3), C(6) and C(7) form a plane (plane 1) with a maximum deviation of 0.034(3) Å whereas atoms C(4) and C(5) are out-of-plane by 1.061(3) and 1.260(3) Å, respectively. The dihedral angle between plane 1 and the C$_6$S$_8$ core is 84.3(2)°.

The molecules are stacked uniformly along the *a*-axis (Fig. 4). Similarly to compounds **2**, **3** and **5**, molecules of compound **6** are arranged in pairs in the crystal (Fig. 5). The intermolecular S···S contacts are close to sum of the van der Waals radii. These distances are 3.753(1) Å [S(1)···S(2′)] and 3.693(1) Å [S(2)···S(2′)]. These contacts are longer than those observed for compounds **2**, **3** and **5**.
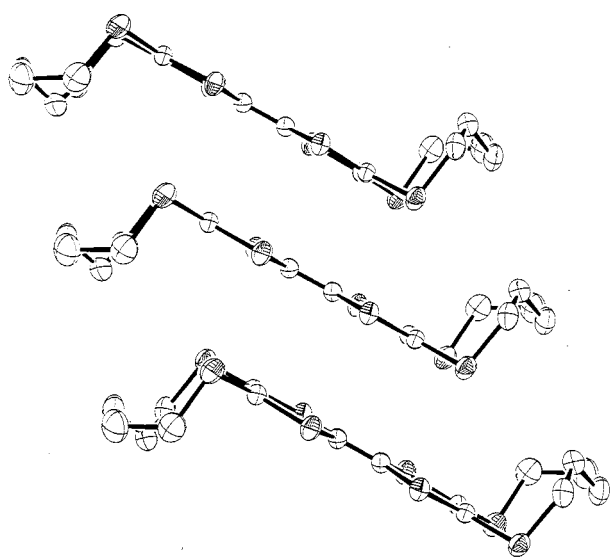
Table 2 Important structural parameters of TTFs **2**, **3**, **4**, **5**, **6**, **7** and **7a**
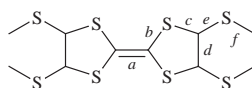
TTF	a (Å)	b (Å)	c (Å)	d (Å)	e (Å)	Shape of C_6S_8 core	Min. S···S distance	Ref.
2[a]	1.319	1.753	1.755	1.328	1.751	Tub	3.482	14
3	1.342(7)	1.754(5)	1.754(5)	1.342(8)	1.737(6)	Planar	3.434(3)	9
4	1.341(4)	1.761(3)	1.764(3)	1.335(4)	1.750(3)	Tub	3.615	3b
5	1.337(4)	1.761(2)	1.756(2)	1.341(2)	1.743(2)	Planar	3.668(1)	4c
6	1.342(4)	1.757(2)	1.753(2)	1.344(3)	1.750(2)	Planar	3.693(1)	This work
7	1.346(5)	1.756(3)	1.768(3)	1.346(4)	1.749(3)	Planar	3.766(2)	This work
7a	1.338(5)	1.768(3)	1.788(3)	1.343(4)	1.754(3)	Folded	—	This work

[a] Estimated standard deviations 0.007–0.012 Å.

Table 3 Crystal data and structure refinement details

Compound	6	7	7a	10
Empirical formula	$C_{16}H_{20}S_8$	$C_{18}H_{24}S_8$	$C_{18}H_{24}S_8$	$C_9H_{12}S_5$
Formula weight	468.81	496.85	496.85	280.49
Temperature (K)	296	293(2)	130(2)	293(2)
Wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2/c$	$P2_1/n$
Unit-cell dimensions (Å)				
a	5.022(1)	8.0783(12)	17.028(7)	5.3869(7)
b	13.036(1)	9.3235(13)	16.148(5)	9.4938(14)
c	15.579(2)	14.863(2)	16.996(5)	24.495(3)
Cell angles (°)				
β	95.08(1)	90.457(12)	109.10(2)	95.106(9)
Volume (Å³)	1015.9(3)	1119.4(3)	4416(3)	1247.8(3)
Z	2	2	8	4
Density (Mg m⁻³)	1.533	1.474	1.495	1.493
Absorption coefficient (mm⁻¹)	0.84	0.800	0.811	0.888
$2\theta_{range}$ (°)	4–50	5–55	5–50	5–55
Index ranges	$0 \leqslant h \leqslant 5$	$0 \leqslant h \leqslant 10$	$-19 \leqslant h \leqslant 20$	$-6 \leqslant h \leqslant 0$
	$0 \leqslant k \leqslant 15$	$0 \leqslant k \leqslant 12$	$-19 \leqslant k \leqslant 0$	$0 \leqslant k \leqslant 12$
	$-18 \leqslant l \leqslant 18$	$-19 \leqslant l \leqslant 19$	$-19 \leqslant l \leqslant 0$	$-31 \leqslant l \leqslant 31$
Reflections collected	2091	2734	7936	3129
Independent reflections	1772	2557	7650	2829
R_{int}	0.014	0.0168	0.0166	0.0108
R_1	0.030	0.0418	0.0300	0.0446
R_w/wR_2	0.031	0.1023	0.0713	0.1105
Goodness of fit (GOF)	1.243	1.025	0.924	1.046
Refined parameters	149	146	661	149
Reflections used	1509 [$I > 3\sigma(I)$]	2557	7650	2826
$(\Delta\rho)_{min}$ (e Å⁻³)	−0.218	−0.354	−0.406	−0.460
$(\Delta\rho)_{max}$ (e Å⁻³)	0.301	0.868	0.242	1.016

Fig. 4 Stacking of compound **6** along a-axis
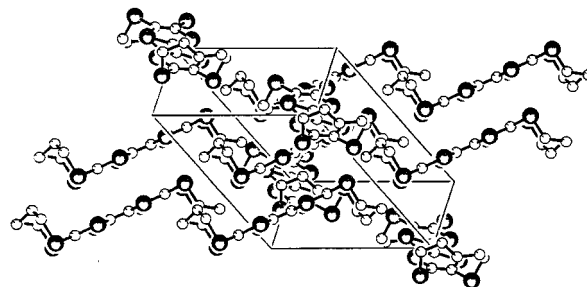
Fig. 5 Packing diagram for compound **6**

Crystal and molecular structure of compound 7

The molecular structure of compound **7** is shown in Fig. 6. Details of the crystal data are given in Table 3. Like molecules **5** and **6**, molecule **7** is also centrosymmetric and the asymmetric units consist of half a molecule which is linked to the remaining half by a centre of inversion. Similar to analogues **2**, **3**, **5** and **6**, molecules of compound **7** are arranged in pairs in the crystal (Fig. 7). The intermolecular S···S contacts are close to
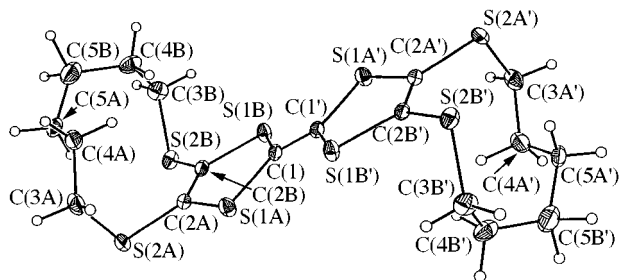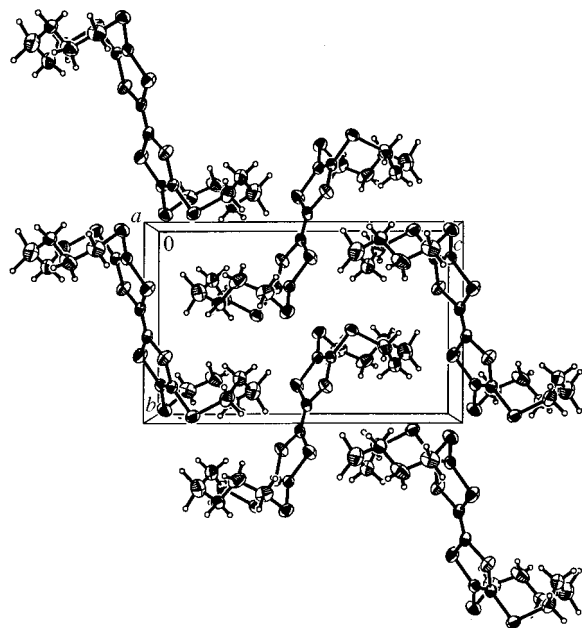
Fig. 6 Molecular diagram of compound **7**

Fig. 7 Packing diagram for compound **7**

Fig. 8 Molecular structure of compound **7a**

Fig. 9 Side-on-view of compound **7a** with atom numbering (A, B, C, D represent the asymmetric units and A and A′, B and B′ *etc.* represent the corresponding half-molecules)

sum of the van der Waals radii [3.766(2) Å]. The two halves of the molecule are tilted with respect to each other with an angle of 8.3°. Owing to this the C_6S_8 core is not as planar as observed in analogues **5** and **6**. The S(1A) and S(1B) atoms are below the mean plane by 0.1266 and 0.1250 Å, respectively, and S(1A′) and S(1B′) are above by 0.1377 and 0.136 28 Å, respectively.

Crystal and molecular structure of compound 7a

The molecular structure of compound **7a** is shown in Fig. 8. The molecule sits on a 2-fold axis in space group *P*2/*c* and there are four half-molecules in the asymmetric unit. Another interesting feature of the structure is that the -(CH₂)₆- bridge is linked across in a 'side-on' way. The 'side-on' bridge gives a 14-membered macrocyclic ring. A side-on-view of the molecule (Fig. 9) shows that the C_6S_8 core is distorted away from its preferred planar geometry as a result of the ring strain. A similar distortion has been reported by Mullen and co-workers,[11] Robert and co-workers,[12] Kilburn and co-workers,[13] and Becher and co-workers.[15] The angles of the planes defined by S(1A), S(2A), C(3A), C(2A) (plane 4) and S(2A′), S(1A′), C(2A′), C(3A′) (plane 5) with respect to the plane defined by S(1A), S(2A), S(2A′), S(1A′) (plane 3) are close to 44.3°. The ring strain forces the central fulvalene double bond out of plane. The angle between central double bond and the planes C(1A), S(1A), S(2A) (plane 1) and C(1A′), S(2A′), S(1A′) (plane 2) is 15.4°. A comparison of the bond lengths of the TTFs of the present study and BEDT-TTF **2** (Table 2) shows no apparent irregularities except for the C–S bond denoted by *c*. This is much longer [1.788(3) Å] as compared with 1.755 Å in BEDT-TTF **2**. However, this is close to the values observed for the same bond in other 'phane'-like TTFs.[11,12,13,15]

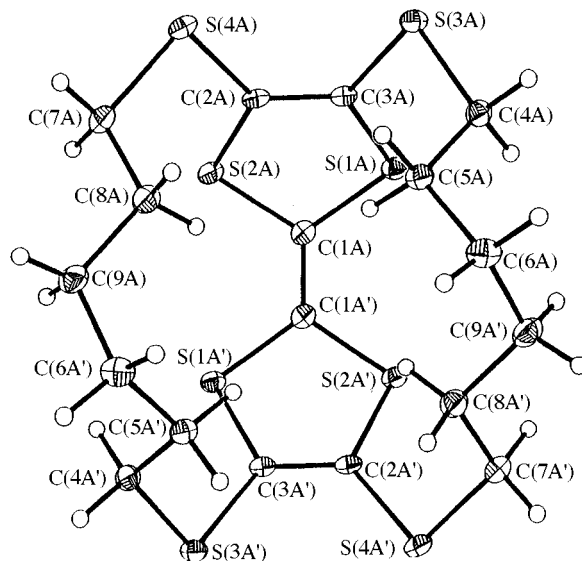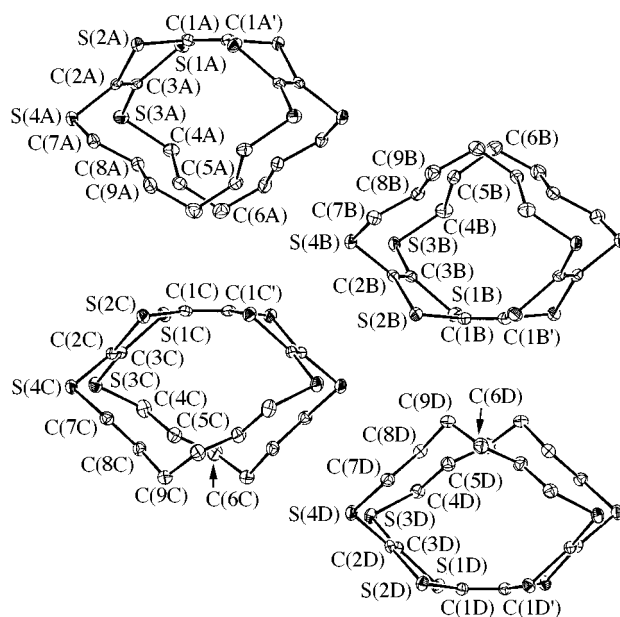The lengthening of this bond indicates that the π conjugation

is disturbed and that the central and the peripheral double bonds are less coupled than in planar TTFs **2**, **3** and **6**. Interestingly, there is a close agreement between the calculated[7] and observed bond lengths and angles for both isomers **7** and **7a** (Table 4). A similar correlation has been observed for the TTF **5**.[7] There are no close S⋯S contacts.

Crystal and molecular structure of compound 10

The molecular structure of compound **10** is shown in Fig. 10. The molecule crystallises in the *P*2₁/*n* space group. Details of the crystal-structure determination and refinement parameters are given in Table 3. The closest intermolecular S⋯S distances are close to the sum of the van der Waals radii (3.724 Å).

Conclusions

The preparation of thione **10** by coupling of the precursor synthons **8** and **9** with 1,6-dibromohexane is slightly more complex than we originally reported.[6] It appears that by subtle control of conditions, both monomeric thione **10** and dimeric thione **12** can be obtained as major products. We believe that in our

Table 4 Comparison of PM3-computed structural parameters and single-crystal X-ray structural parameters for isomers **7** and **7a**

| Compound **7**	Geometric parameters (Å and deg)					
	a, A	*b, B*	*c, C*	*d, D*	*e*	*f*
PM3[7]	1.349	1.759	1.757	1.356	1.748	1.827
	123.4	96.6	111.9	105.6		
X-Ray	1.346(5)	1.756(3)	1.768(3)	1.346(4)	1.749(3)	1.828(3)
	123.5(3)	95.54(12)	118.0(2)	117.6(2)		

Geometric parameters

a, C(1)–C(1′)#1; *b*, C(1)–S(1B); *c*, C(2B)–S(1B); *d*, C(2A)–C(2B); *e*, C(2B)–S(2B); *f*, C(3B)–S(2B)
A, C(1′)#1–C(1)–S(1B); *B*, C(1)–S(1B)–C(2B); *C*, S(2B)–C(2B)–S(1B); *D*, C(4B)–C(3B)–C(2B)

Compound **7a**	Geometric parameters (Å and deg)					
	a, A	*b, B*	*c, C*	*d, D*	*e, T1*	*f, T2*
PM3[7]	1.347	1.765	1.773	1.361	1.738	1.838
	122.5	92.8	121.8	107.9	162	46 and 57
X-Ray	1.338(5)	1.768(3)	1.788(3)	1.343(4)	1.754(3)	1.830(3)
	124.3(3)	91.92(12)	117.4(2)	114.5(2)	160.73	51.47

Geometric parameters

a, C(1A)–C(1A′)#1; *b*, C(1A)–S(1A); *c*, C(3A)–S(1A); *d*, C(3A)–C(2A); *e*, C(3A)–S(3A); *f*, S(3A)–C(4A)
A, C(1A′)#1–C(1A)–S(1A); *B*, C(1A)–S(1A)–C(3A); *C*, S(3A)–C(3A)–S(1A); *D*, C(5A)–C(4A)–S(3A); *T1*, C(1A)–S(1A)–C(3A)–S(3A); *T2*, C(7A)–S(4A)–C(2A)–S(2A)
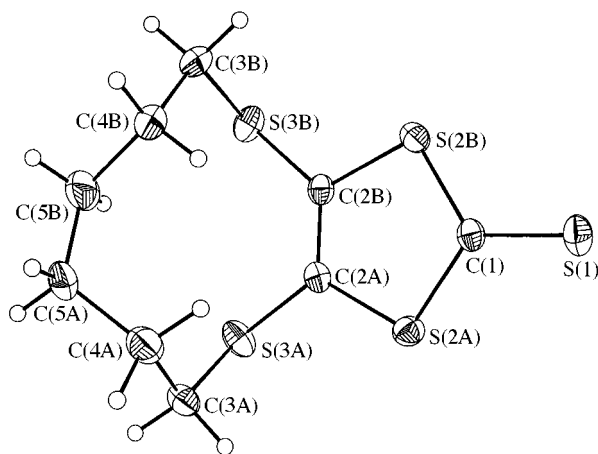
Fig. 10 Molecular structure of compound **10**

previous report[6] probably both the thiones **10** and **12** were obtained in different reactions. However, it was thione **12** which was coupled to give the TTF **7a**, and the thione **10** and the TTF **7** were not observed. The present work unambiguously identifies all the thiones and the TTFs and establishes a convenient method for the preparation of both the thiones and the corresponding TTFs. As predicted by Molecular Modelling studies,[7] we have demonstrated that both the isomers with a -(CH₂)₆- system, *i.e.* 'D_{2h}' **7** and the 'phane'-form **7a**, can be isolated. We have also demonstrated that dimeric thiones of type **12** and **14** where alkyl chains are involved as 'spacers' can be conveniently synthesised in moderate to good yields by using the [Zn-(dmit)₂]²⁻ synthon. It appears that the metal ion acts as a 'template' for formation of the dimer. The TTF **7a** has not yielded any charge-transfer complexes when treated with CuCl₂ or HgCl₂. The low reactivity of compound **7a** is due to its 'phane'-like structure. It is concluded that for 'D_{2h}' symmetry TTFs, *i.e.* compounds **1**–**7** the colour, cyclic voltammetry (CV) properties and reactivity are generally similar to those of BEDT-TTF **2**. However, for the 'phane'-like TTFs the usual orange-red colour is lost and CV showed only one irreversible peak at ~1 V. For alkyl chains -(CH₂)ₙ- *n* ≥ 5 both isomers are possible and their isolation depends on the method of preparation. According to PM3 calculations, the 'vertical' ionisation energies of this series of compounds were found to increase as the size of the exterior alkyl ring increases.[7] A look at the ease of formation and conducting behaviour of the charge-transfer

complexes of these donors shows the same trend. The room temperature (rt) conductivities of the charge-transfer complexes derived from donors **3** and **5** fall in the range of 10^{-2}–10^{-3}, while those of the higher analogues **6** and **7a** fall in the range of 10^{-6}–10^{-7} S cm⁻¹. Charge-transfer complexes **26** and **27** behaved as semiconductor and metal, respectively, at low temperatures.

Experimental

General methods
All the solvents used were dried and deoxygenated prior to use. The reactions were carried out in an inert atmosphere. Mps were determined with a VEEGO melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba elemental analyser model 1106. IR spectra were recorded for samples as KBr pellets on a Nicolet Impact 400 FT-IR spectrometer. UV–Visible spectra were recorded on a Shimadzu UV-160A spectrophotometer. ¹H and 2D-NMR spectra were recorded on a Varian VXR 300 MHz instrument with Me₄Si as internal standard and CDCl₃ as solvent. Solid-state ESR spectra were recorded on a Varian E-112 ESR spectrometer using tetracyanoethylene as **g**-marker at rt. The solid-state conductivities were measured on powdered samples at rt by the two-probe method; samples were manually compressed between two steel probes and the sample's resistance was monitored with a Keithley digital multimeter. Temperature-variant electrical conductivity measurements were done on the compressed pellets (annealed at 75 °C) by van der Pauw's four-probe method over the temperature range 10–300 K. Mass spectra were obtained on a JEOL D-300 mass instrument, operating at 70 eV. CV experiments were performed on a Bio-Analytical systems (BAS) instrument which consisted of a one-compartment cell with a platinum working electrode, a counter-electrode and a Ag/AgCl or standard calomel electrode (SCE) (reference electrode). All solutions were purged with argon or nitrogen and retained under the inert atmosphere while the CV data were recorded.

5,6,7,8,9,10-Hexahydro-1,3-dithiolo[4,5-*b*][1,4]dithiacyclo-decene-2-thione[6] 10
To a suspension of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione **9** (8.12 g, 20 mmol) in absolute ethanol (20 cm³) was added a stirred solution of sodium ethoxide (sodium 0.96 g, 42 mmol) in absolute ethanol (10 cm³). The mixture was stirred for

45 min and diluted with absolute ethanol (500 cm³). 1,6-Dibromohexane (4.69 g, 20 mmol) as a solution in ethanol (500 cm³) was added dropwise at ~75 °C during *ca.* 4 h, and the reaction mixture was further stirred at rt until completion of the reaction (TLC, 3 h). The resulting viscous yellow precipitate, obtained by decantation of the solvent, was washed with ethanol and dissolved in chloroform. The solution was then filtered and the filtrate was washed with water, dried and chromatographed on silica gel. Elution with light petroleum (60–80 °C)–ethyl acetate (99:1) gave the title thione **10** as the major compound (1.33 g, 29%) followed by the thione **11** (0.530 g, 5%) and the dimeric thione **12** (traces). Compound **10** was obtained as yellow crystals, mp 128 °C (Found: C, 38.48; H, 4.32. Calc. for $C_9H_{12}S_5$: C, 38.57; H, 4.28%); δ_H(CDCl₃) 1.66 (m, 4 H), 1.91 (m, 4 H) and 2.90 (m, 4 H, SCH₂); *m/z* 280 (M·⁺, 100%).

4,5-Bis-(6-bromohexylthio)-1,3-dithiole-2-thione 11. Red viscous liquid, δ_H(CDCl₃) 1.46 (m, 8 H), 1.69 (m, 4 H), 1.87 (m, 4 H), 2.88 (t, 4 H, SCH₂) and 3.41 (t, 4 H, CH₂Br); δ_C(CDCl₃) 27.65, 29.50, 32.55, 33.67, 36.65, 136.30 and 211.30; *m/z* 525 (M·⁺, 100%).

5,6,7,8,9,10,16,17,18,19,20,21-Dodecahydrobis[1,3]dithiolo[4,5-*b*:4′,5′-*l*][1,4,11,14]tetrathiacycloeicosene-2,13-dithione 12
To a solution of the Zn[dmit]₂²⁻ synthon **8** (4.705 g, 5 mmol) in acetone (50 cm³) was added a solution of 1,6-dibromohexane (2.34 g, 10 mmol) in acetone (10 cm³). The solution was stirred for 4 h at rt. The solution turned greenish and a yellow sticky precipitate started separating out. Stirring was continued for an additional 1 h and the sticky precipitate was collected by decantation. The precipitate was washed with CHCl₃ several times to give the *title compound* **12** as yellow powder (0.85 g, 30%), mp 158 °C (Found: C, 38.57; H, 4.65. $C_{18}H_{24}S_{10}$ requires C, 38.57; H, 4.28%); ν(KBr)/cm⁻¹ 1080 (C=S); δ_H(CDCl₃) 1.48 (m, 8 H), 1.69 (m, 8 H) and 2.89 (t, 8 H); *m/z* 560 (M⁺, 100%).

The collected filtrate was chromatographed on silica gel. Elution with light petroleum (60–80 °C)–ethyl acetate (99:1) gave the thiones **10**, as yellow crystals (7%) and **11**, as a red viscous liquid (5%).

Compound **13** was synthesised following the method used for the thione **10**.

5,6,7,8,9,10,11,12,13,14,15,16-Dodecahydro-1,3-dithiolo-[4,5-*b*][1,4]dithiacyclohexadecene-2-thione 13. *Yellow crystalline solid*, mp 64 °C (Found: C, 49.19; H, 6.52. $C_{15}H_{24}S_5$ requires C, 49.45; H, 6.59%); δ_H(CDCl₃) 1.34 (br, 12 H), 1.47 (m, 4 H), 1.69 (m, 4 H) and 2.89 (t, 4 H, SCH₂); δ_C(CDCl₃) 26.05, 26.72, 27.01, 28.79, 36.90, 136.60 and 211.79; *m/z* 364 (M·⁺, 100%).

Compound **14** was synthesised following the method used for thione **12**.

6,7,8,9,16,17,18,19-Octahydro-5*H*,15*H*-bis[1,3]dithio[4,5-*b*:4′,5′-*k*]cyclooctadecene-2,12-dithione 14. *Yellow powder* (0.48 g, 18%), mp 210 °C (decomp.) (Found: C, 36.11; H, 3.66. $C_{16}H_{20}S_{10}$ requires C, 36.09; H, 3.75%); δ_H(CDCl₃) 1.56 (m, 4 H), 1.71 (m, 8 H) and 2.87 (m, 8 H, CH₂S); *m/z* 532 (M·⁺, 70%).

Synthesis of bi(5,6,7,8,9,10-hexahydro-1,3-dithiolo[4,5-*b*][1,4]-dithiocyclodecen-2-ylidene) BHDT-TTF 7
Method I. To anhydrous, degassed ethanol (100 cm³) was added a solution of sodium ethoxide (sodium 0.190 g, 8 mmol) in ethanol (10 cm³) followed by 2,3,6,7-tetrakis(2′-cyanoethylthio)tetrathiafulvalene[8] (0.521 g, 0.96 mmol). The mixture was stirred for 4 h after which a solution of 1,6-dibromohexane (1.21 g, 5 mmol) in ethanol (50 cm³) was introduced through a dropping funnel over a period of 2 h and the solution was stirred overnight. The solvent was evaporated off *in vacuo* and the precipitate was re-dissolved in CH₂Cl₂, the solution was washed with water (100 cm³) and the organic product was column chromatographed (silica gel; hexane) to obtain title compound **7** (0.105 g, 22%).
Method II. To anhydrous, degassed ethanol (30 cm³) was

added a solution of sodium ethoxide (sodium 0.190 g, 8 mmol) in ethanol (10 cm³) followed by 2,3,6,7-tetrakis(2′-cyanoethylthio)tetrathiafulvalene[8] (0.521 g, 0.96 mmol). The mixture was stirred for 4 h after which a solution of 1,6-dibromohexane (1.21 g, 5 mmol) in ethanol (5 cm³) was introduced through a syringe and the solution was stirred overnight. The solvent was evaporated off *in vacuo* and the precipitate was re-dissolved in CH₂Cl₂, the solution was washed with water (100 cm³), and the organic product was subjected to column chromatography over silica gel using hexane–ethyl acetate (98:2) to obtain compounds **7**, **18** and **19**. Compound **7** was obtained first (0.025 g, 5%), followed by compound **19** (0.085 g, 12%) and compound **18** (0.168 g, 20%).

Method III. The thione **10** (1.68 g, 6 mmol) was taken up in triethyl phosphite (10 cm³) and the mixture was heated and stirred at 120 °C; the solution became orange after 15 min and an orange crystalline precipitate started to form. Reflux was continued for 1 h and the precipitate was filtered off, washed with diethyl ether, and recrystallised from dichloromethane to afford tetracycle **7** as orange crystals (0.223 g, 15%) (Found: C, 43.34; H, 5.01. $C_{18}H_{24}S_8$ requires C, 43.54; H, 4.83%); mp 242 °C (decomp.); δ_H(CDCl₃) 1.66 (m, 8 H), 1.87 (m, 8 H) and 2.84 (m, 8 H); δ_C(CDCl₃) 22.59, 25.68, 35.94 and 131.3; *m/z* 496 (M·⁺, 100%).

4,4′,5,5′-Tetrakis(6-bromohexylthio)tetrathiafulvalene 18. Red viscous liquid, δ_H(CDCl₃) 1.45 (m, 16 H), 1.64 (m, 8 H), 1.87 (m, 8 H), 2.82 (t, 8 H, CH₂S) and 3.41 (t, 8 H, CH₂Br); δ_C(CDCl₃) 27.82, 29.74, 32.8, 33.95, 36.30, 110.32 and 127.98; *m/z* 984 (M·⁺, 100%).

2-[4,5-Bis(6-bromohexylthio)-1,3-dithiol-2-ylidene]-5,6,7,8,9,10-hexahydro[1,3]dithiolo[4,5-*b*][1,4]dithiacyclodecene 19. Orange crystalline, mp 62 °C (Found: C, 38.84; H, 4.85. $C_{24}H_{36}Br_2S_8$ requires C, 38.91; H, 4.86%); δ_H(CDCl₃) 1.46 (m, 8 H), 1.64 (m, 8 H), 1.87 (m, 8 H), 2.83 (m, 8 H, SCH₂) and 3.42 (t, 4 H, CH₂Br); δ_C(CDCl₃) 22.60, 25.67, 27.82, 29.75, 32.79, 33.93, 36.02 and 131.37; *m/z* 742 (M·⁺, 100%).

***cis,cis*-4,4′;5,5′-Bis(hexamethylenedithio)tetrathiafulvalene 7a[6]**
The thione **12** (0.70 g, 1.25 mmol) was taken up in triethyl phosphite (10 cm³) and heated and stirred at 100–110 °C for 3 h. Removal of the triethyl phosphite under reduced pressure and chromatographic separation of the residue on silica gel using light petroleum–ethyl acetate (95:5) as eluent yielded title 'phane' **7a** as a pale yellow crystalline material (0.074 g, 12%), mp 228 °C (decomp.) (Found: C, 43.18; H, 5.00. $C_{18}H_{24}S_8$ requires C, 43.54; H, 4.83%); δ_H(CDCl₃) 1.38 (m, 16 H), 2.35 (m, 4 H) and 3.20 (m, 4 H); δ_C(CDCl₃) 26.63, 27.82, 35.34 and 128.74; *m/z* 496 (M·⁺, 100%).

The TTF **15** was synthesised following the procedure used as for the TTF **7** (both the coupling and the tetrathiolate route[8]). In the tetrathiolate route, the partially cyclised TTF **20** was also isolated.

Bi(5,6,7,8,9,10,11,12,13,14,15,16-dodecahydro-1,3-dithiolo-[4,5-*b*][1,4]dithiocyclohexadecen-2-ylidene) 15. *Orange crystalline solid*, mp 180 °C (Found: C, 54.63; H, 7.16. $C_{30}H_{48}S_8$ requires C, 54.21; H, 7.22%); δ_H(CDCl₃) 1.33 (br, 24 H), 1.44 (m, 8 H), 1.65 (m, 8 H) and 2.82 (t, 8 H); δ_C(CDCl₃) 27.16, 27.76, 28.02, 28.22, 28.39, 28.73, 29.11, 29.97, 30.11, 31.36, 34.86, 35.80, 110.38, 127.16 and 130.81; *m/z* 664 (M·⁺, 60%).

The TTF **16** was synthesised following the method used for TTF **7a**.

***cis,cis*-4,5;4′,5′-Bis(pentamethylenedithio)tetrathiafulvalene 16.** *Yellow crystals* (0.086 g, 14%), mp >200 °C (decomp.) (Found: C, 41.08; H, 4.68. $C_{16}H_{20}S_8$ requires C, 41.02; H, 4.27%); δ_H(CDCl₃) 1.61 (m, 8 H), 1.78 (m, 4 H), 2.61 (m, 4 H) and 3.07 (m, 4 H); δ_C(CDCl₃) 29.98, 30.58, 36.55, 132.08 and 133.08; *m/z* 468 (M·⁺, 100%).

2-[4,5-Bis(12-bromododecylthio)-1,3-dithiol-2-ylidene]-5,6,7,8,9,10,11,12,13,14,15,16-dodecahydro[1,3]dithiolo[4,5-*b*]-[1,4]dithiacyclohexadecene 20. Red viscous liquid; δ_H(CDCl₃)

1.27 (br, 32 H), 1.39 (m, 16 H), 1.64 (m, 12 H), 2.81 (m, 8 H) and 3.40 (t, 4 H, CH$_2$Br); δ_C(CDCl$_3$) 25.75, 25.92, 26.63, 27.11, 27.83, 28.00, 28.23, 28.34, 28.41, 28.64, 28.82, 29.15, 29.56, 29.74, 29.84, 32.89, 34.09, 35.28, 35.92, 36.35, 110.38, 127.16 and 130.76; m/z 992 (M$^{\cdot+}$, 100%).

Synthesis of iodine complexes with π-donors

(BMeEDT-TTF)I$_5$ 21. To a solution of BMeEDT-TTF **3** (0.0412 g, 0.1 mmol) in chloroform (20 cm^3) was added a solution of iodine (0.0508 g, 2 mmol) in chloroform (15 cm^3). The reaction mixture was then stirred for 20 min at rt and the resulting grey precipitate was filtered off, washed with chloroform (50 cm^3), and dried *in vacuo* over anhydrous CaCl$_2$ to afford a *grey-black powder* (0.045 g, 44%), mp 197–198 °C (Found: C, 13.39; H, 1.53. C$_{12}$H$_{12}$S$_8$I$_5$ requires C, 13.76; H, 1.14%); λ_{max}(CH$_2$Cl$_2$)/nm 486.5, 418.5, 306 and 262; λ_{max}-(CH$_3$CN)/nm 354, 334, 292 and 260.5; $\sigma_{rt} = 5.51 \times 10^{-3}$ S cm^{-1}; g = 2.0087.

Compounds **22**, **23** and **24** were synthesised similarly, following the general method used for compound **21**.

(BBDT-TTF)·I$_5$ 22. *Greenish black powder* (0.050 g, 51%), mp 181–183 °C (Found: C, 15.81; H, 1.85. C$_{14}$H$_{16}$S$_8$I$_5$ requires C, 15.63; H, 1.48%), λ_{max}(CH$_2$Cl$_2$)/nm 299.5 and 263; $\sigma_{rt} = 2.5 \times 10^{-3}$ S cm^{-1}; g = 2.0027.

(BPtDT-TTF)·I$_7$ 23. *Black-brown crystalline material* (0.042 g, 38%), mp 174–176 °C (Found: C, 13.59; H, 1.67. C$_{16}$H$_{20}$S$_8$I$_7$ requires C, 14.15; H, 1.47%); λ_{max}(CH$_2$Cl$_2$)/nm 302 and 259; λ_{max}(CH$_3$CN)/nm 362, 332, 292 and 258; $\sigma_{rt} = 1.1 \times 10^{-6}$ S cm^{-1}; g = 1.9938.

(7a)·I$_5$ 24. *Black crystalline material* (0.054 g, 59%), mp 202–204 °C (Found: C, 20.15; H, 1.90. C$_{18}$H$_{24}$S$_8$I$_5$ requires C, 19.10; H, 2.12%); λ_{max}(CH$_2$Cl$_2$)/nm 392, 359, 327, 320, 290 and 260; λ_{max}(CH$_3$CN)/nm 591, 359, 340, 290 and 262; $\sigma_{rt} = 1.12 \times 10^{-7}$ S cm^{-1}; g = 2.002 77.

Synthesis of CuCl$_2$ complexes with π-donors

(BBDT-TTF)$_2$·(CuCl$_2$)$_3$ 25. To a stirred solution of BBDT-TTF **5** (0.040 g, 0.09 mmol) in acetonitrile (20 cm^3) was added a solution of CuCl$_2$·2H$_2$O (0.015 g, 0.09 mmol) in acetonitrile (20 cm^3). The colour of the solution turned from orange to greenish black. The mixture was stirred at rt for an additional 1 h and the greenish black precipitate was filtered off, washed successively with dichloromethane (50 cm^3) and acetonitrile (50 cm^3), and dried *in vacuo* (0.048 g, 83%), mp 188–189 °C (Found: C, 26.19; H, 3.32. C$_{28}$H$_{32}$S$_{16}$Cu$_3$Cl$_6$ requires C, 26.17; H, 2.49%); λ_{max}(CH$_2$Cl$_2$)/nm 602, 442, 376, 280 and 263.5; λ_{max}(CH$_3$CN)/nm 590, 442, 382, 306 and 262; $\sigma_{rt} = 2.9 \times 10^{-6}$ S cm^{-1}; g = 1.9968.

(BMeEDT-TTF)$_{8/3}$·(CuCl$_2$) **26** was synthesised following the reported procedure.[6]

Under identical conditions the 'phane' **7a** has not produced any copper complex.

Synthesis of HgCl$_2$ complex with π-donors

(BMeEDT-TTF)$_2$·(HgCl$_3$) 27. A solution of mercury(II) chloride (0.027 g, 0.1 mmol) in acetonitrile (30 cm^3) was added to a stirred solution of BMeEDT-TTF **3** (0.040 g, 0.097 mmol) in acetonitrile (30 cm^{-3}). The reaction mixture was further stirred and refluxed for 6 h, then was filtered, and concentrated to half its volume and left for slow evaporation at rt. After a week, glistening black crystals were obtained from the mother liquor; these were washed with hot acetonitrile and dried *in vacuo* to give *complex* **27** (0.046 g, 59%), mp 193–194 °C (Found: C, 25.59; H, 1.96. C$_{24}$H$_{24}$S$_{16}$HgCl$_3$ requires C, 25.46; H, 2.12%); λ_{max}(CH$_2$Cl$_2$)/nm 378 and 263; λ_{max}(CH$_3$CN)/nm 376, 299, 281 and 260; $\sigma_{rt} = 7.51 \times 10^{-3}$ S cm^{-1}; g = 2.002 77.

Compound **28** was synthesised similarly following the method used for compound **27**.

(BBDT-TTF)$_3$·(HgCl$_3$)$_2$ 28. *Black-brown powder* (0.032 g, 55%), mp 197–198 °C (Found: C, 26.49; H, 2.33. C$_{42}$H$_{48}$S$_{24}$-Hg$_2$Cl$_6$ requires C, 26.05; H, 2.48%); $\sigma_{rt} = 1.486 \times 10^{-2}$ S cm^{-1}; g = 2.002 77.

X-Ray data collection and processing for compound 6

The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). All the hydrogen atoms were located from the difference Fourier map and were refined isotropically. Table 3 summarises the crystal data. The non-hydrogen atoms were refined with anisotropic temperature factors. The structures were solved by SHELXS-86 and refined by SHELX-76.[16]

X-Ray data collection and processing for compounds 7 and 10

The intensity data were collected on a Siemens diffractometer with graphite-monochromated Mo-Kα radiation. All the hydrogen atoms were located from the difference Fourier map and were refined isotropically. Table 3 summarises the crystal data. The non-hydrogen atoms were refined with anisotropic temperature factors. Refinement used full-matrix least squares on F^2. Atoms C(5A) of molecule **7** and **10** are disordered over two positions [C(5A), C(5AA)]. The structures were solved and refined using SHELXTL.[17]

X-Ray data collection and processing for compound 7a

The intensity data were collected on a Siemens R3m/v four-circle diffractometer using a low-temperature dry nitrogen stream as coolant with graphite-monochromated Mo-Kα radiation. All the hydrogen atoms were located from the difference Fourier map and were refined isotropically. Table 3 summarises the crystal data. The non-hydrogen atoms were refined with anisotropic temperature factors. Refinement method was by full-matrix least squares on F^2.§[18]

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