Bis[naphthalene-1,8-diylbis(methylthio)]tetrathiafulvalene (BNMT-TTF) and Bis(tetramethylenedithio)tetrathiafulvalene (BMDT-TTF):† New Electron Donors

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The title compounds **7**,**9** have been synthesised and characterised, and cyclic voltammetric data show that the donors undergo two one-electron oxidations; the crystal structure of **9** is presented.

Cation radical salts based on the electron donor molecule bis(ethylenedithio)tetrathiafulvalene, (BEDT-TTF) **1**, have yielded several organic superconductors.[1,2] The highest recorded superconducting transition for an organic superconductor is T_c = 12.5 K for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.[3,4] The presence of two-dimensional S···S networks in the cation–radical salts of BEDT-TTF is generally believed to be pivotal in suppressing instabilities inherent to low-dimensional systems. Moreoever, weak interactions between the anion and the 'CH$_2$ cavity' in which the anions reside play an important role in governing the lattice's softness. Therefore, new donors derived from various chemical modifications of BEDT-TTF and TTF are of immense current interest.[5–9] By modifying the size of the outer ring of BEDT-TTF, various donors‡ such as BMDT-TTF **2**, and BPDT-TTF **3** have been obtained. The incorporation of tetramethylene or pentamethylene bridges in place of ethylene in **1** should not only lead to an enlarged unit cell but also result in a larger spatial extension of the outer sulphurs (part of eight- and nine-membered outer rings). These donors with 'CH$_2$ cavities' of different shapes and sizes may provide a mechanism for the fine tuning of interstack S···S distances.[10]

Underhill and coworkers[11,12] have reported the synthesis of some related macrocyclic cage compounds incorporating the tetrathiafulvalene unit. The reaction of 4,5-dimercapto-1,3-dithiole-2-thione disodium salt **4** with 2,6-bis(bromomethyl)pyridine, instead of capping the anion and forming a nine-membered ring, resulted in the formation of a macrocyclic π-donor.[11] We now describe the first example of a TTF incorporating a nine-membered outer ring. Also reported herein is the first synthesis and unique structure of the tetramethylenedithio compound (BMDT-TTF) **9**.

The dimercapto disodium salt **4** was prepared from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione following the procedure developed by Underhill *et al.*[13] Treatment of **4** with 1,8-bis(bromomethyl)naphthalene and dibromobutane led to

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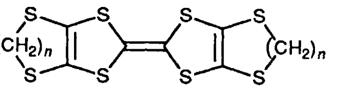
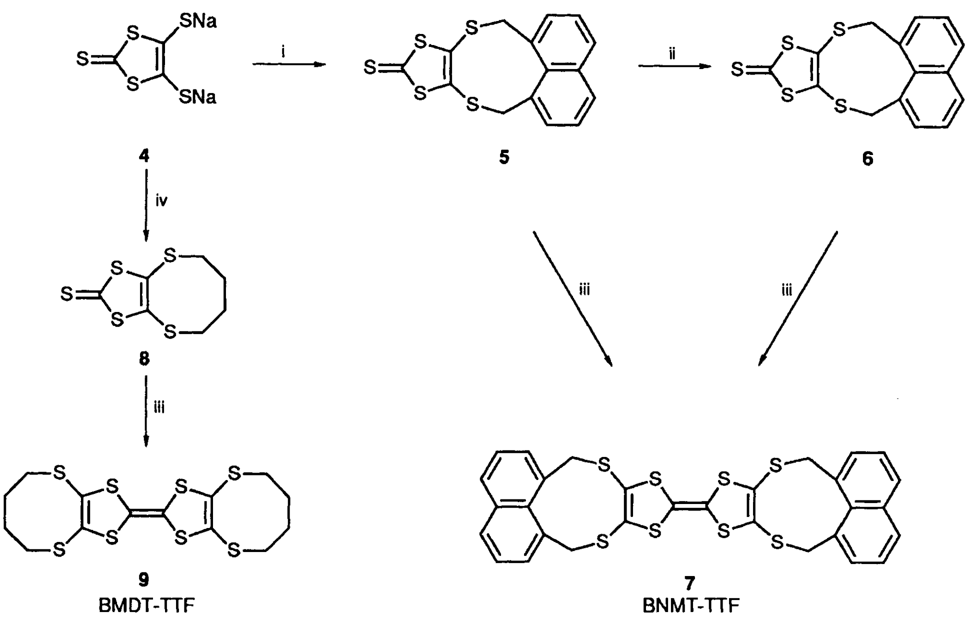
† BNMT-TTF = bi(7*H*,13*H*-[1,3]dithiolo[4,5-*b*]naphtho[1,8-*fg*]-[1,4]dithionin-10-ylidene); BMDT-TTF = bi(6,7,8,9-tetrahydro-5*H*-1,3-dithiolo[3,4-*b*]dithionin-2-ylidene).

‡ BMDT-TTF = bis(methylenedithio)tetrathiafulvalene; BPDT-TTF = bis(propylenedithio)tetrathiafulvalene.



n = 2, BEDT-TTF **1**
n = 1, BMDT-TTF **2**
n = 3, BPDT-TTF **3**



Scheme 1 *Reagents and conditions*: i, $C_{10}H_6(CH_2Br)_2$, MeOH; ii, $Hg(OAC)_2$, $CHCl_3$–AcOH, room temp.; iii, $P(OEt)_3$, 120 °C; iv, $Br(CH_2)_4Br$

the isolation of compounds **5** and **8** respectively.§ Conventional coupling of the thione **5** with triethyl phosphite provided the compound **7** in poor yield. However, coupling of **6** and **8** with triethyl phosphite resulted in moderate yields of **7** and **9** (Scheme 1).§

The X-ray diffraction study¶ of **9** showed that it crystallises with the same space group as that of the BMDT-TTF, BEDT-TTF and BPDT-TTF.[14] Although the molecule has a centre of symmetry like BMDT-TTF, it assumes a *trans* configuration (Fig. 1). The unique feature of the structure is the high planarity of the C_6S_8 core which is non-planar in BEDT-TTF and BPDT-TTF. This is probably due to the incorporation of the eight-membered exterior ring. Very recently Saito *et al.* have reported the structure of tetrakis(octylthio)tetrathiafulvalene which also has a planar C_6S_8

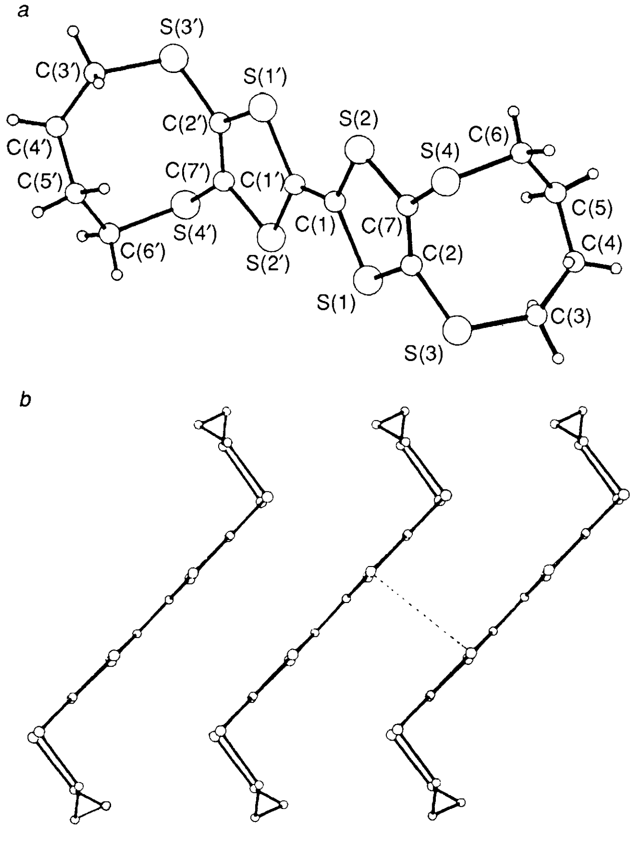


Fig. 1 (*a*) Molecular structure of BMDT-TTF; (*b*) stacking arrangement along the *a* axis

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§ Compound **5**, yield 89%, m.p. 225 °C (decomp.). Compound **6**, yield 61%, m.p. 211 °C (decomp.). Compound **7**, prepared in 26% yield from **6** and in 11% yield from **5**, m.p. 243–244 °C (decomp.). Compound **8**, yield 63%, m.p. 109 °C. Compound **9**, yield 37% from **8**. m.p. 151 °C. Satisfactory elemental analyses were obtained for all new compounds.

¶ *Crystal data*: $C_{14}H_{16}S_8$, $M = 440.75$, monoclinic, space group $P2_1/c$, unit cell: $a = 5.233(10)$, $b = 14.247(4)$, $c = 13.430(3)$ Å, $\beta = 109.44(2)°$, $V = 944.10$ Å^3, $Z = 2$, $D_c = 1.551$ mg mm^{-3}, λ = (Mo-Kα) = 0.7107 Å, μ (Mo-Kα) = 0.857 mm^{-1}, $F(000) = 456$. Final $R = 0.0403$ and $R_w = 0.0400$ for 2167 observed reflections with $|F_o| \geq 3\sigma(|F_o|)$.

Intermolecular interactions: $S(2)\cdots S(2)^{(i)}$ 3.686(1) Å; (i) $2 - x$, $1 - y, z$ [shown with dotted line in Fig. 1], $S(1)\cdots S(4)^{(ii)}$ 3.668(1) Å; (ii) $-1 + x, y, z$ and $S(3)\cdots S(4)^{(iii)}$ 3.705(1) Å; (iii) $-1 + x, 3/2 - y + z$. Details to be published in *Acta Crystallogr. Sect. C.* Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 Cyclic voltammetric data (in volts)[a]

Compound	$E^1{}_{1/2}$	$E^2{}_{1/2}$	ΔE	C/mol dm^{-3}
1 BEDT-TTF	0.530	0.937	0.407	5×10^{-4}
9 BMDT-TTF	0.525	0.950	0.425	5×10^{-4}
7 BNMT-TTF	0.525	1.060	0.535	5×10^{-4}

[a] *Conditions*: Volts *vs.* Ag/AgCl reference electrode, 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate in CH_2Cl_2, scan rate 0.2 V s^{-1}, Pt working electrode.

core.[15] The BMDT-TTF molecules stack uniformly along the *a* axis. The intermolecular $S\cdots S$ contacts are close to the sum of the van der Waals radii (3.70 Å).

Table 1 compares cyclic voltammetric data for the title compound with other analogous compounds. The cyclic voltammograms of BNMT-TTF and BMDT-TTF showed, as expected, two reversible redox waves. The first ionisation potentials of **7** and **9** are very similar to those of BEDT-TTF **1** while ($E^2{}_{1/2}$) for the new donors is higher than that of BEDT-TTF (measured under identical conditions).

Both BMDT-TTF and BNMT-TTF form 1:1 charge transfer‖ with π-acceptors TCNQ (tetracyanoquinodimethane) and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). Conductivities of the BMDT-TTF complexes measured on compressed pellets by the two-probe method were $\sigma_{rt} = 4.9 \times 10^{-4}$ and 2.7×10^{-3} S cm^{-1} respectively, while that of BNMT-TTF were in the insulator range, *i.e.* $\sigma_{rt} = 5.8 \times 10^{-7}$ and 7.7×10^{-7} S cm^{-1} respectively.

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‖ BMDT-TTF:TCNQ, yield 59%, m.p. 242 °C (decomp.). BMDT-TTF:DDQ, yield 53%, m.p. 224 °C (decomp.). BNMT-TTF:TCNQ, yield 65%, m.p. 194 °C (decomp.). BNMT-TTF:DDQ, yield 52%, m.p. 212 °C (decomp.).

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