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Preparation, Crystal Structure and Electrical Properties of Dimethyl Substituted Unsymmetrical 2,5-Bis(1′,3′-dithiol-2′-ylidene)-1,3,4,6-tetrathiapentalenes

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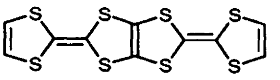
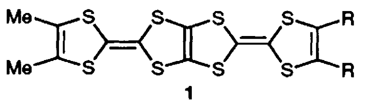
Preparation, crystal structure and electrical properties of the title compounds **1a–g** are described; these donors gave several conducting salts showing metallic temperature dependence.

2,5-Bis(1′,3′-dithiol-2′-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) which is a bis-fused tetrathiafulvalene (TTF), and its derivatives[1] are promising donors for the preparation of organic metals.[2–4] A characteristic of BDT-TTP is a ladder-like arrangement of sulfur atoms, as is observed in bis(ethylenedithio)-TTF (BEDT-TTF) which has yielded most organic superconductors.[4] Therefore BDT-TTP is also expected to give two-dimensional (2-D) metals stable down to low temperature, while TTF gives generally 1-D metals that inherently show metal–insulator transitions at low temperature. In fact BDT-TTP and its derivatives recently synthesized by us have yielded many metallic salts.[5–8] In this context synthesis of a series of BDT-TTP derivatives is needed in order to elucidate electrical properties of conducting salts based on BDT-TTP donors. Herein we describe the synthesis, crystal structure and electrochemical properties of dimethyl-substituted unsymmetrical BDT-TTPs (**1a–g**), and electrical properties of their conducting salts.



BDT-TTP



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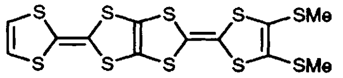
a; R = H
b; R = CO_2Me
c; R = SMe
d; R-R = -SCH_2S-
e; R-R = -$S(CH_2)_2S$-
f; R-R = -$S(CH_2)_3S$-
g; R-R = -$O(CH_2)_2O$-



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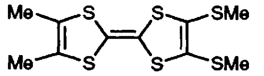

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Table 1 Electrical properties of TCNQ complexes and cation radical salts of **1**

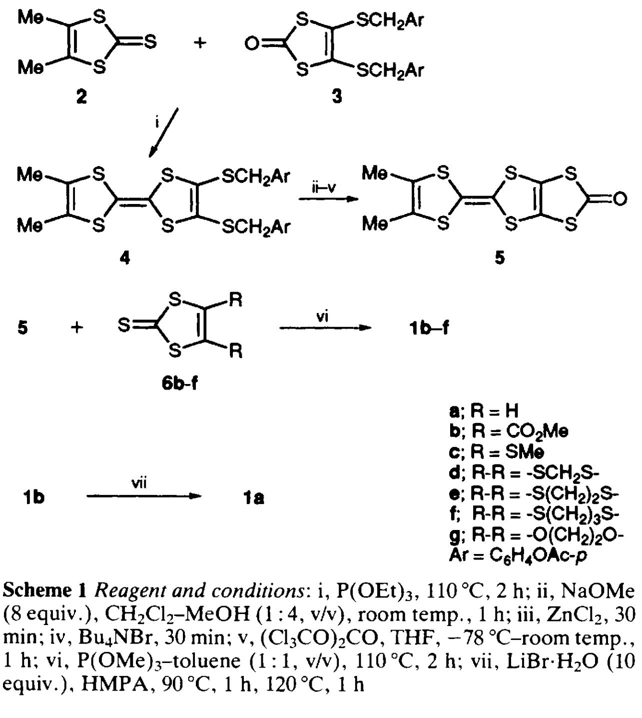
Donor	Anion	D : A[a]	σ_{rt}/S cm^{-1} [b]	Conducting behaviour[c]
1a	TCNQ	1 : 1	60	Metallic, T_{MI} = 200 K
	I_3	8 : 3	20	Metallic, T_{MI} = 170 K
1c	TCNQ	1 : 1	0.8	Semiconducting, E_a = 0.040 eV
	I_3	8 : 3	2	Metallic, T_{MI} = 200 K
1d	TCNQ	1 : 1	30	Metallic down to 4.2 K
	I_3	8 : 3	40	Metallic down to 4.2 K
1e	TCNQ	1 : 1	20	Metallic, T_{MI} = 190 K
	I_3	8 : 3	9	Semiconducting, E_a = 0.013 eV
1g	TCNQ	1 : 1	60	Metallic, T_{MI} = 180 K
	I_3	3 : 1	5	Semiconducting, E_a = 0.026 eV

[a] Determined based on elemental analyses. [b] Room temp. conductivity measured by a four-probe technique on a compressed pellet obtained at an applied pressure of 4 bar. [c] T_{MI} = metal to semiconductor transition temp.

The new BDT-TTPs were synthesized by a similar method to that described before (see Scheme 1).[5–7]† However, tetramethyl-BDT-TTP could not be obtained by the cross-coupling between **2** and **5**. The cyclic voltammogram (CV) of bis(methylthio)-**1** (**1c**) exhibited four pairs of redox waves at +0.43, +0.68, +0.98 and +1.17 V [0.1 mol dm^{-3} Bu_4NClO_4 in PhCN, Pt electrode, 25 °C, scan rate 50 mV s^{-1}, V *vs.* saturated calomel electrode (SCE)]. Satisfactory CVs could not be obtained for other donors as these were less soluble in common solvents. The E_1 value of **1c** is lower by 0.06 V than that of bis(methylthio)-BDT-TTP (**7**, +0.49 V),[6] suggesting that the donor ability is enhanced by introduction of electron-donating methyl groups. However, the E_1 value of **1c** is slightly higher by 0.03 V compared with the corresponding TTF (**8**, E_1 = +0.40, E_2 = +0.75 V)‡ in spite of extension of apparent π-conjugation. On the other hand the $E_2 - E_1$ value (0.25 V) is smaller by 0.1 V than that of **8** (0.35 V), suggesting that on-site Coulombic repulsion in the dication state of **1c** decreases due to increase of redox-active 1,3-dithioles.

Fig. 1 shows the molecular structure of **1c** determined by X-ray diffractional analysis.§ The BDT-TTP skeleton has almost planar structure, though the 1,3-dithiole ring substituted with methylthio groups is slightly puckered. The molecules are stacking in a heat-to-tail manner (see Fig. 2) along the *b*-axis, and also form sheet-like networks along the *a*-axis, as is observed in tetrakis(methylthio)-BDT-TTP.[5] However, there are no short S···S contacts within the sum of van der Waals radii (3.70 Å), the shortest one being 3.720(2) Å.

The electrical properties of tetracyano-*p*-quinodimethane (TCNQ) complexes and cation radical salts using **1** are summarized in Table 1. All salts show high conductivity



Scheme 1 *Reagent and conditions*: i, $P(OEt)_3$, 110 °C, 2 h; ii, NaOMe (8 equiv.), CH_2Cl_2–MeOH (1 : 4, v/v), room temp., 1 h; iii, $ZnCl_2$, 30 min; iv, Bu_4NBr, 30 min; v, $(Cl_3CO)_2CO$, THF, −78 °C–room temp., 1 h; vi, $P(OMe)_3$–toluene (1 : 1, v/v), 110 °C, 2 h; vii, LiBr·H_2O (10 equiv.), HMPA, 90 °C, 1 h, 120 °C, 1 h

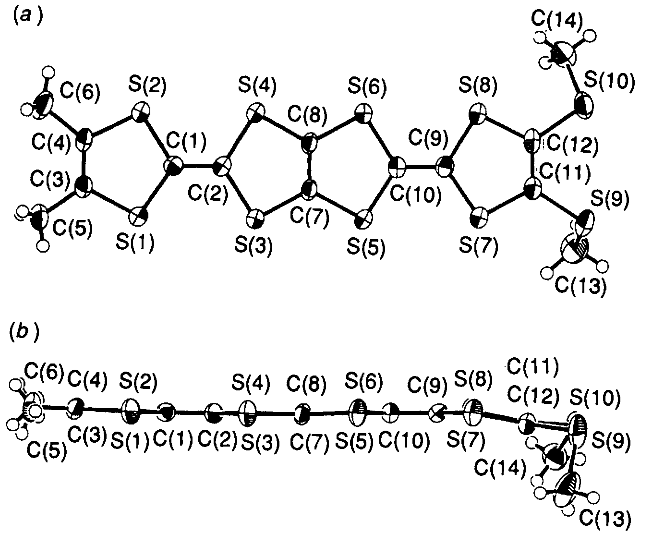


Fig. 1 Molecular structure of (*a*) **1c** and (*b*) the side view; bond lengths (Å): S(1)–C(1) 1.746(4), S(1)–C(3) 1.752(4), S(2)–C(1) 1.752(4), S(2)–C(4) 1.763(4), S(3)–C(2) 1.768(4), S(3)–C(7) 1.736(4), S(4)–C(2) 1.768(4), S(4)–C(8) 1.743(4), S(5)–C(7) 1.754(4), S(5)–C(10) 1.761(4), S(6)–C(8) 1.742(4), S(6)–C(10) 1.771(4), S(7)–C(9) 1.751(4), S(7)–C(11) 1.757(4), S(8)–C(9) 1.754(4), S(8)–C(12) 1.753(4), S(9)–C(11) 1.750(4), S(9)–C(13) 1.799(7), S(10)–C(12) 1.745(4), S(10)–C(14) 1.769(5), C(1)–C(2) 1.347(6), C(3)–C(4) 1.318(6), C(3)–C(5) 1.508(6), C(4)–C(6) 1.496(6), C(7)–C(8) 1.324(6), C(9)–C(10) 1.341(6), C(11)–C(12) 1.340(6)

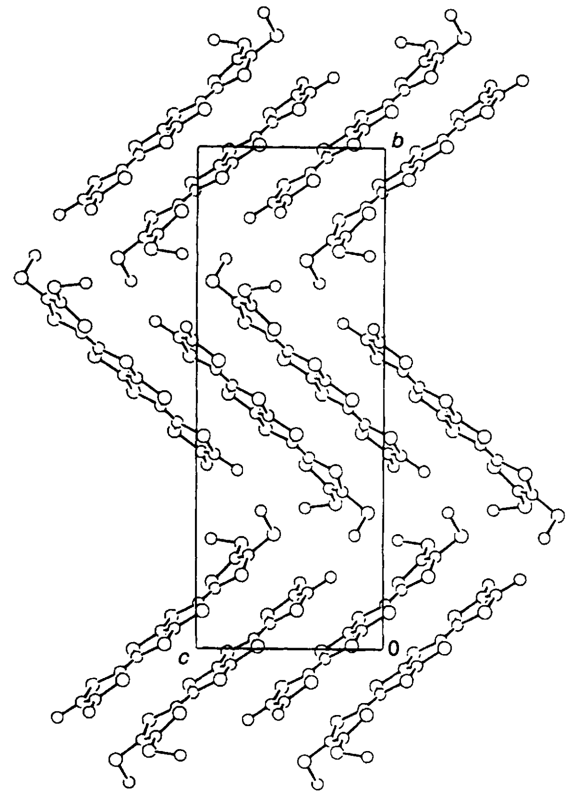


Fig. 2 Crystal structure of **1c** viewed along the *a*-axis

(0.8–60 S cm^{-1} at room temp.) on compressed pellets, and many of them exhibit metallic conducting behaviour. It is noteworthy that TCNQ complex and I_3 salts of **1d** are metallic down to 4.2 K. The other metallic salts show metal to semiconductor transition around 170–200 K. Further investigations, in particular, preparation of single crystals suitable for X-ray structure analysis are in progress.

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Footnotes

† *Selective data* for **1**. ^{1}H NMR data 90 MHz in CS_2–[$^2H_6$]benzene. **1a**: 72% yield; brown powder; mp 179–180 °C (decomp.); δ 1.77 (6 H, s), 5.96 (2 H, s); MS *m/z* 408 (M^+). **1b**: 79% yield; black lustre microcrystals; mp 190–191 °C (decomp.); δ 1.65 (6 H, s), 3.45 (6 H, s); MS *m/z* 524 (M^+). **1c**: 56% yield; red plates; mp 182–183 °C (decomp.); δ 1.77 (6 H, s), 2.22 (6 H, s); MS *m/z* 500 (M^+). **1d**: 53% yield; reddish-brown powder; mp 189–190 °C (decomp.); δ 1.70 (6 H, s), 4.42 (2 H, s); MS *m/z* 470 (M^+). **1e**: 59% yield; reddish-brown powder; mp 202–203 °C (decomp.); δ 1.72 (6 H, s), 2.82 (4 H, s); MS *m/z* 484 (M^+). **1f**: 34% yield; reddish-brown powder; mp 214–215 °C (decomp.); δ 0.85–0.88 (2 H, m), 1.69 (6 H, s), 2.33 (4 H, t); MS *m/z* 498 (M^+). **1g**: 28% yield; red powder; mp 193–194 °C (decomp.); δ 1.73 (6 H, s), 4.24 (4 H, s); MS *m/z* 466 (M^+).

‡ Compound **8** was prepared by treatment of **4** with an excess of sodium methoxide, followed by the reaction with an excess of iodomethane in a quantitative yield. This methodology for synthesis of unsymmetrical TTF has been recently developed (J. D. Kilburn, H. Uech and A. E. Underhill, *Tetrahedron. Lett.*, 1992, **33**, 3923).

§ *Crystal data* for **1c**: $C_{14}H_{12}S_{10}$, $M = 500.85$, monoclinic, space group $P2_1/c$, $a = 7.523(3)$, $b = 26.218(3)$, $c = 9.944(2)$ Å, $\beta = 94.29(2)°$, $V = 1955.7(8)$ Å^3, $Z = 4$, $D_c = 1.701$ g cm^{-3}, Cu-Kα radiation, $\lambda = 1.54178$ Å, $\mu = 104.17$ cm^{-1}, $F(000) = 1024$. The data were collected on a Rigaku AFC5R diffractometer equipped with graphite monochromated Cu-Kα radiation using the ω–2θ scan technique to a maximum 2θ of 120.2°. The structure was solved by direct methods and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.056$, $R_w = 0.084$ for 2407 observed ([$I \geqslant 3\sigma(I)$]) reflections from 3009 unique data. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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