

2-(1',3'-Dithiol-2'-ylidene)-5-(thiopyran-4''-ylidene)-1,3,4,6-tetrathiapentalene: a Novel Bis-fused π -Electron Donor

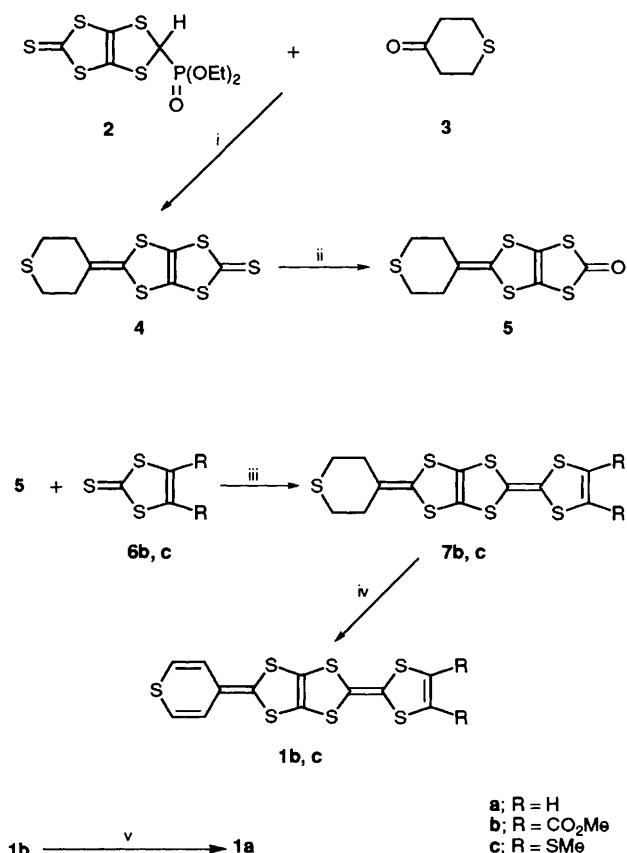
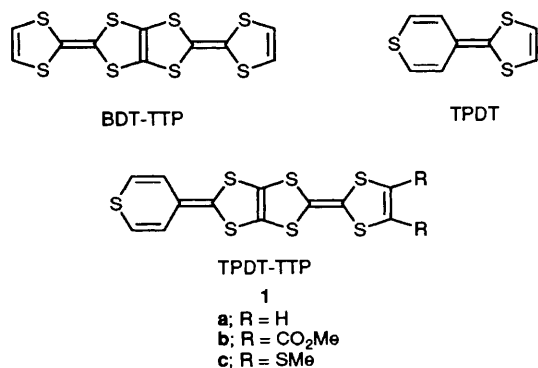
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The synthesis and electrochemical properties of the title compound and its derivatives are described; the electrical properties of their charge-transfer complexes and cation radical salts are also presented.

π -Electron donors possessing more than two 1,3-dithiol-2-ylidenes are of current interest for the development of organic conductors because on-site Coulombic repulsion in their dications decreases owing to delocalization of two positive charges over the whole redox-active 1,3-dithiol-2-ylidenes.¹ In order to simultaneously realize a multistage redox property

and two-dimensional electrical conductivity²⁻⁴ as is observed in superconducting bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts,⁵ we have recently synthesized several derivatives of 2,5-bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP), the bis-fused TTF, which afforded highly conducting cation radical salts showing metallic tem-



Scheme 1 Reagents and conditions: i, LDA, THF, -78°C , 20 min; ii, Hg(OAc)₂ (2.5 equiv.), CHCl₃-AcOH (1:1, v/v), room temp., 2 h; iii, P(OEt)₃, 80°C , 2 h; vi, DDQ (2.3–2.8 equiv.), xylene, reflux, 30 min; v, LiBr·H₂O (10 equiv.), HMPA, 90°C , 1 h and 130°C , 30 min.

perature dependence on conductivities.⁴ In this connection 2-(1',3'-dithiol-2'-ylidene)-5-(thiopyran-4''-ylidene)-1,3,4,6-tetrathiapentalene (TPDT-TTP, **1**), a bis-fused donor composed of TTF and 2-(thiopyran-4'-ylidene)-1,3-dithiole (TPDT),⁶ has similar properties to those mentioned above. In this communication we report the synthesis and electrochemical properties of a new bis-fused donor **1** and its derivatives, and electrical properties of their charge-transfer (CT) complexes and cation radical salts.

Synthesis of TPDT-TTPs was achieved as shown in Scheme 1. Treatment of a phosphorous reagent for a Wittig-Horner reaction **2** with an equimolar amount of lithium diisopropylamide (LDA) in the presence of tetrahydrothiopyran-4-one **3** in tetrahydrofuran (THF) at -78°C gave a 1,3-dithiole-2-thione **4** in 67% yield. Reaction of **4** with an excess of

Table 1 Redox potentials of **1a** and **c** and their related compounds^a

Compound	E_1	E_2	E_3	E_4^b	$E_2 - E_1$
1a	+0.37	+0.60	+0.94	+1.11	0.23
1c	+0.38	+0.63	+0.93	+1.10	0.25
TTF	+0.35	+0.77			0.42
TPDT	+0.28	+0.69			0.41

^a Bu₄NClO₄ 0.1 mol dm⁻³ in PhCN, Pt electrode, 25°C , scan rate 50 mV s⁻¹, V vs. saturated calomel electrode (SCE). ^b Irreversible steps. Anodic peak potentials.

Table 2 Electrical properties of TCNQ complexes and I₃ salts of **1**

Donor	Acceptor	D : A ^a	$\sigma_{\text{r}}/\text{S cm}^{-1b}$	E_{a}/eV
1a	TCNQ	1 : 1	37	0.019
1a	I ₃	2 : 1	6.0	0.021
1c	TCNQ	1 : 1	1.8	0.009–0.032
1c	I ₃	3 : 2	0.4	0.064

^a Determined based on elemental analyses. ^b Measured on the compressed pellets using the four-probe technique.

mercury(II) acetate in chloroform-acetic acid (1:1, v/v) afforded the corresponding 1,3-dithiol-2-one **5** in 92% yield. When the ketone **5** was cross-coupled with 4,5-bis(methoxycarbonyl)- and 4,5-bis(methylthio)-1,3-dithiole-2-thiones (**6a**, **b**) in neat triethylphosphite at 80°C , the corresponding tetrahydro derivatives of **1** (**7a**, **b**) were obtained in yields of 73 and 44%, respectively. Dehydrogenation of **7** was carried out by treatment with an excess of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in refluxing xylene to give bis(methoxycarbonyl)- and bis(methylthio)-derivatives of **1** (**1b**, **c**) in 83 and 79% yields, respectively. The parent TPDT-TTP **1a** was obtained by heating **1b** with an excess of LiBr·H₂O in hexamethylphosphoramide (HMPA) at 90 – 130°C in 45% yield.†

Cyclic voltammograms of **1a** and **c** consisted of four pairs of single-electron redox waves similarly to those of BDT-TTPs; a satisfactory voltammogram of **1b** could not be obtained because of its extremely low solubility for the common solvents. The redox potentials of **1a** and **c** are summarized in Table 1 together with those of TTF and TPDT. The first oxidation potential (E_1) of **1a** (+0.37 V vs. SCE) was almost equal to that of TTF (+0.35 V), but was higher by ca. 0.1 V than that of TPDT (+0.28 V) measured under the identical condition. On the other hand the ΔE ($= E_2 - E_1$) value (0.23 V) was smaller by ca. 0.2 V than those of TTF (0.42 V) and TPDT (0.41 V), suggesting that the on-site Coulombic repulsion in its dication decreased by delocalization of two positive charges in the whole molecule to an extent.

The donors **1a** and **c** reacted with tetracyano-*p*-quinodimethane (TCNQ) and tetra-*n*-butylammonium triiodide to afford the corresponding TCNQ complexes and I₃ salts. The compressed pellets of these salts showed high electrical conductivities in the range of 0.4–37 S cm⁻¹ at room temperature (Table 2). Furthermore the activation energies (E_{a}) of these salts were very small (0.009–0.064 eV),

† TPDT-TTPs. **1a**: orange plate-like microcrystals; m.p. 200 – 201°C (decomp.); ¹H NMR (90 MHz, CS₂-[²H₆]benzene) δ 5.78–5.92 (4H, m), 6.75 (2H, s); MS m/z 374 (M⁺). **1b**: dark-brown microcrystals; m.p. 218°C (decomp.); ¹H NMR spectrum could not be obtained owing to its insolubility; MS m/z 490 (M⁺). **1c**: orange plate-like microcrystals; m.p. 183 – 184°C (decomp.); ¹H NMR (90 MHz, CS₂-[²H₆]acetone) δ 2.40 (6H, s), 6.08 (2H, s), 6.17 (2H, s); MS m/z 466 (M⁺).

suggesting their single crystals are expected to exhibit metallic conductive behaviour. We are currently engaged in the preparation of a single crystals of these conducting salts.

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