

Bis(phenylethylenedithio)tetrathiafulvalene (BPhEDT-TTF)

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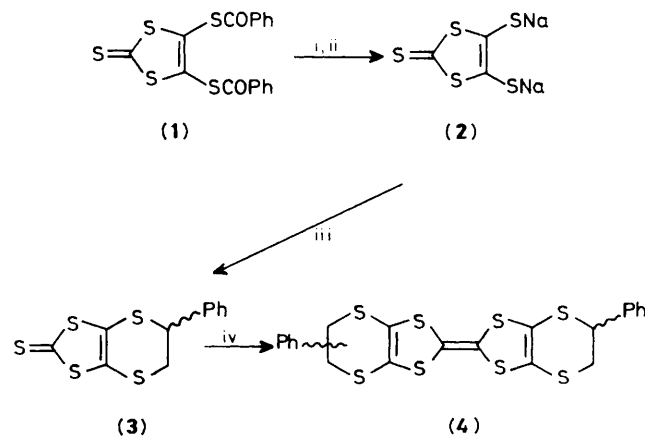
The title compound, synthesized from (\pm)-4,5-phenylethylenedithio-1,3-dithiole-2-thione *via* triethyl phosphite coupling, has been prepared and characterized; some electrochemically prepared salts of this new π -donor are described.

The symmetrical organic π -donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), and its cation-radical salts have been the subject of numerous studies owing to the superconducting properties of some of the salts.^{1,2} Dunitz and co-workers have reported the novel chiral organic donor, *S,S,S,S*-bis-(dimethylethylenedithio)tetrathiafulvalene (TMET), and some of its cation-radical salts.^{3,4} Recently, new organic superconductors derived from the unsymmetrically substituted donor dimethyl(ethylenedithio)diselenadithiafulvalene (DMET) have been reported.⁵ We now report the synthesis of the first asymmetrically-substituted phenyl derivative of BEDT-TTF, BPhEDT-TTF (**4**), albeit as a mixture of possible isomers. The introduction of bulky phenyl groups into BEDT-TTF may prevent inversion of the sp^3 carbons of the dihydrodithiin rings, an important process affecting the structural and electronic properties of the salts of unsubstituted BEDT-TTF.

The 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**1**) was converted in quantitative yield to the dimercapto disodium salt (**2**) by deprotection using sodium ethoxide at room temperature. The salt (**2**) precipitates as a crystalline red compound in large excess of dry ether and was isolated using Schlenk techniques.⁶ We have previously used (**2**) for an improved synthesis of BEDT-TTF⁶ and in the construction of 1,4-dithiino ring systems.⁷⁻⁹

Treatment of (**2**) with an equimolar amount of (\pm)-1,2-

dibromoethylbenzene in dry methanol provided (\pm)-4,5-phenylethylenedithio-1,3-dithiole-2-thione (**3**)[†] in 60–65% yield [(**3**), m.p. 148–150 °C; i.r. (KBr, cm^{-1}): 1085 (C=S); ¹H



Scheme 1. Reagents and conditions: i, NaOEt, EtOH, 20 °C, 20 min; ii, excess dry ether, 20 °C, 10 min; iii, (\pm)-CH₂BrCHBrPh, MeOH, 20 °C, 18 h; iv, P(OEt)₃, 100–130 °C, 30 min.

[†] Satisfactory elemental analysis obtained.

n.m.r. (CDCl_3 , δ): 3.51 (m, 2H), 4.7 (m, 1H), 7.33 (m, 5H); ^{13}C n.m.r. (CDCl_3 , δ): 35.73(CH_2), 48.73(CH), 121.79(Ph-C), 125.02(Ph-C), 127.66(Ph-C), 129.18(Ph-C), 129.34(Ph-C), 137.63(C=C), 208.25(C=S), m/z M^+ : 300].

Thione (3) was coupled in triethyl phosphite at 100–130 °C to afford the title compound as a mixture of possible isomers [(4)‡ in 45–50% yield; m.p. 207–210 °C (decomp.); i.r. (KBr, cm^{-1}): 3059w, 3027w, 2915w, 1630m, 1490m, 1407m, 1291w, 906m, 772m, 726m, 696m; ^1H n.m.r. (CDCl_3 , δ): 3.57 (m, 4H), 4.7 (m, 2H), 7.36 (m, 10H); ^{13}C n.m.r. (CDCl_3 , δ): 36.52 (CH_2), 48.88 (CH), 127.6 (Ph-C), 128.6 (Ph-C), 129 (Ph-C), 138.4 (C=C); u.v. (cyclohexane, nm) λ_{max} (log ϵ), 218 (5.23), 308 (4.75), 344 sh (4.60).

Cyclic voltammetry of (4) in dichloromethane (0.1 M Bu_4NPF_6 , Pt working electrodes, 20 mV s^{-1}) shows two reversible one-electron oxidation waves at +0.47 V and +0.62 V [vs. Standard Calomel Electrode (SCE)]. The corresponding values for BEDT-TTF (measured under identical conditions) are +0.49 and +0.64 V. The phenyl substituent in (4) clearly aids the stabilization of the cation-radical as well as the dication species.

Electrochemical growth of charge-transfer salts with the inorganic anions PF_6^- , ClO_4^- , and I_3^- has been accomplished using a constant voltage (2.5 V) at room temperature in 1,1,2-trichloroethane (TCE). Elemental analysis for the ClO_4^- salt shows it to be a 1 : 1 salt containing one molecule of

‡ Fast atom bombardment mass spectrometry of the title compound (4) in *m*-nitrobenzyl alcohol gave not unexpectedly^{10,11} an abundant M^+ ion at m/z 536 with an isotopic pattern ($M + 1$: 35.0%, $M + 2$: 41.2%, $M + 3$: 12.8%, $M + 4$: 8.2%). This is very close to the expected values calculated for $\text{C}_{22}\text{H}_{16}\text{S}_8$ with 5% protonation. ($M + 1$: 36.6%; $M + 2$: 41.8%; $M + 3$: 13.3%; $M + 4$: 7.7%).

solvent, *i.e.* (BPhEDT-TTF) ClO_4 (TCE). The electrical conductivity measured along the needle axis of a single crystal of the perchlorate salt by a standard four-probe technique at room temperature was $2 \times 10^{-6} \text{ S cm}^{-1}$.

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