

New π -Electron Donors for Organic Metals: Synthesis of Substituted Tetrathiafulvalenes with Eight- and Nine-Membered Dithiaheterocycles: Crystal Structure of 5,6,7,8-Tetrahydro-1,3-dithiolo[4,5-*b*][1,4]dithiocine-2-thione

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Reaction of the dimercapto disodium salt **2** with 1,4-dibromobutane, dibromo-*o*-xylene, 1,8-bis(bromomethyl)naphthalene and 1,2,4,5-tetrakis(bromomethyl)benzene gave the thiones **3**, **5**, **8** and **11** respectively. The thiones **5** and **8** were oxidised to give the oxo derivatives **6** and **9**. Coupling of the thiones **3**, **5** and **8** or their oxo derivatives **6** and **9** in neat triethyl phosphite afforded new π -donors **4**, **7** and **10** respectively. Reaction of **2** with dimethyltellurium dichloride gave di(dithiolo)tetrathiocinedithione **15**. The oxidation potentials of the donors **4**, **7** and **10** are reported along with the preparation and electrical conductivity measurements of their charge-transfer complexes with 7,7,8,8-tetracyano-*p*-quinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. The crystal structure of 5,6,7,8-tetrahydro-1,3-dithiolo[4,5-*b*][1,4]dithiocine-2-thione **3** was determined by single-crystal X-ray diffraction. Compound **3** crystallizes in the monoclinic space group *P*2₁/*n* with unit-cell dimensions *a* = 4.8048(6) Å, *b* = 9.029(1) Å, *c* = 23.250 Å, β = 93.22(1), *V* = 1028.0(2) Å³, *Z* = 4 and *R* = 0.046.

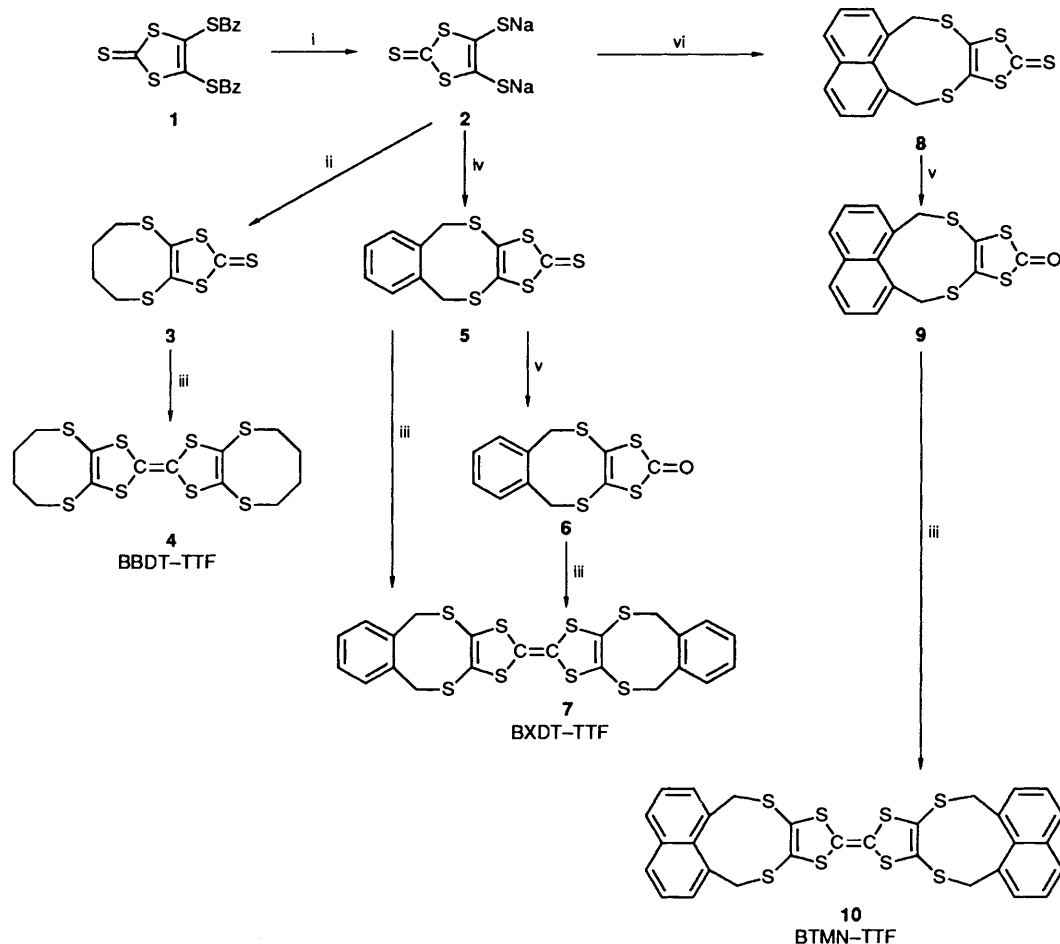
Substituted tetrathiafulvalenes (TTF) and their selenium and tellurium analogues have attracted much interest in the field of organic metals and superconductors.¹ Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has yielded several ambient pressure superconductors and the superconducting transition temperature of these materials has been rapidly rising. A *T*_c of ca. 10.5 K in κ -(BEDT-TTF)₂Cu(NCS)₂ was reported² in 1988 and with the recent findings³ of *T*_c ca. 12.5 K in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl under pressure of 0.3 kbar, a new high in *T*_c for organic systems has now been achieved. An ambient pressure superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Br with *T*_c = 11.6 K has also been reported.⁴ The presence of two-dimensional S...S networks in the radical cation salts of BEDT-TTF is now believed to be responsible for suppressing instabilities inherent to the low-dimensional systems. Consequently, there is great interest in the synthesis of new donor molecules with similar structures.^{5,6} An analogous tuning of the S...S interactions is in principle possible with the replacement of ethylene bridges in BEDT-TTF by propylene bridges in bis(propylenedithio)tetrathiafulvalene (BPDT-TTF).⁷ We report here the synthesis of three donors, bis(butylenedithio)tetrathiafulvalene (BBDT-TTF), bis(*o*-xylenedithio)tetrathiafulvalene (BXDT-TTF) and bis(1,8-thiomethylnaphthalene)tetrathiafulvalene (BTMN-TTF) which incorporate annulated eight- and nine-membered dithiaheterocycles. The presence of bulkier butylene and pentylene bridges should not only lead to expansion of the unit cell but also enhance hydrogen bonding with anions in the charge-transfer salts and thereby favourably affect the electronic properties. Goldenberg *et al.*⁸ have reported the synthesis of BXDT-TTF without experimental details and full characterisation data. We have synthesised BXDT-TTF by a different route with high overall yield.

Another approach in the development of organic metals involves incorporation of several sulphur atoms and other heteroatoms in the TTF skeleton, thereby increasing the intermolecular interactions between the heteroatoms. Recently, some organic multi-sulphur donors,⁹ new TTFs incorporating *N*-heterocyclic moieties¹⁰ and polyether units¹¹ have been

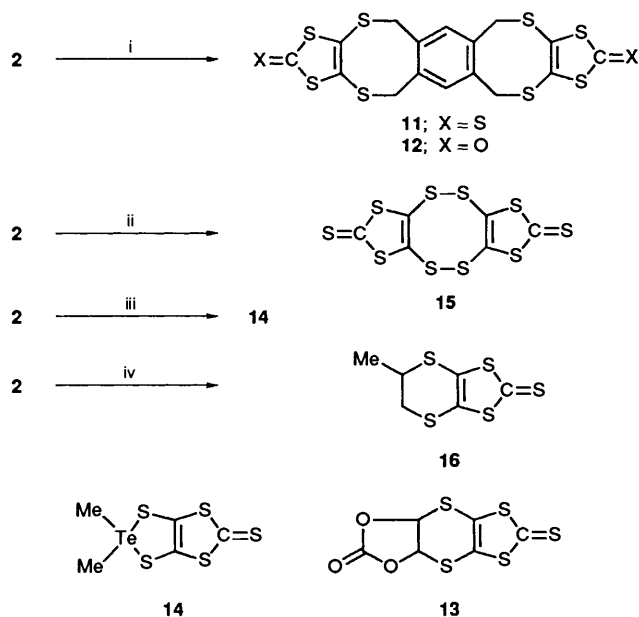
reported. We also report herein our attempts to synthesise such a multi-sulphur TTF donor and incorporation of tellurium, oxygen and phosphorus in the outer ring of BEDT-TTF. An X-ray diffraction study of **3** was carried out to ascertain the mode and extent of S...S interactions and the conformation in the new precursor to organic metals. A portion of this work has already been communicated.¹²

Results and Discussion

The dimercapto disodium salt **2** was obtained from dithia-benzoyl ester¹³ **1** by deprotection using sodium methoxide at room temperature. The salt was isolated following the method of Underhill *et al.*¹⁴ Treatment of **2** with 1,4-dibromobutane, dibromo-*o*-xylene and 1,8-bis(bromomethyl)naphthalene provided the corresponding thiones **3**, **5** and **8** in good yield. Oxidation of the thiones **5** and **8** with mercuric acetate yielded their oxo analogues **6** and **9** respectively in moderate yield. The novel substituted TTFs, BBDT-TTF **4**, BXDT-TTF **7** and BTMN-TTF **10** were obtained by the coupling of the thiones **3**, **5** and **8** or their oxo analogues **6** and **9** with triethyl phosphite in moderate yield (Scheme 1). In an attempt to synthesise a TTF with more than ten sulphur atoms, the bis(thione) **11** was prepared in 84% yield by slight modification of the reported procedure.⁹ Oxidation of **11** with mercuric acetate gave the dioxo derivative **12** in poor yield. Coupling reactions of **11** and **12** with triethyl phosphite were not successful. In an attempt to incorporate 1,3-dioxolan-2-one and dimethyl telluride in the outer ring of BEDT-TTF, 4,5-dichloro-1,3-dioxolan-2-one and dimethyltellurium dichloride were allowed to react with **2**. The reaction, instead of capping the anion to produce the expected thiones **13** and **14**, resulted in di(dithiolo)tetrathiocinedithione **15** (Scheme 2). Dimethyltellurium(IV) dichloride was reduced to dimethyltellurium(II) which could be identified by a comparison of its NMR spectral and TLC characteristics with those of an authentic sample. Recently Rauchfuss *et al.*¹⁵ have reported the preparation of **15** from the treatment of 'zincate synthon' with SO₂Cl₂. Compound **15** is a useful precursor to dithiacyclopentenone derivatives.



Scheme 1 Reagents and conditions: i, NaOMe-MeOH; ii, Br(CH₂)₄Br; iii, P(OEt)₃, heat; iv, dibromo-*o*-xylene; v, Hg(OAc)₂-AcOH; vi, 1,8-bis(bromomethyl)naphthalene



Scheme 2 Reagents: i, 1,2,4,5-tetrakis(bromomethyl)benzene; ii, 4,5-dichloro-1,3-dioxolan-2-one; iii, (CH₃)₂TeCl₂; iv, 1,2-dibromopropane

Papavassiliou *et al.*¹⁶ have reported the synthesis of the thione **16** in good yield from the reaction of the 'zincate synthon' with 1,2-dibromopropane. Reaction of the latter with **2**, in our hands, afforded **16** in very low yield. Our attempts to induce **2** to

react with phenylphosphine dichloride, 3,4-dibromothiophene, 1,2-dibromobenzene and dichloromalononitrile were unsuccessful.

The π -donors and their precursors were identified by elemental analysis and mass spectrometry. All the compounds have shown molecular ion peaks. The ¹H NMR spectra of the thione **8** and its oxo analogue **9** showed interesting features. The CH₂ proton resonances of these compounds appeared as an unresolved AB quartet at room temperature. However, a variable temperature ¹H NMR spectroscopic study of **8** and **9** yielded a well resolved AB quartet at -30 °C which coalesces upon warming to 20 °C (Fig. 1). A similar type of AB spectrum has been observed by Guttenberger *et al.*¹⁷ for 3*H*,7*H*-naphtho[1,8-*de*]-1,2-dithiepin which suggests the presence of chair and boat geometries in solution. The ¹³C NMR chemical shift data for substituted TTFs are rather limited because of the poor solubility of most of the compounds. The new π -donor **4** showed three peaks at δ 27.47 (CH₂), 38.41 (SCH₂) and 140.16 (C=C) respectively. Cyclic voltammetry of donors **4**, **7** and **10** showed two reversible one-electron oxidation waves at 0.525, 0.950, 0.515, 0.980 and 0.525, 1.06 V respectively. Comparison of these values with those for BEDT-TTF at 0.530 and 0.937 V, measured under identical experimental conditions, shows that substitution of bulkier alkylthio groups in BEDT-TTF aids the stabilization of the cation radicals and not the dication species.

Both BBDT-TTF **4** and BTMN-TTF **10** form 1:1 C-T complexes with π -acceptors TCNQ and DDQ. The C-T complexes of BBDT-TTF are conducting (**4**·TCNQ = 4.9×10^{-4} , **4**·DDQ = 2.7×10^{-3} S cm⁻¹) while that of BTMN-TTF are insulators (**10**·TCNQ 5.8×10^{-7} , **10**·DDQ = 7.7×10^{-7} S

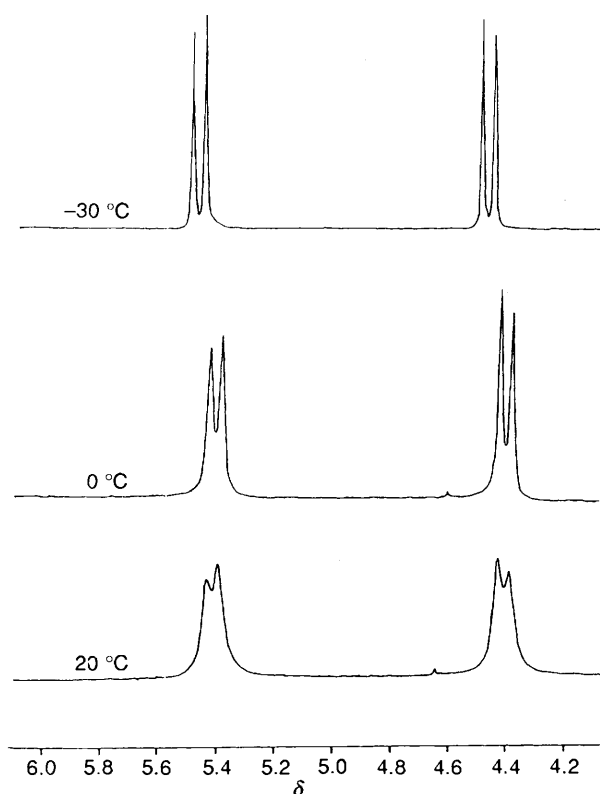


Fig. 1 300 MHz ^1H NMR spectra of the CH_2 protons of **8** in CDCl_3 at 20, 0 and -30°C

Table 1 Positional parameters for $\text{S}_5\text{C}_7\text{H}_8$

Atom	x	y	z
S(1)	0.677 1(3)	0.106 1(2)	0.558 36(7)
S(2)	0.700 5(3)	0.220 3(2)	0.698 01(7)
S(3)	1.075 3(3)	0.352 5(2)	0.542 01(7)
S(4)	1.084 7(3)	0.452 2(2)	0.659 09(7)
S(5)	1.421 3(4)	0.612 9(2)	0.577 8(1)
C(1)	0.872(1)	0.254 1(5)	0.587 7(2)
C(2)	0.876(1)	0.300 9(5)	0.642 4(2)
C(3)	1.207(1)	0.479 7(6)	0.591 7(3)
C(4)	0.881(1)	-0.098 8(7)	0.643 6(3)
C(5)	0.955(1)	0.089 0(7)	0.726 2(3)
C(6)	0.876(1)	-0.056 9(6)	0.580 3(3)
C(7)	1.078(1)	-0.010 3(7)	0.683 5(3)
H(1)	1.07(1)	-0.044(7)	0.569(3)
H(2)	0.85(1)	0.042(6)	0.757(2)
H(3)	1.19(1)	-0.082(6)	0.704(2)
H(4)	1.19(1)	0.041(8)	0.659(3)
H(5)	0.70(1)	-0.090(6)	0.660(2)
H(6)	0.94(1)	-0.202(7)	0.646(2)
H(7)	0.78(1)	-0.127(7)	0.551(3)
H(8)	1.10(2)	0.14(1)	0.751(4)

cm^{-1}). BXDT-TTF **7** does not react with TCNQ, however, it forms 1:1 C-T complex with DDQ which is an insulator ($7 \cdot \text{DDQ} = 9.4 \times 10^{-8} \text{ S cm}^{-1}$).

ESR spectra of the C-T complexes showed a singlet, which was superimposable with the marker (TCNE) signal. The g factor (2.00) is almost the same for all the complexes and is very close to the free electron value, suggesting that the signal was due to an unpaired electron on TCNQ and DDQ. The degree of charge-transfer in organic conductors could be monitored by the examination of $\nu(\text{CN})$ for TCNQ 18 and $\nu(\text{CO})$ for DDQ. 19 The method is applicable only to conducting materials, however for the complexes synthesised the IR spectroscopic data are

Table 2 Bond lengths (\AA) and bond angles ($^\circ$) with esds in parentheses for compound **3**

S(1)-C(1)	1.759(5)	S(4)-C(3)	1.726(7)
S(1)-C(6)	1.824(6)	S(5)-C(3)	1.643(6)
S(2)-C(2)	1.753(5)	C(1)-C(2)	1.339(8)
S(2)-C(5)	1.817(7)	C(4)-C(6)	1.517(9)
S(3)-C(1)	1.739(6)	C(4)-C(7)	1.529(9)
S(3)-C(3)	1.728(6)	C(5)-C(7)	1.491(1)
S(4)-C(2)	1.737(5)		
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C(1)-S(1)-C(6)	103.5(3)	S(4)-C(2)-C(1)	115.9(4)
C(2)-S(2)-C(5)	100.4(3)	S(3)-C(3)-S(4)	112.1(3)
C(1)-S(3)-C(3)	97.8(3)	S(3)-C(3)-S(5)	125.0(4)
C(2)-S(4)-C(3)	98.0(3)	S(4)-C(3)-S(5)	122.9(4)
S(1)-C(1)-S(3)	118.0(3)	C(6)-C(4)-C(7)	115.6(5)
S(1)-C(1)-C(2)	125.8(4)	S(2)-C(5)-C(7)	116.6(5)
S(3)-C(1)-C(2)	116.2(4)	S(1)-C(6)-C(4)	116.8(5)
S(2)-C(2)-S(4)	117.9(3)	C(4)-C(7)-C(5)	117.0(6)
S(2)-C(2)-C(1)	126.1(4)		

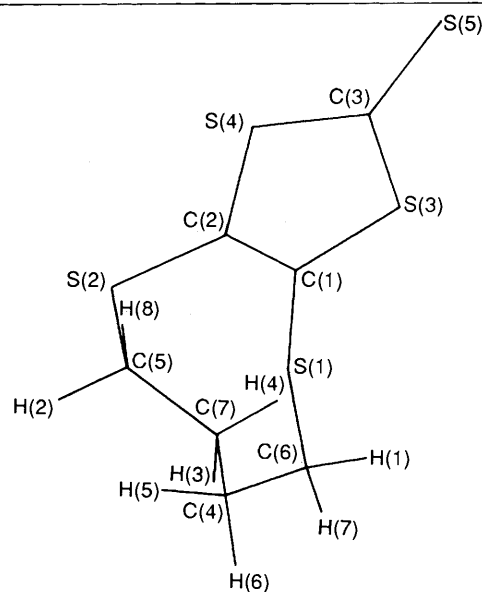


Fig. 2 Molecular structure of **3**

different from those of the components. The $\nu(\text{CN})$ band of TCNQ $^\circ$ (2230 cm^{-1}) is observed *ca.* 2210 cm^{-1} indicating partial charge transfer [$\text{Na}^+\text{TCNQ}^{\cdot-}$ $\nu(\text{CN}) = 2180 \text{ cm}^{-1}$]. In the case of DDQ complexes, $\nu(\text{CO})$ at 1680 cm^{-1} is absent. Characteristic absorption for the phenoxy radical appeared at $1560\text{--}1565 \text{ cm}^{-1}$ and the $\nu(\text{CN})$ bands of DDQ $^\circ$ (2222 cm^{-1}) is only slightly shifted. Attempts to prepare a perchlorate cation-radical salt by electrochemical oxidation of donor **4** have not yielded isolable crystals so far.

Crystal and Molecular Structure of 3.—Atomic coordinates are listed in Table 1. The bond lengths and bond angles are gathered in Table 2. The molecular structure of **3** is shown in Fig. 2 with the atomic numbering scheme. The crystal structure of the title compound consists of discrete molecules linked by weak intermolecular $\text{S} \cdots \text{S}$ interactions. As in the case of BBDT-TTF **4** 12 the heterocyclic five-membered dithiole ring is highly planar. The maximum deviation from a least-squares plane defined by the dithiole ring atoms is 0.004 \AA which is comparatively much less than that observed in 4,5-bis(methylthio)-2*H*-1,3-dithiole-2-thione (BTDDT) and its 2-oxo analogue (BTDTO). 20 The exterior S atoms, *i.e.* S(1), S(2) and S(5), are also coplanar with the dithiole ring and the deviations from plane 1 are 0.024, 0.046 and 0.041 \AA respectively. The coplanarity of the outer S atoms S(1) and S(2) is further reflected by the conformation angles which are *ca.* 180° . Pronounced

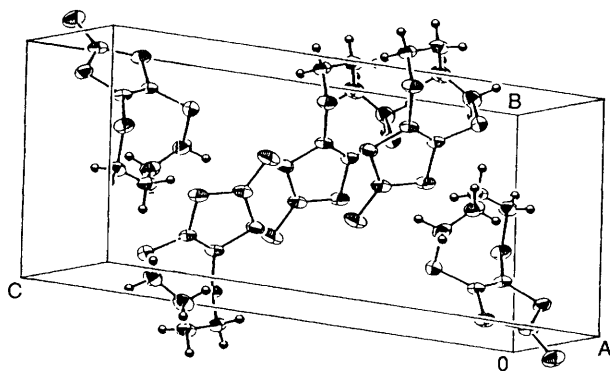


Fig. 3 Packing diagram of 3

double bond character is indicated by the bond length of 1.339(8) Å for C(1)–C(2). The thione bond length of 1.643(6) Å for C(3)–S(5) is in good agreement with that of BTDTT.²⁰ It is observed that the C–S bond distances [$<1.739(6)$ Å] within the five-membered ring are shorter than the outer C–S bond distances (C–sp³) [$>1.753(5)$ Å]. This is probably due to delocalised π -bonding through the interaction of sulphur d orbitals with C=C and C=S π bonds. In addition the bond lengths and bond angles of 2-thioxo-1,3-dithiole-4,5-dithiolate unit are similar to those found in a variety of metal complexes formed by this ligand.^{21–22} This has been interpreted in terms of covalent bonding in both cases.²⁰ In this molecule, there are three weak intermolecular S...S contacts which are less than 3.7 Å [S(3)...S(1), (1 + x, y, z), 3.698(3), S(3)...S(5), (2 – x, 1 – y, 1 – z), 3.609(3), S(1)...S(1), (1 – x, – y, 1 – z), 3.677(4) Å].

The X-ray structure determination of BBTD-TTF 4²³ showed that the 'Z' shaped molecules stack along the *a* axis and incorporation of the bulkier butylene residue in the exterior ring has not affected the S...S intermolecular interactions. The conformation of the eight-membered ring both in 3 and 4 is tub-shaped and the C₃S₅ and C₆S₈ cores highly planar.

Experimental

M.p.s were determined with a Kettan melting point apparatus and are uncorrected. Elemental analysis for C, H and N were carried out with Carlo Erba elemental analyser model 1106. IR spectra were recorded as KBr discs on a Perkin-Elmer 681. UV spectra were recorded on a Shimadzu UV-260 spectrophotometer (CH₂Cl₂ as solvent). ¹H and ¹³C NMR spectra were recorded with Varian VXR 300 MHz instrument with TMS as internal standard (CDCl₃ as solvent); *J* values are given in Hz. Mass spectra were obtained on a Shimadzu QP 1000 mass spectrometer operating at 70 eV. Solid-state ESR spectra were recorded on Varian E-112 ESR spectrometer using tetracyanoethylene as *g*-marker at room temperature. Cyclic voltammetry (CV) experiments were performed in a one-compartment cell with platinum working, platinum wire counter electrode and silver-silver chloride reference electrode. Measurements were made with a BAS model CV-1B electrochemical analyser. The solution of donor (5×10^{-4} mol dm⁻³, with tetrabutylammonium hexafluorophosphate (0.1 mol dm⁻³) as supporting electrolyte in dry dichloromethane (15 cm³) were purged with argon and retained under an inert atmosphere throughout the CV experiments. The scan rate was 100 mV s⁻¹. All the solid-state conductivities were measured on powdered samples at room temperature by the two-probe method; samples were manually compressed between two steel probes and the sample resistance monitored with a Keithley Digital multimeter.

5,6,7,8-Tetrahydro-1,3-dithiole[4,5-b][1,4]dithiocine-2-thione

3.—To a suspension of finely powdered 4,5-bis(benzoylthio)-1,3-dithiole-2-thione 1 (4.06 g, 10 mmol) in absolute methanol (10 cm³) was added a stirred solution of sodium methoxide (sodium 0.48 g, 21 mmol) in absolute methanol (10 cm³) under an inert atmosphere. After 20 min, solvent was evaporated and the red precipitate was washed with ether and dried. The disodium salt 2 was redissolved in methanol (55 cm³). To this solution was added dibromobutane (2.16 g, 10 mmol) in methanol (10 cm³) dropwise over a period of 10 min. The mixture was stirred at room temperature overnight after which the yellow precipitate was filtered off, washed with methanol and dried. Chromatography on silica gel with dichloromethane–light petroleum (b.p. 60–80 °C) (1:1) as the eluent yielded the *title compound* 3 (1.6 g, 63%) as a yellow solid; recrystallisation from chloroform–methanol gave yellow crystals, m.p. 109 °C (Found: C, 32.85; H, 3.15. C₇H₈S₅ requires C, 33.30; H, 3.19%); ν_{\max} (KBr)/cm⁻¹ 1066 (C=S); λ_{\max} (CH₂Cl₂)/nm 357, 273 and 245; δ_{H} (CDCl₃) 2.05 (s, 4 H, CH₂) and 3.05 (s, 4 H, SCH₂); δ_{C} (CDCl₃) 140.16 (C=C), 38.41 (SCH₂) and 27.47 (CH₂); *m/z* 252 (M⁺, 100%).

Bi(5,6,7,8-Tetrahydro-1,3-dithiole[4,5-b][1,4]dithiocine-2-ylidene) 4.—The thione 3 (0.5 g, 0.2 mmol) dissolved in triethyl phosphite (20 cm³) was refluxed and stirred at 120 °C for 2 h to give an orange coloured solution. The mixture was then evaporated and the residue was chromatographed on silica gel with dichloromethane as eluent to yield 4 as an orange solid; recrystallisation from dichloromethane–methanol gave orange crystals (0.16 g, 37%), m.p. 151 °C (Found: C, 38.25; H, 3.85. C₁₄H₁₆S₈ requires C, 38.15; H, 3.66%); ν_{\max} (KBr)/cm⁻¹ 1498, 1300 and 544 (CS), with absence of 1066 peak (C=S); λ_{\max} (CH₂Cl₂)/nm 310 and 227; δ_{H} (CDCl₃) 2.00 (s, 8 H, CH₂) and 2.96 (s, 8 H, SCH₂); δ_{C} (CDCl₃) 131.37 (C=C), 37.78 (SCH₂) and 27.54 (CH₂); *m/z* 440 (M⁺, 100%).

5H,10H-Dithiole[2,3-b][2,5]benzodithiocine-2-thione 5.—The disodium salt 2 (prepared as described in 3) was dissolved in methanol (55 cm³) and to this solution was added dibromo-*o*-xylene (2.63 g, 10 mmol) in tetrahydrofuran (THF) (20 cm³) dropwise over a period of 20 min. The mixture was stirred for 3 h at room temperature to give a yellow precipitate. The precipitate was filtered off, washed with methanol several times and dried to yield 5 as a yellow solid; recrystallisation from dioxane gave yellow crystals (2.52 g, 84%), m.p. 205 °C (lit.⁸ 207 °C) (Found: C, 43.75; H, 2.65. Calc. for C₁₁H₈S₅: C, 43.96; H, 2.68%); ν_{\max} (KBr)/cm⁻¹ 1066 (C=S); λ_{\max} (CH₂Cl₂)/nm 374 and 245; δ_{H} (CDCl₃) 4.37 (s, 4 H, SCH₂) and 7.19–7.30 (m, 4 H, ArH); δ_{C} (CDCl₃) 139.26 (C=C), 133.95 (quaternary ArC), 130.68, 128.98 (tertiary ArC) and 38.53 (SCH₂); *m/z* 300 (M⁺, 100%).

5H,10H-Dithiole[2,3-b][2,5]benzodithiocine-2-one 6.—The thione 5 (0.2 g, 0.67 mmol) was dissolved in chloroform (25 cm³) and to this solution was added mercuric acetate (1.68 g, 1.68 mmol) and acetic acid (20 cm³). The mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and the filtrate washed successively with water, aqueous sodium hydrogen carbonate and water, and then dried (Na₂SO₄) and evaporated to give 6 as a white solid; recrystallisation from chloroform–methanol gave white crystals (98 mg, 52%), m.p. 167–169 °C (Found: C, 46.6; H, 3.25. C₁₁H₈O₄S₄ requires C, 46.45; H, 2.84%); ν_{\max} (KBr)/cm⁻¹ 1678 (C=O); λ_{\max} (CH₂Cl₂)/nm 249; δ_{H} (CDCl₃) 4.35 (s, 4 H, SCH₂) and 7.19–7.28 (m, 4 H, ArH); δ_{C} (CDCl₃) 134.08 (C=C), 130.31 (quaternary ArC), 130.67, 128.75 (tertiary aromatic carbons) and 38.19 (SCH₂); *m/z* 284 (M⁺, 25%).

Bi(5H,10H-dithiole[2,3-b][2,5]benzodithiocine-2-ylidene) 7.—

Method A. The oxo compound **6** (0.09 g, 0.32 mmol) dissolved in triethyl phosphite (5 cm³) under dry argon atmosphere was refluxed and stirred at 110–120 °C for 1 h. The reaction mixture was cooled to room temperature and the precipitate was filtered off, washed with ether and dried to yield **7** (15 mg, 18%) as an orange coloured solid.

Method B. The thione **5** (1.3 g, 4.33 mmol) was suspended in triethyl phosphite (25 cm³) under dry argon atmosphere and refluxed and stirred at 110–120 °C for 2 h. The mixture was cooled to room temperature and the orange coloured precipitate was filtered off, washed with ether and dried. When chromatographed on silica gel with dichloromethane as the eluent it yielded **7** as an orange solid; recrystallisation from chloroform gave orange crystals (710 mg, 61%), m.p. 265–267 °C (decomp.) (lit.,⁸ 269 °C) (decomp.) (Found: C, 49.0; H, 3.2. C₂₂H₁₆S₈ requires C, 49.22; H, 3.0%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1480, 508 (C=S) with absence of 1066 peak (C=S); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 340, 286, 243 and 231; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.24 (s, 8 H, SCH₂) and 7.16–7.27 (m, 8 H, ArH); m/z 536 (M⁺, 38%).

7H,13H-1,3-Dithiolo[1,8-fg]naphtho[4,5-b][1,4]dithionine-10-thione 8.—The disodium salt **2** (prepared as described in **3**) was dissolved in methanol (55 cm³) and to this solution was added 1,8-bis(bromomethyl)naphthalene (3.14 g, 10 mmol) in THF (45 cm³) dropwise over a period of 30 min. The mixture was stirred for 5 h at room temperature to give a yellow precipitate. The precipitate was filtered off, washed with methanol several times and dried to yield compound **8** as yellow powder; recrystallisation from dioxane gave yellow crystals (3.1 g, 89%), m.p. 225 °C (decomp.) (Found: C, 51.7; H, 3.0. C₁₅H₁₀S₅ requires C, 51.39; H, 2.88%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1066 (C=S); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 381, 302 and 238; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.39–4.44 (4 H, AB system, *J* 16), 5.40–5.44 (4 H, AB system, *J* 14) and 7.41–7.82 (m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 134.86 (C=C), 131.59, 130.58 (quaternary ArC), 132.89, 130.92 and 125.41 (tertiary ArC); m/z 350 (M⁺, 100%).

7H,13H-1,3-Dithiolo[1,8-fg]naphtho[4,5-b][1,4]dithionin-2-one 9.—The thione **8** (0.16 g, 0.46 mmol) was dissolved in chloroform (30 cm³) and to this solution was added mercuric acetate (0.37 g, 1.15 mmol) and acetic acid (10 cm³). The mixture was stirred at room temperature for 3 h. The reaction mixture was filtered and the filtrate washed successively with water, aqueous sodium hydrogen carbonate and water and then dried (Na₂SO₄) and evaporated to give a white solid; recrystallisation of this from chloroform–methanol gave white crystals (92 mg, 61%), m.p. 211 °C (decomp.) (Found: C, 54.4; H, 3.3. C₁₅H₁₀OS₄ requires C, 53.86; H, 3.01%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1660 (C=O); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 300 and 237; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.39–4.42 (4 H, AB system, *J* 9), 5.39–5.41 (4 H, AB system, *J* 6) and 7.39–7.81 (m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 134.89 (C=C), 132.87, 130.74, 125.29 (tertiary ArC), 131.71 and 130.69 (quaternary ArC), m/z 334 (M⁺, 100%).

Bi(7H,13H-dithiolo[1,8-fg]naphtho[4,5-b][1,4]dithionin-10-ylidene) 10.—**Method A.** The thione (**8**) (0.1 g, 0.29 mmol) was suspended in triethyl phosphite (5 cm³) under a dry argon atmosphere and refluxed and stirred at 130 °C for 2 h. The reaction mixture was cooled to room temperature. The orange precipitate was filtered off, washed with ether and dried to yield compound **10** as an orange solid (10 mg, 11%).

Method B. The oxo compound **9** (0.88 g, 2.63 mmol) dissolved in triethyl phosphite (25 cm³) under a dry argon atmosphere was stirred and refluxed at 120–130 °C for 2 h. The reaction mixture was cooled to room temperature to give an orange coloured solid which was filtered off, washed with ether and dried; recrystallisation from dichloromethane gave orange crystals (220 mg, 26%), m.p. 243–244 °C (decomp.) (Found: C,

55.85; H, 3.15. C₃₀H₂₀S₈ requires C, 56.57; H, 3.17%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1516, 670 and 562 (CS) with absence of 1660 peak (C=S); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 334, 294, 237, 220 and 204; m/z 636 (M⁺).

Benzo[1,2-g:4,5-g']bis[1,3]dithiolo[4,5-b][1,4]dithiocine-2,10-dithione 11.—The disodium salt **2** (prepared as described in **3**) was redissolved in methanol (20 cm³) and to this solution was added tetrakis(bromomethyl)benzene (0.55 g, 1.23 mmol) in THF (25 cm³) dropwise over a period of 15 min. The mixture was stirred for 2 h at room temperature to give a yellow precipitate. The precipitate was filtered off, washed with methanol several times and dried to yield compound **11** as a yellow solid; recrystallisation from dioxane gave yellow crystals (0.54 g, 84%), m.p. 270–272 °C (decomp.) (Found: C, 36.5; H, 2.2. C₁₆H₁₀S₁₀ requires C, 36.75; H, 1.93%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1066 (C=S); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 378 and 278; m/z 522 (M⁺, 7%).

Benzo[1,2-g:4,5-g']bis[1,3]dithiolo[4,5-b][1,4]dithiocine-2,10-dione 12.—The bis(thione) **11** (0.27 g, 1.56 mmol) was suspended in chloroform (150 cm³) and to this suspension was added mercuric acetate (0.5 g, 1.56 mmol) and acetic acid (30 cm³). The mixture was refluxed for 2 h then cooled to room temp. The mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. Evaporation of the solvent after drying over anhydrous sodium sulphate gave a white solid (0.03 g, 12%), m.p. 203–205 °C (decomp.), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1680 (C=O) with absence of 1066 peak (C=S); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 265; m/z 490 (M⁺, 17%).

1,2,5,6-Tetrathiocinedi[1,3]dithiolo-2,7-dithione 15.—The dimercapto disodium salt **2** (prepared as described in **3**) was redissolved in methanol (20 cm³) and to this solution was added dimethyltellurium dichloride²⁴ (0.57 g, 2.46 mmol) in methanol (15 cm³) dropwise over a period of 10 min. The mixture was stirred for 15 min to give a red precipitate. The precipitate was filtered off, washed with methanol and ether several times and dried. The solid was extracted with carbon disulphide and evaporation of the solvent gave a red solid (0.23 g, 49%), m.p. 149 °C (decomp.), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 454m, 508m, 688s, 706s, 814w, 850m, 886m, 1048w, 1066vs, 1120w, 1426vs, 1570vs and 1606vs; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 234, 272 and 372; m/z 392 (M⁺, 22%).

5,6-Dihydro-5-methyldithiolo[4,5-b]dithiine 16.—The dimercapto disodium salt **2** (prepared as described in **3**) was redissolved in methanol (15 cm³) and to this solution was added 1,2-dibromopropane (0.49 g, 2.46 mmol) in methanol (7 cm³) dropwise over 5 min. The mixture was stirred overnight at room temperature to give a yellow precipitate which was filtered off, washed with methanol several times and dried to yield compound **16** as a yellow solid; recrystallisation from ethanol gave yellow crystals (50 mg, 9%), m.p. 53–54 °C (lit.,¹⁶ 55 °C) (Found: C, 31.1; H, 3.25. C₆H₆S₅ requires C, 30.23; H, 2.54%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1084 (C=S); m/z 238 (M⁺, 50%).

Synthesis of Charge-transfer Complexes.—All the complexes were synthesized by essentially similar methods and the following experiment is typical of those carried out.

Preparation of BBDT-TTF-TCNQ Complex.—A warm acetonitrile solution (20 cm³) of BBDT-TTF (20 mg, 0.045 mmol) was added to a warm acetonitrile solution of TCNQ (9.18 mg, 0.045 mmol). The reaction mixture was refluxed for 20 min and then cooled to room temperature to give the complex as a black powder. The latter was filtered off, washed with acetonitrile and dried to yield the charge-transfer complex

(17 mg, 59%), m.p. 242 °C (decomp.) (Found: C, 47.75; H, 3.1; N, 8.5. $C_{14}H_{16}S_8 \cdot C_{12}H_4N_4$ requires C, 48.41; H, 3.12; N, 8.68%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2210 (C≡N); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 399, 328, 311 and 231.

BBDT-TTF-DDQ (53%), m.p. 224 °C (decomp.) (Found: C, 39.6; H, 2.95; N, 4.9. $C_{14}H_{16}S_8 \cdot C_8Cl_2N_2O_2$ requires C, 39.56; H, 2.42; N, 4.19%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2218 (C≡N); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 776, 417, 325, 289 and 236.

BXDT-TTF-DDQ (60%), m.p. 240 °C (decomp.) (Found: C, 47.5; H, 2.25; N, 4.1. $C_{22}H_{16}S_8 \cdot C_8Cl_2N_2O_2$ requires C, 47.17; H, 2.11; N, 3.66%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2200 (C≡N); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 339, 256 and 236.

BTMN-TTF-TCNQ (65%), m.p. 194 °C (decomp.) (Found: C, 60.6; H, 2.45; N, 7.1. $C_{30}H_{20}S_8 \cdot C_{12}H_4N_4$ requires C, 59.97; H, 2.88; N, 6.66%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2210 (C≡N); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 400, 295 and 234.

BTMN-TTF-DDQ (52%), m.p. 212 °C (decomp.) (Found: C, 53.5; H, 2.55; N, 3.9. $C_{30}H_{20}S_8 \cdot C_8Cl_2N_2O_2$ requires C, 52.82; H, 2.33; N, 3.24%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2218 (C≡N); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 890, 703, 412, 336, 290, 264 and 235.

Attempted Electrochemical Preparation of (BBDT-TTF)₂-ClO₄.—BBDT-TTF (3 mmol) dissolved in dry, degassed 1,1,2-trichloroethane (5 cm³) was added to the anode compartment of an H-Cell, which was separated from the cathode compartment by a glass frit. A solution of tetrabutylammonium perchlorate (120 mmol) in 1,1,2-trichloroethane (20 cm³) was added to both the cathode and anode compartments to level both sides. The solutions were then purged with argon before the platinum wire electrodes were inserted. After 8 weeks at 5 μA constant current no crystal growth was observed. However, during electrolysis, the colour of the solution changed from orange to dark black indicating oxidation of the donor.

Crystal Structure Determination.—The crystal structure determination was performed at Keene State College. The X-ray data were collected on a Rigaku AFC6S diffractometer using graphite monochromated Mo-K α radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from least-squares refinement using the setting angle of zero carefully centred reflections in the range $<2\theta$ corresponded to a monoclinic cell with dimensions: $a = 4.9048(6)$ Å, $b = 9.029(1)$ Å, $c = 23.250(3)$ Å, $V = 1028.0(2)$ Å³, $\beta = 93.22(1)^\circ$. For $Z = 4$ and $M = 252.44$. The calculated density is 1.631 g/cm³. Based on the systematic absences of $h0l: h + l = 2n$; $0k0: k = 2n$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$. The data were collected at a temperature of 23 ± 1 °C using the ω - 2θ scan technique to a maximum 2θ value of 50.0°. Of the 2182 reflections which were collected, 1941 were unique. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods.^{25,26} The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-square refinement was based on 1375 observed reflections [$I > 3.00 \sigma(I)$] and 142 variable parameters and converged with unweighted and weighted agreement factors of: $R = \sum \|F_o\| - |F_c| / \sum |F_o| = 0.046$; $R_w = [(\sum_w (|F_o| - |F_c|)^2) / \sum_w F_o^2]^{1/2} = 0.072$. Neutral atom scattering factors were taken from Cromer and Waber.²⁷ Anomalous dispersion effects were included in F_{calc} .²⁸ The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.²⁹ All calculations were performed using the TEXSAN³⁰ crystallographic software package of the Molecular Structure Corporation, PLUTO³¹ and ORTEP³² packages.

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