

New Symmetrical and Unsymmetrical Tetrathiafulvalene π -Donors containing the Dithiinoquinoxaline Ring System

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2,3-Dichloroquinoxaline when treated with the multi-sulphur dithiolate (**1**) gave the thione (**2**), which was coupled using neat triethyl phosphite to give the bisquinoxalinodithiin-fused tetrathiafulvalene, BQDT-TTF (**3**). Cross-coupling of thione (**2**) with 4,5-bis(methylthio)-1,3-dithiole-2-thione and 5,6-dihydro-1,3-dithiol[4,5-*b*][1,4]dithiin-2-thione afforded the unsymmetrical donors (**4**) and (**5**) respectively. The oxidation potentials of donors (**4**) and (**5**) are reported along with the preparation and electrical conductivity measurement of a tri-iodide cation-radical salt of BQDT-TTF (**3**).

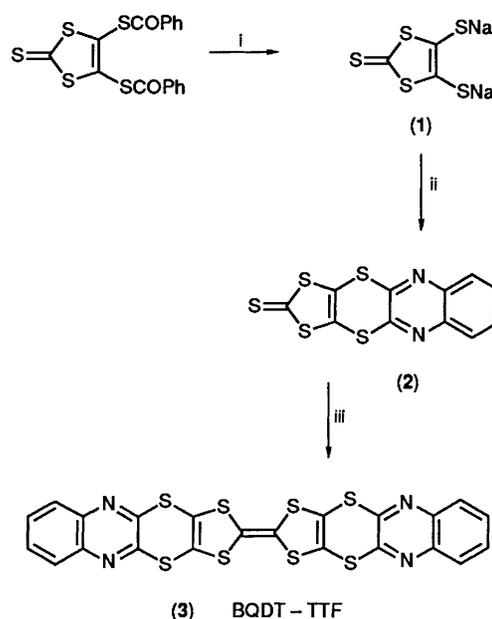
The search for new organic π -donors for the preparation of organic metals, semiconductors, and superconductors has led to extensive synthetic studies on sulphur-, selenium-, and tellurium-based organic molecules.^{1,2} Most of these donors are structurally based on tetrathiafulvalene and key intermediates in their preparation have been synthons containing the 1,3-dithiole-2-thione or trithiocarbonate functionality.^{2,3} This type of intermediate has been recently exploited to give metal dithiolene complexes which have been shown to have useful solid-state electronic and magnetic properties.^{4,5}

One of the desired properties which these donor or ligand systems should display is the ability of their corresponding conducting salts to form segregated stacks within which there should be appreciable intermolecular non-bonding contacts between the chalcogen atoms. These electronic contacts help in overcoming the Peierl's instability or transition from a metallic state to either a semiconducting or insulating one at low temperatures. Recently, some organic multi-sulphur donors incorporating *N*-heterocyclic moieties have been reported which show enhanced intrastack stabilization through S...N and S...S contacts shorter than the corresponding van der Waals distances.^{6,7}

In an effort to further synthetic studies in these donors and *S*-ligands, we have investigated the reactivity of an important multi-sulphur dithiolate, disodium 2-thioxo-2*H*-1,3-dithiole-4,5-dithiolate (**1**) in the nucleophilic substitution of halogen atoms in 2,3-dichloroquinoxaline. In our earlier reports,⁸⁻¹² the dithiolate (**1**) was demonstrated to be a good synthon to build π -donors, ligands, and macrocycles containing multi-sulphur rings. In this paper we report the ability of dithiolate (**1**) to bring about nucleophilic substitutions in *N*-heterocyclic systems, leading to new tetrathiafulvalene donors.

Results and Discussion

The thione (**2**) was obtained in excellent yield from the reaction of the dithiolate sodium salt (**1**) with 2,3-dichloroquinoxaline. The structure of this dithiole-thione (**2**) was confirmed by the expected strong 1 077 cm^{-1} band for the C=S group. To the best of our knowledge, this is the first example of the nucleophilic substitution of heteroaryl halides by the dithiolate (**1**) directly to provide tetrathiafulvalene (TTF) precursors. The coupling of thione (**2**) was achieved by heating it with freshly distilled triethyl phosphite to afford the new *N*-hetero π -donor (**3**) (Scheme 1). Compound (**3**) is insoluble in all the common

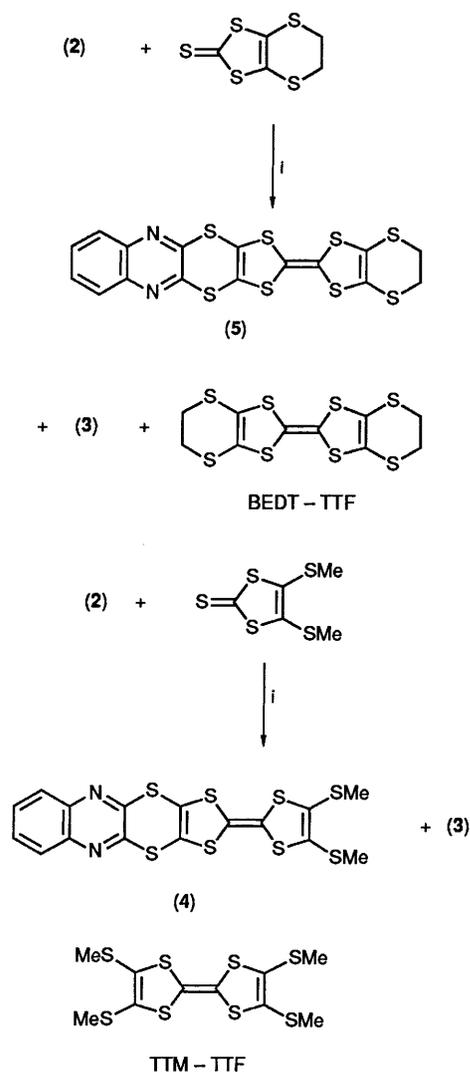


Scheme 1. Reagents and conditions: i, NaOEt-EtOH, followed by excess of dry diethyl ether; ii, 2,3-dichloroquinoxaline; iii, P(OEt)₃, heat.

organic solvents but can be recrystallized from 1,2,4-trichlorobenzene.

Elucidation of the electronic properties of donor (**3**) proved to be difficult due to the solubility problem. Hence a cyclic voltammogram has not been obtained. We have, however, attempted to prepare a tri-iodide cation-radical salt by electrochemical oxidation of donor (**3**) in the presence of tri-iodide anion (see Experimental section). Although no crystal growth was observed on the electrode, slow evaporation of the solution from the anodic compartment produced black needles of a 1:1 stoichiometric complex of compound (**3**) with tri-iodide of reasonable quality, albeit with low conductivity (room temperature conductivity, σ_{RT} 4.5×10^{-6} S cm^{-1} measured using the standard four-probe method).

Oxidation of the donor (**3**) in hot trichlorobenzene solution with tetracyanoquinodimethane (TCNQ) produces a blue solution which is indicative of the presence of radical ion species. Repeated attempts to isolate the solid charge-transfer complex



Scheme 2. Reagents and conditions: i, P(OEt)₃, heat.

were unsuccessful, probably due to the very low solubility of these compounds even in the high boiling trichlorobenzene (see Experimental section).

In an attempt to improve upon the solubility and electronic properties of donor (3), we turned our attention to the synthesis of the unsymmetrical donors (4) and (5). The syntheses were straightforward and involved heating the thione (2) with the respective thiones in triethyl phosphite (Scheme 2). The coupled products were in both cases completely separated by flash column chromatography on silica gel. The by-products (3), TTM-TTF, and BEDT-TTF were all identified using authentic samples. The new unsymmetrical tetrathiafulvalenes (4) and (5) have been characterised. Compound (5) was shown to be homogeneous by TLC on silica with hexane-dichloromethane (1:1) as developer, and the structure was confirmed using mass spectrometry which showed the expected isotopic pattern in the molecular-ion cluster with M^+ at m/z 484 for the presence of eight sulphur atoms. For confirmation of structure (5) the most important fragmentation seen in the mass spectrum is the $M^+ - 28$ fragment, which indicates the presence of the aliphatic dithiine ring. Cyclic voltammetry of donor (4) showed two reversible one-electron waves, at 0.78 and 1.27 V. Comparison of these values with those for donor (5) at 0.82 and 1.06 V shows that while formation of the radical-cation species is slightly easier in compound (4), the formation of a dication species is

more easily achieved in compound (5). The formation of dication species is probably more favoured in rigid cyclic systems as is the case for donor (5). The parent π -donor, tetrathiafulvalene (TTF), oxidises reversibly at 0.43 and 0.85 V when measured under identical conditions.

We anticipate that electrochemically grown cation-radical salts of the donors described in this paper will show enhanced intrastack stabilisation through S...N and S...S contacts, thereby providing interesting new materials for further physical studies.

Experimental

M.p.s were determined with a Büchi melting-point apparatus and are uncorrected. IR spectra were recorded as KBr discs on a Perkin-Elmer 1720 FTIR spectrophotometer. UV spectra were recorded on a Shimadzu UV-160 spectrophotometer [absolute EtOH as solvent; compounds (2), (3), and (5) were not completely dissolved in EtOH, therefore only the λ_{\max} -values are given]. Mass spectra were recorded on a Varian MAT 311A (70 eV) or a Kratos MS50TC instrument. Cyclic voltammograms were obtained on an EG & G Model 264 A polarographic analyser [Pt electrodes; 0.1M-tetrabutylammonium tetrafluoroborate in 1,1,2-trichloroethane; 100 mV s^{-1} scan rate; vs SCE (standard calomel electrode)].

The homogeneity of compounds (2), (4), and (5) was tested by TLC on plastic sheets precoated with silica gel 60 F₂₅₄ (Merck 5734 and 5554) (0.2 mm thickness). Preparative column chromatography was carried out using the 'flash' technique on silica gel 60 (finer than 230 mesh ASTM) (Merck 7729).

4,5-Dimercapto-1,3-dithiole-2-thione Disodium Salt (1).—To a stirred suspension of finely powdered 4,5-bis(benzoylthio)-1,3-dithiole-2-thione^{13,14} (16.24 g, 40 mmol) in absolute ethanol (50 ml) was added a solution of sodium ethoxide [obtained by dissolving sodium (1.86 g, 0.81 g-atom) in absolute ethanol (20 ml)] under nitrogen. After 0.5 h the clear red dithiolate solution was poured slowly into stirred, dry diethyl ether (1.5 l). After 0.25 h the resulting crimson-red precipitate was filtered off under nitrogen, using the Schlenk technique, and washed well with dry diethyl ether. The salt (1) was dried *in vacuo* for 0.5 h and was then used directly in the next step without further purification. A quantitative yield of salt (1) (9.68 g) was obtained.

1',3'-Dithiolo[4',5':5,6][1,4]dithiino[2,3-b]quinoxaline-2-thione (2).—2,3-Dichloroquinoxaline (4.96 g, 40 mmol) was added in one portion to a solution of the disodium salt (1) (9.68 g, 40 mmol) in dry tetrahydrofuran (200 ml). The mixture was then stirred at room temperature overnight. The resulting yellow precipitate was filtered off, washed successively with water and methanol, and dried *in vacuo* to yield compound (2) (12.3 g, 95%) as a yellow powder; recrystallisation from benzene gave *crystals* m.p. 304 °C (decomp.) (Found: C, 41.0; H, 1.2; N, 8.4. C₁₁H₄N₂S₅ requires C, 40.72; H, 1.24; N, 8.63%); m/z 324 (M^+); ν_{\max} (KBr) 1 077 cm^{-1} (C=S); λ_{\max} (abs. EtOH) 387, 297, 263, and 227 nm.

Bisquinoxalinodithiino-tetrathiafulvalene (3).—The thione (2) (4 g, 12 mmol) was heated with freshly distilled triethyl phosphite (10 ml) at 130–140 °C under nitrogen for 0.5 h in an oil-bath. The resulting pink solid was filtered off, and washed successively with methanol and diethyl ether to yield compound (3) (0.6 g, 69%) as a pink powder; recrystallisation from 1,2,4-trichlorobenzene gave *crystals*, m.p. 350–351 °C (decomp.) (Found: C, 43.7; H, 1.3; N, 9.2. C₂₂H₈N₄S₈·H₂O requires C, 43.83; H, 1.67; N, 9.29%); m/z 584 (M^+); ν_{\max} (KBr) 1 452 and 1 406 cm^{-1} , with absence of 1 077 cm^{-1} peak (C=S); λ_{\max} (abs. EtOH) 378 and 256 nm.

Preparation of Unsymmetrical Donor (4).—The thione (2) (3.24 g, 10 mmol) was heated with 4,5-bis(methylthio)-1,3-dithiole-2-thione¹³ (2.26 g, 10 mmol) in freshly distilled triethyl phosphite (10 ml) at 120–130 °C under nitrogen for 40 min in an oil-bath. The resulting orange-red precipitate obtained on cooling the reaction mixture to room temperature was filtered off, and washed successively with ethanol and diethyl ether to yield a mixture (ca. 1.2 g) of compounds (3), (4) and tetrakis-(methylthio)tetrathiafulvalene (TTM-TTF).¹⁴ A portion of the precipitate (0.5 g) containing the three compounds was completely separated by silica gel (ca. 50 g) flash column chromatography (hexane–dichloromethane; 2:1). The yields of compounds (3), (4) and TTM-TTF were 20, 40, and 30 mg, respectively. **Compound (4)** is a red solid, m.p. 179–181 °C (Found: C, 39.4; H, 2.1; N, 5.6. C₁₆H₁₀N₂S₈ requires C, 39.48; H, 2.07; N, 5.75%; *m/z* 486 (*M*⁺); *v*_{max}(KBr) absence of C=S peaks; *λ*_{max}(abs. EtOH) (log *ε*) 445 (3.35), 337 (4.09), 307 (4.11), and 247 nm (4.34).

TTM-TTF was a dark orange powder.

Preparation of Unsymmetrical Donor (5).—The thione (2) (3.24 g, 10 mmol) was heated with 5,6-dihydro-1,3-dithiol[4,5-*b*]-[1,4]dithiin-2-thione^{13,15} (2.24 g, 10 mmol) in freshly distilled triethyl phosphite (8 ml) at 120–130 °C under nitrogen for 0.5 h in an oil-bath. The resulting dark orange precipitate obtained on cooling the reaction mixture to room temperature was filtered off, and washed successively with ethanol and diethyl ether to yield a mixture (ca. 1 g) of compounds (3), (5), and BEDT-TTF. A portion of the precipitate (0.5 g) containing the three compounds, (3), (5), and BEDT-TTF was completely separated by silica gel (ca. 50 g) flash column chromatography (hexane–dichloromethane; 1:1) in yields of 10, 40, and 30 mg, respectively. **Compound (5)** is a red solid, m.p. 252–255 °C (Found: C, 44.45; H, 2.9; N, 6.8. C₁₆H₈N₂S₈·0.75C₆H₄Cl₂ requires C, 44.82; H, 3.40; N, 5.10%), which was shown to be homogeneous by TLC [silica; hexane–dichloromethane (1:2)]. The compound was characterised by its mass spectrum: *m/z* (%) 484 (78), 456 (20), 384 (8), 336 (20), 292 (24), 284 (20), 216 (54), and 88 (100). The MS showed a molecular-ion cluster at *m/z* 484 (100), 485 (24.74), and 486 (37); these relative intensities correspond well to the expected molecular formula C₁₆H₈N₂S₈; peak matching gave *M*, 483.8443 as the average of 4 measurements; C₁₆H₈N₂S₈ requires *M*, 483.8453; *v*_{max}(KBr) absence of C=S peaks; *λ*_{max}(abs. EtOH) 307 nm.

BEDT-TTF was obtained as a dark orange solid, m.p. 246–248 °C (decomp.).

Electrochemical Preparation¹ of BQDT-TTF Tri-iodide (3)⁺ I₃⁻.—BQDT-TTF (3) (1 mmol) was partially dissolved in dry, degassed 1,2-dichlorobenzene (30 ml) and the suspension was placed in the anode compartment of an H-cell, and which was separated from the cathode compartment by a glass frit. A solution of tetrabutylammonium tri-iodide (5 mmol) in dichlorobenzene (50 ml) was added to both the cathode and anode compartments to level both sides. The solutions were then purged with argon and the platinum wire electrodes were

inserted. The cell was then heated at 50 °C in a water-bath to ensure a sufficient concentration of the donor (3) in solution. After 6 weeks at 2 μA constant current, no crystal growth was observed. Evaporation of the filtered anodic solution over a period of ca. 8 weeks gave black shiny needles, which were carefully washed with dry dichloromethane to remove any residual ammonium salt (Found: C, 30.4; H, 0.9; N, 4.1. C₂₂H₈N₄S₈·C₆H₄Cl₂ requires C, 30.23; H, 1.08; N, 5.00%).

Attempted Preparation of Charge-transfer Complex.—BQDT-TTF (3) (0.58 g, 1 mmol) and TCNQ (0.4 g, 2 mmol) were refluxed together in dry, degassed 1,2,4-trichlorobenzene until a blue colour in the solution persisted. This took ca. 10 h. The expected solid charge-transfer complex was not obtained on cooling the blue solution to room temperature. The solvent was then distilled off and again no solid residue was observed. However, on evaporation of the solution to near dryness a blue coating was evident around the bottom half of the flask, but this could not be isolated. Chromatographic separations could not be used owing to insolubility of the product formed.

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