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Efficient synthesis of brominated tetrathiafulvalene (TTF) derivatives: solid-state structure and electrochemical behaviour

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Abstract—An efficient synthesis is reported for 4,5-dibromo-[1,3]dithiole-2-thione (**1**) and 4-bromo-1,3-dithiole-2-thione (**7**) by bromination of lithiated vinylene trithiocarbonate. Compound **1** acts as a convenient precursor to a number of asymmetric electron donors. This is exemplified by the formation of 4,5-dibromo-4′,5′-bis(2′-cyanoethylsulfanyl)TTF (**3**) by cross-coupling methodology and subsequent conversion into 4,5-dibromo-4′,5′-ethylenedithioTTF (**4**) by reaction with caesium hydroxide and 1,2-dibromoethane. The new donor 4,5-dibromo-4′,5′-ethylenedithiodiselenadithiafulvalene (**5**) was prepared by cross-coupling of **1** and 4,5-ethylenedithio-1,3-diselenol-2-one (**6**). The X-ray structures of **3** and **5** are reported.

1. Introduction

Within the field of molecular conductors, organosulfur and organoselenium donor molecules have been a major focus for research in the preparation of conductive molecular systems.[1] Tetrathiafulvalene (TTF) and its derivatives have played a leading role in the formation of charge-transfer complexes and radical ion salts since the planarity and high chemical stability of the radical cation favours the intermolecular delocalisation of charge carriers.[2] Studies have concentrated on the electrical and magnetic properties[3] but extend to include an examination of the role of intermolecular S···S attractions, polymorph formation and phase transitions. It is in this context that crystal engineering has emerged as a key topic.[4]

Close inter-stack S···S interactions increase the dimensionality in most TTF derivatives,[1] but the role played by intermolecular hydrogen bonding and interactions involving halogen atoms have gained increasing attention.[5] The addition of halogen substituents to TTF reduces the π-electron donating ability and this effect is additive with the increasing number of halogens on the TTF system.[5] The key motivation of this work was the study of new brominated derivatives and the role played by the halogen atoms in modifying the donating ability of the new donors.

2. Results and discussion

According to the literature,[6] reactions to obtain iodinated derivatives of TTF[7] have proven until recently difficult and even unreliable, but conversely the synthesis of brominated derivatives seemed to be more straightforward[8] although the proportion of monobrominated versus dibrominated derivatives seemed to be difficult to control. In the simplest reaction, direct bromination of the TTF leads to good yields of the monobrominated derivative, but treatment of the TTF core with more than 1 equiv of LDA produced a mixture of mono- and polybrominated derivatives, which proved difficult to separate and were recovered in very low yields.[9] In order to overcome this problem, the lithiation of vinylene trithiocarbonate followed by reaction with a series of brominating agents (e.g., *p*-toluenesulfonyl bromide[6] or 1,2-dibromotetrachloroethane[10]) has been attempted by various groups. However, these attempts[6] have been reported to yield a mixure of mono- and dibromo derivatives in comparatively low yields (25–30%). In our hand, the use of 1,2-dibromotetrachloroethane, which had been previously utilised to obtain **4** in good yields from direct lithiation and bromination of the parent ethylenedithioTTF,[8] produced a much more reliable reaction, allowing mono- or dibrominated derivatives to be selectively prepared in good yields (~80%). The extent of bromination could be controlled by adjusting the amount of lithiating agent in the mixture, i.e., reaction of vinylene trithiocarbonate with 1 equiv of LDA followed by treatment with 1,2-dibromotetrachloroethane produced exclusively the monobrominated derivative **7**, whereas reaction with 3 equiv of LDA led to the isolation of the dibrominated derivative **1** (Scheme 1).

There are numerous routes to functionalised TTFs,[11] although coupling (or cross-coupling) of two 1,3-2-thione (or dithiocarbonate) half-units, usually in the presence of a trialkyl phosphite is the most widespread. In order to ascertain the possibility of using **1** and **7** as building blocks in the

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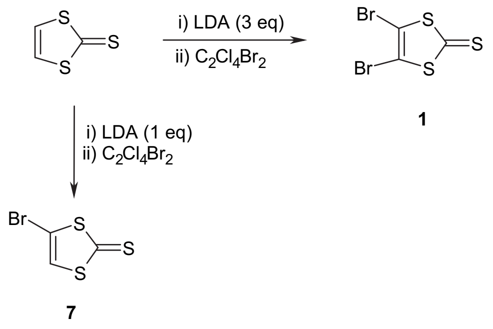


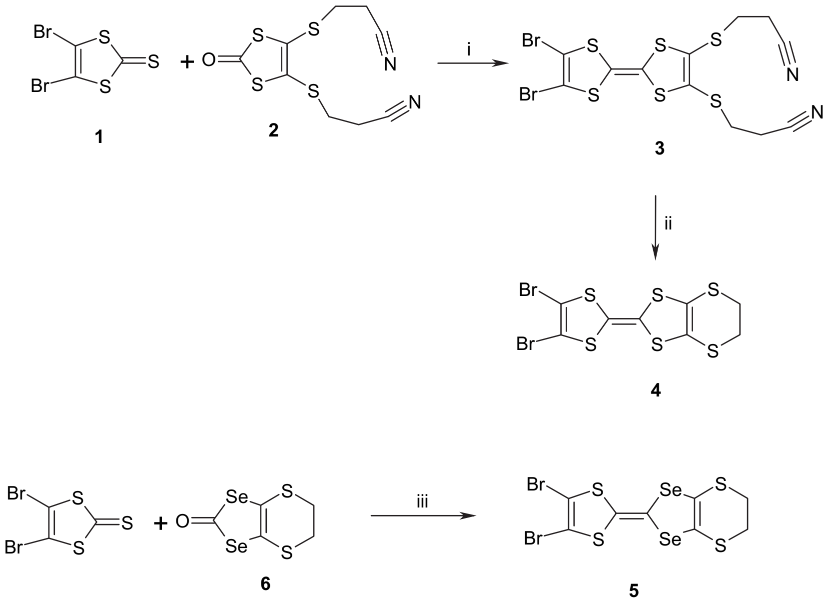
Scheme 1.

synthesis of brominated TTF derivatives, the synthesis of the known donor **4** and the new donor **5** was attempted.

Cross-coupling of **1** with **2** (Scheme 2) gave the TTF derivative **3** with no loss of bromine in good yields (60–70%). Removal of the cyanoethyl groups under Becher's conditions[12] generated the dithiolate species, which was trapped in situ with 1,2-dibromoethane to afford **4**.

In order to illustrate the application of this methodology to the synthesis of Se containing derivatives, **1** was cross-coupled with the selenium analogue **6** affording the new donor **5**, which was recovered in high yields by column chromatography.

In previous reports,[6] crystallisation of **3** from dichloromethane yielded a polymorph, which crystallised in the orthorhombic space group *Pbca*.[†] In our hands, a new polymorph, which crystallised in the orthorhombic space group *Pca*2_1 with one molecule in the asymmetric unit, was isolated



X-Ray crystal structures

	3	5
Empirical Formula	$C_{12}H_8Br_2N_2S_6$	$C_8H_4Br_2S_4Se_2$
T/K	180(2)	293(2)
λ/Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space Group	$Pca2_1$	$P2_1/n$
***a*/Å**	29.988(6)	6.67520(10)
***b*/Å**	8.7474(17)	8.1972(2)
***c*/Å**	6.9526(14)	24.320(5)
α/°	90	90
β/°	90	96.35(3)
γ/°	90	90
V /Å^3	1823.8 (6)	1322.5(3)
μ **/mm^{-1}**	5.126	12.232
F(000)	1040	1016
θ **range/°**	$3.80 \leq \theta \leq 22.50$	$2.62 \leq \theta \leq 22.50$
Reflections collected	8580	8910
Unique reflections	2084	1713
R_1 (I > 2σ(I)]	0.0288	0.0635
***w*R_2 (all data)**	0.0651	0.1266
Largest peak/hole eÅ^{-3}	0.71 and -0.34	0.95 and -0.85

Scheme 2. Reaction conditions: (i) $P(OEt)_3$, toluene, reflux; (ii) CsOH, THF–methanol, then dibromoethane; (iii) $P(OEt)_3$, toluene, reflux.

[†] Unit cell dimensions a=14.609(4) Å, b=11.607(4) Å, c=21.020(5) Å.

from acetonitrile. In this new polymorph, the planes of the rings form a pseudo-butterfly conformation along the long axis of the molecule (Figs. 1–3), with increased deviation from planarity ca. 35° compared to previously reported structures ca. 3°.[6]

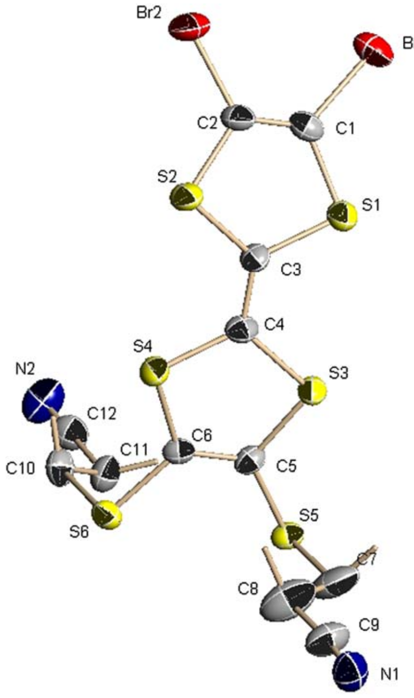


Figure 1. Asymmetric unit of **3** with numbering scheme.

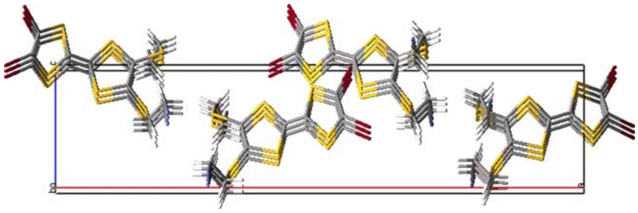


Figure 2. View of the stacks, approximately down the *b*-axis.

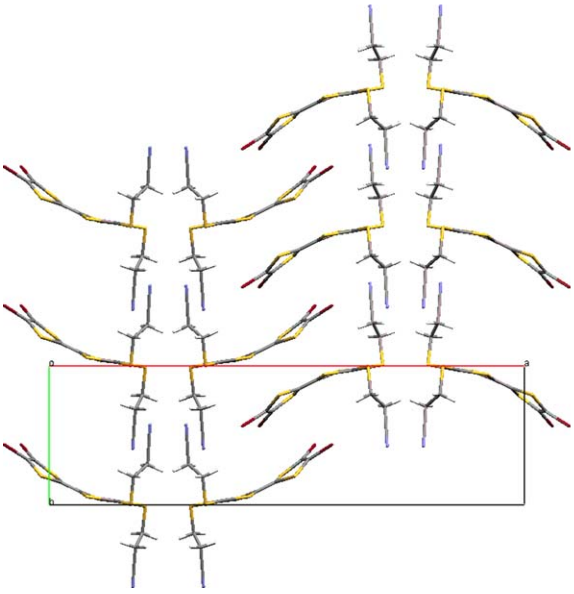


Figure 3. View perpendicular to the *ab* plane.

There are no contacts less than the sum of the van der Waals radii between the softer Br and S atoms, which are expected to contribute most significantly to dispersion forces. The shortest contact 3.873(3) Å is comparable with the sum of the van der Waals radii (~3.5 Å). In the current case the CH_2CH_2CN groups adopt a trans conformation with respect to the dithiole rings, which facilitates CN···H interactions (2.612–2.658 Å) generating chains along the *b*-axis. The adoption of this alternative trans geometry may arise out of solvation effects in which the polar HCH_2CN may provide competing sites as improved solvation of the CH_2CH_2CN substituents in the trans orientation.

In order to illustrate the application of this methodology to the synthesis of brominated Se containing derivatives, **1** was cross-coupled with the selenium analogue **6** affording the new donor **5**, which was recovered in high yields by column chromatography.

The molecular structure and packing diagram of **5** are shown in Figure 4.

The introduction of two bromine atoms into the framework leads to a slight lengthening of the C=C bonds of the TTF core, as expected due to the stronger electron-withdrawing ability of Br compared with S. The bromine atoms and the TTF core are essentially co-planar, with the maximum deviation from the least-squares plane being 0.4321(2) Å. Compound **5** packs in the centrosymmetric group $P2_1/n$. There is only one S···Br contact, which is less than the sum of the van der Waals radii [Br(1)···S(3) 3.388(4) Å], whilst all the other intermolecular contacts fall beyond the van der Waals distances.

Figure 5 illustrates the traditional herring-bone motif associated with this space group.

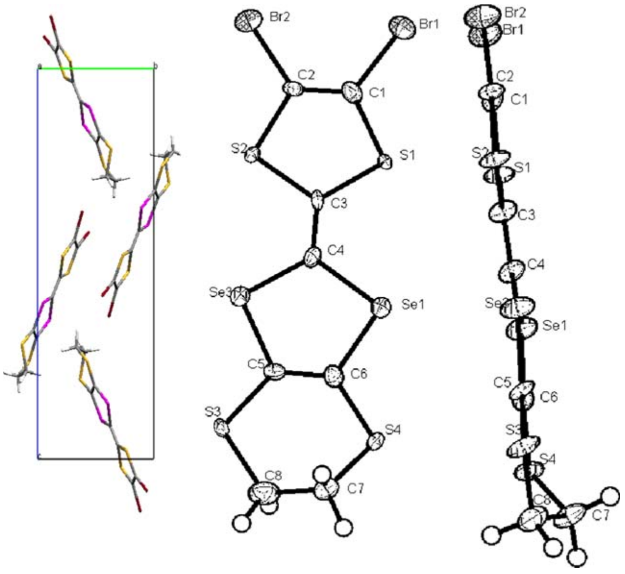


Figure 4. Packing diagram of **5** (left), and molecular structure and numbering scheme (centre and right).

Figure 5. View perpendicular to the *bc* plane.

3. Solution electrochemical data

The solution electrochemical data, obtained by cyclic voltammetry for the two halo-TTF derivatives reported herein, along with model compounds for comparison are collated in Table 1.

Table 1

Compound	$E_1^{1/2}$/mV	$E_2^{1/2}$/mV	ΔE
EDT-TTF	340	700	360
4	640	910	270
5	510	830	320
BETS	230	480	250

A comparison of **4** and **5** with their nonhalogenated derivatives reveals the expected trend resulting from halogen substitution, i.e., both the first and second oxidation potentials are raised significantly, in agreement with previous observations.[6]

Despite the poorer donor ability of **5** in relation to BETS, it was possible to isolate a charge transfer salt of **5** with tetracyano-*p*-quinodimethane (TCNQ) from slow evaporation of a dichloromethane solution, which yielded very small malformed dark needles (elemental analysis supports a 2:1 (**5**:TCNQ) complex) and showed conductivities (compressed pellet measurements) of 0.5×10^{-1} S cm^{-1}. We have so far been unable to grow crystals of similar charge-transfer compounds with **4**. Experiments to obtain single crystals of the CT-complexes and radical-cation salts by electrocrystallisation are underway.

4. Conclusion

This study shows that although the halogenated derivatives (**4**, **5**) display lower donor abilities, their oxidation potentials are comparable to those of BEDTF-TTF, which is a well-known donor. Indeed it is possible to form charge-transfer complexes with them. The availability of the brominated derivatives in synthetically useful amounts will enable further charge-transfer complexes and ion radical salts to be obtained, enhancing the understanding of the role that halogen substituents play in this class of material.

5. Experimental

5.1. General

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-400 MHz spectrometer. Mass spectra were recorded on a Kratos MS890-EI mass spectrometer. Elemental analyses were recorded on an Exeter CE-440 Elemental Analyser. Cyclic voltammetric data were obtained on an Autolab Electrochemical Instrument with PGSTAT20 (0.001 M solution of donor in acetonitrile, 0.1 M tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum working and counter electrodes, Ag/AgCl reference electrode, 20 °C). Conductivity data were obtained using routine four-probe methods.

Reactions were carried out under a nitrogen atmosphere; reagents were used as supplied; solvents were dried where necessary using standard procedures and distilled. Compounds **2**[13] and **6**[14] were synthesised as previously described.

5.1.1. 4,5-Dibromo-[1,3]dithiole-2-thione 1. To a stirred solution of diisopropylamine (0.3 g, 5 mmol) in THF (5 mL) at −78 °C was added *n*-butyl lithium (4 mL, 5.3 mmol of a 1.6 M solution in hexane) and the mixture stirred for 1 h. Vinylene trithiocarbonate (200 mg, 1.49 mmol) in diethyl ether (20 mL) was added dropwise, and the solution stirred at −78 °C for a further 3 h. A solution of 1,2-dibromotetrachloroethane (1.45 g, 4.4 mmol) in diethyl ether (10 mL) was added, the solution stirred at −78 °C for a further 3 h, and then the solution was allowed to reach room temperature overnight.

The solvent was removed in vacuo, and the residue extracted with dichloromethane. The organic extract was washed with water, separated, dried ($MgSO_4$) and evaporated to afford the crude product. Chromatography on a silica column (eluent hexane/toluene 4:1 v/v) afforded **1** as golden yellow crystals, mp 90–92 °C [lit. 90–92 °C[6]] (324 mg, 81%) (Analysis found: C, 12.41; $C_3Br_2S_3$ requires: C, 12.33%); *m*/*z* (EI) 292 (M^+, 100%); δ_C ($CDCl_3$) 106.7, 207.8. The NMR data were consistent with that described in the literature.[6]

5.1.2. 4,5-Dibromo-4′,5′-bis(2′-cyanoethylsulfanyl)tetrathiafulvalene 3. A solution of **1** (100 mg, 0.35 mmol) and **2** (400 mg, 1.4 mmol) in toluene (15 mL) was heated to reflux and then triethyl phosphite (0.35 mL, 2.0 mmol) was added dropwise, the mixture was refluxed for a further 2 h.

Removal of the solvent in vacuo gave a crude product, which was purified by chromatography on a silica column, with dichloromethane as eluent to afford **3** as yellow crystals, mp 132–134 °C [lit. 132–134 °C[6]] (138 mg, 76%) (Analysis found: C, 27.48; H, 1.49; N, 4.94; $C_{12}H_8Br_2N_2S_6$ requires: C, 27.07%; H, 1.51%; N, 5.26%); δ_H ($CDCl_3$) 3.09 (4H, t, *J*=7 Hz), 2.73 (4H, t, *J*=7 Hz). The NMR data were consistent with that described in the literature.[6]

5.1.3. 4,5-Dibromo-4′,5′-ethylenedithiotetrathiafulvalene 4. To a stirred solution of **3** (118 mg, 0.22 mmol) in tetrahydrofuran (20 mL) at 20 °C was added a solution of caesium hydroxide hydrate (35 mg, 0.21 mmol) in methanol (5 mL). Stirring was continued for 0.5 h whereupon 1,2-dibromoethane (260 mg, 0.22 mmol) was added. The mixture was stirred at room temperature overnight. Removal of the solvent in vacuo gave a crude product, which was purified on a silica column with CS_2 as eluent to yield **4** as red crystals, mp 169 °C [lit. 166–168 °C[8]] (60 mg, 61%) (Analysis found: C, 21.41; H, 1.11; $C_8H_4Br_2S_6$ requires: C, 21.24%; H, 0.89%); δ_H ($CDCl_3$–CS_2) 3.29 (s, 4H); *m/z* (EI) 452 M^+; δ_C ($CDCl_3$–CS_2) 113.9, 112.1, 111.3, 101.6, 30.3. The NMR data were consistent with that described in the literature.[8]

5.1.4. 4,5-Dibromo-4′,5′-ethylenedithiodiselenadithiafulvalene 5. A solution of **1** (200 mg, 0.7 mmol) and **6** (180 mg, 0.7 mmol) in toluene (20 mL) was refluxed and then triethyl phosphite (10 mL, 60 mmol) added dropwise over 5 min. The reaction mixture was refluxed for a further 2 h. Removal of the solvent in vacuo gave a crude product, which was purified by chromatography on a silica column, with CS_2 as eluent to afford **5** as dark red crystals (305 mg, 80%) (Analysis found: C, 17.54; H, 0.63; $C_8H_4Br_2S_4Se_2$ requires: C, 17.60%; H, 0.73%), mp 271 °C; IR (KBr) 3075, 3021 cm^{-1}; δ_H ($CDCl_3$–CS_2) 3.33 (s, 4H); δ_C ($CDCl_3$–CS_2) 117.3, 114.8, 101.7, 100.6, 31.1.

5.1.5. 4-Dibromo-[1,3]dithiole-2-thione 7. To a stirred solution of diisopropylamine (0.09 g, 1.5 mmol) in THF (5 mL) at −78 °C was added *n*-butyl lithium (1.2 mL, 1.6 mmol of a 1.6 M solution in hexane) and the mixture stirred for 1 h. Vinylene trithiocarbamate (200 mg, 1.49 mmol) in diethyl ether (20 mL) was added dropwise, and the solution stirred at −78 °C for a further 3 h. A solution of 1,2-dibromotetrachloroethane (0.75 g, 2.2 mmol) in diethyl ether (10 mL) was added, the solution stirred at −78 °C for a further 3 h, and then the solution was allowed to reach room temperature overnight.

The solvent was removed in vacuo, and the residue extracted with dichloromethane. The organic extract was washed with water, separated, dried ($MgSO_4$) and evaporated to afford the crude product. Chromatography on a silica column (eluent hexane/toluene 4:1 v/v) afforded **7** as yellow crystals, mp 92–94 °C [lit. 92–95 °C[6]] (231 mg, 72%) (Analysis found: C, 17.40; H, 0.61; C_3HBrS_3 requires: C, 16.90%; H, 0.47%); *m/z* (EI) 214 (M^+, 100%); δ_H (DMSO-d_6) 7.71(s). The NMR data were consistent with that described in the literature.[6]

5.1.6. Complex $[5]_2\cdot$TCNQ. Solutions of compound **5** in dry dichloromethane and TCNQ in dry dichloromethane were mixed at 20 °C and allowed to slowly evaporate to afford tiny black crystals (Analysis found: C, 26.01; H, 1.12; N, 4.14; $C_{28}H_{12}Br_4N_4S_8Se_4$ requires: C, 25.94%; H 0.93%; N 4.32%).

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 298122 and 298123. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2006.06.006.

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