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Synthesis of Some Functionalised Isomeric Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and Dithiophenetetrathiafulvalene (DTTTF) π-Donors

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Abstract: The synthesis of some functionalised, isomeric, symmetrical tetrathiafulvalene derivatives containing 4,5-(ethylenedithio)-1,3-dithiole and 4,5-(propylenedithio)-1,3-dithiole units is described. These contain hydroxy, chloro and cyano functionalities (**4**, **6**, **9** and **12**). Interestingly, attempted coupling of 4,5-bis(propargylthio)-1,3-dithiole-2-thione **13**, to obtain the corresponding TTF, **14** afforded the novel thione, 5-methylthieno[2,3-d]-1,3-dithiole-2-thione **15**. Self coupling of thione **15** in the presence of trimethyl phosphite afforded new functionalised dithiophenetetrathiafulvalene **16**. The X-ray crysal structures of 4,5-bis(propargyldithio)-1,3-dithiole-2-thione **13** and 5-methylthieno[2,3-d]-1,3-dithiole-2-thione **15** are described.
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INTRODUCTION

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has yielded several organic superconductors.[1] The S...S intermolecular interactions and C-H...anion interactions play a key role in determining the solid state properties of the superconductors. In this context, BEDT-TTF type donors with (i) increased dimensionality,[2] (ii) lower oxidation potential and multi-stage redox behaviour,[3] (iii) bearing appropriate functionality,[4] and having κ-phase structure,[1] are challenging targets. Recently, it has been demonstrated that incorporation of hydrogen-bonding substituents in tetrathiafulvalene derivatives is a promising strategy for isolating κ-phase structures. For example, 4-(hydroxymethyl)-4,5-ethylenedithiotetrathiafulvalene forms ion-radical salts with κ-type structures.[5] Recently, hydroxyl group substituted tetrathiafulvalene vinologs which exhibit good π–donor ability have also been reported.[5] Synthesis and structure of 4-(N-methylthioamido)tetrathiafulvalene, the first example of a neutral tetrathaiafulvalene derivative and hydroxy functionalised TTF derivatives having donor-donor hydrogen bonding have been reported by Bryce and co-workers.[6] Furthermore, tetrathiafulva-lenes containing hydroxyl group functionality have been employed as a precursor for the synthesis of bis- and tris-TTFs.[7]

While several functionalised TTF derivatives are known, there are very few reports of functionalised BEDT-TTF derivatives.[8] In exploring the structure-property relationship in BEDT-TTF analogs,[9] we contemplated the synthesis of functionalised BEDT-TTF derivatives **4** and **9** since these have, (i) the desired BEDT-TTF framework, and (ii) functional groups (-OH, and -Cl respectively) which have the ability to participate in hydrogen bonding/intermolecular interactions.

Further, new functionalised tetrathiafulvalene donors, incorporating olefinic/acrylate substituents have also attracted considerable current interest.[4b,10] In this context, a monovinyl-TTF derivative was isolated few years ago and reported to polymerise slowly on standing.[11] Recent work by Bryce *et.al.*[12] shows that vinyl-TTFs are stable if pure. The tetravinyl-TTF derivative could not be isolated owing to its rapid polymerisation.[13] In this respect, we have attempted to synthesise TTF derivatives **12** and **14** with unsaturated substituents *viz.*, cyano and propargyl groups. In this article we report the synthesis of three new functionalised BEDT-TTF derivatives **4**, **9** and **12**. The preparation of known TTF **6** which was isolated during the attempted synthesis of **4** is also described.

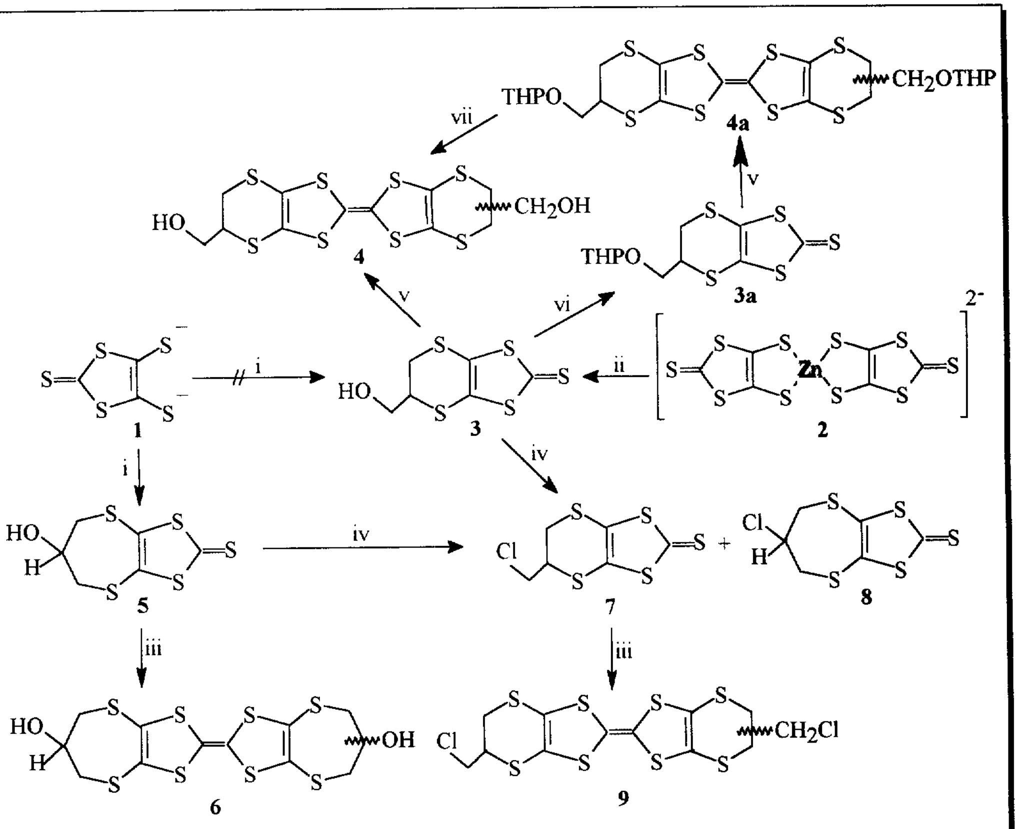
Engler *et.al,* Rovira *et.al.* and others have reported the synthesis of thiophene annulated TTFs.[14-17] We report here a new approach towards the synthesis of the precursor thione **15** with a methyl substituent on the thiophene ring at fifth position and its TTF **16**. The X-ray crystallographic structures of the thiones **13** and **15** are described.

RESULTS AND DISCUSSION

The synthesis of thione **3** was attempted by the reaction of sodium salt of 4,5-dimercapto-1,3-dithiole-2-thione **1** (generated *in situ* from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione[18] by deprotection using sodium ethoxide in anhydrous ethanol at room temperature)[19] with (±) 2,3-dibromo-1-propanol. The reaction afforded thione **5** with seven-membered exocyclic ring instead of the expected thione **3** with six-membered exocyclic ring. Alternatively, cyclisation of the complex $[Zn(dmit)_2]^{2-}$ **2** with (±) 2,3-dibromo-1-propanol in refluxing acetone gave the thione **3** in 50% yield (Scheme 1). The structure of **3** was inferred from ^1H NMR spectrum, which showed the expected triplet for the -OH proton of $CH_2O\underline{H}$, whereas thione **5** in DMSO-d_6 showed a well resolved doublet for the hydroxyl proton indicating the presence of $-CHO\underline{H}$. Ultimate unambiguous proof for the structure of **5** was finally obtained from a X-ray diffraction study.[20] While this work was in progress, synthesis of the compound **5** by different routes [reduction of 4,5-(propanonedithio)-1,3-dithiole-2-thione[21] and by reaction of **2** with 1,3-dibromo-propan-2-ol or by reaction of 1,3-dibromo-propan-2-ol in DMF with caesium salt of 4,5-dimercapto-1,3-dithiole-2-thione)] and its structure were reported by Bryce *et.al.*[8]

The formation of **5** presumably proceeds *via* abstraction of the hydroxyl proton by the base (EtO^-) present in the reaction mixture followed by the formation of an epoxide intermediate and cyclisation (Scheme 2). The IR spectra of the thiones **3** and **5** showed the characteristic absorptions at 3350-3000 cm^{-1} for the OH group which disappeared on increasing dilution (CH_2Cl_2). The disappearance of the above band

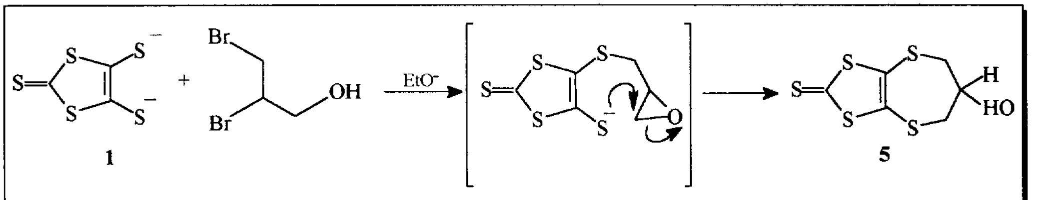
and the appearance of a sharp band at 3600-3650 cm^{-1} (free -OH band) on dilution might be interpreted in terms of intermolecular hydrogen-bonding in the concentrated solution and even in solid state. The weak intermolecular hydrogen-bonding in **5** has been further supported with single crystal X-ray structure determination by us[20] and others.[8] When **5** was subjected to chlorination by reaction with thionyl chloride and pyridine as the base, interestingly we obtained **7** as the major product, in addition to **8** as the minor product.



Reaction conditions: i. (±) 2,3-dibromopropanol, EtOH, 1 h;
ii. (±) 2,3-dibromopropanol, acetone, Δ, 3 h;
iii. $(EtO)_3P$, 120°C, Δ, 2h; iv. $SOCl_2$, pyridine, 0°C, 1 h, then reflux;
v. $(EtO)_3P$, Δ; vi. DHP, CAN, THF, 2 h; vii. AcOH, THF, H_2O, Δ, 6 h.

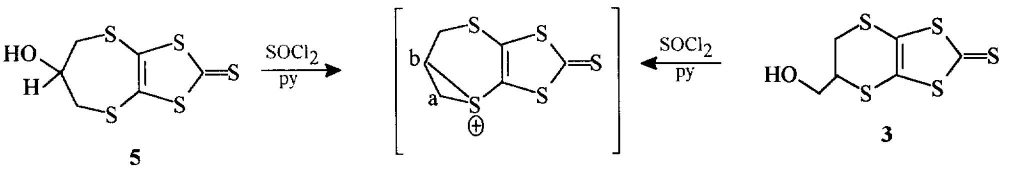
Scheme 1

^1H NMR spectra served to identify the isomers **7** and **8**. An AB pattern for $-CH_2Cl$ group for **7** at δ 3.90 whereas a triplet for -CHCl for **8** at δ 4.45 were observed. Unambiguous proof for the structure **7** was finally obtained by comparing the spectroscopic data, melting point and TLC with an authentic sample of 7 prepared from **3**. Similarly chlorination of **3** under identical conditions afforded a mixture of 7 and **8** in yields identical to those obtained for the chlorination of **5** and might be explained *via* the formation of a common intermediate in both the reactions (Scheme 3). While the formation of the major product 7 presumably occurs through a favoured SN^2 attack by the nucleophile at less substituted carbon atom (a), the attack of the nucleophile (Cl$^-$) at (b) leads to **8** having the seven-membered exocyclic ring.[22]



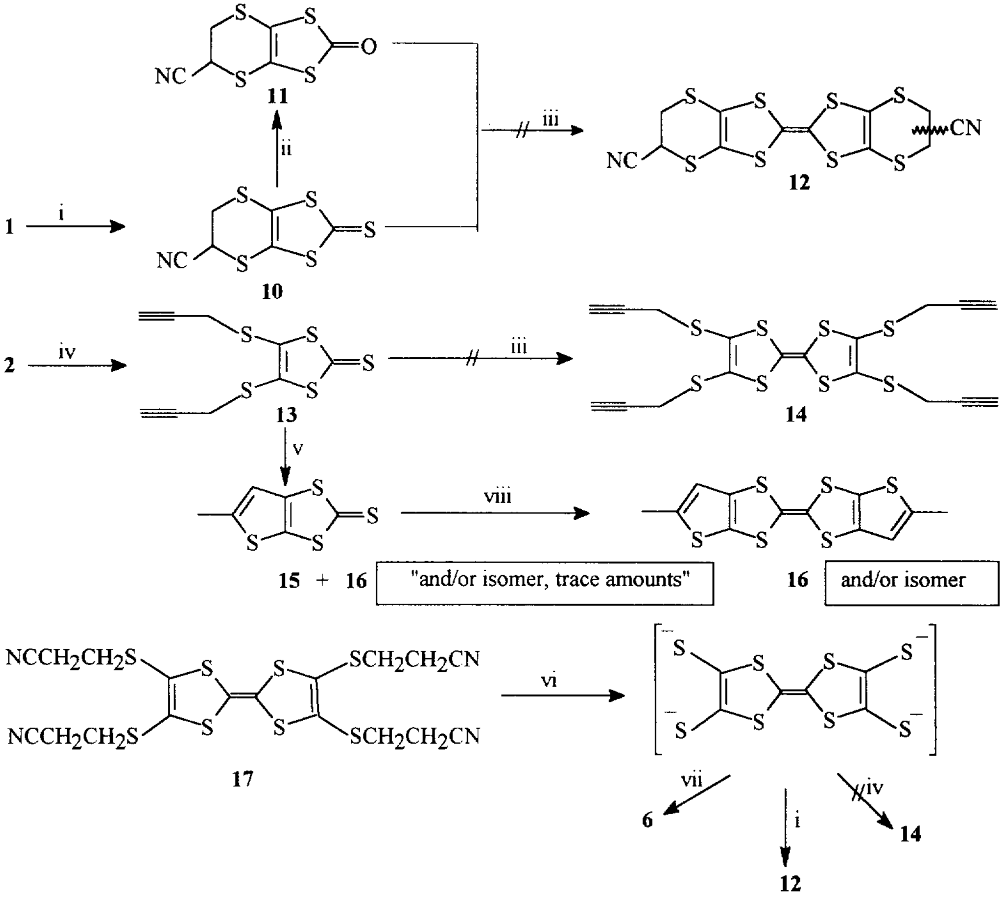
Scheme 2

Thiones 3, **5** and 7 were coupled in neat boiling (EtO)$_3$P or (MeO)$_3$P to give the corresponding tetrathiafulvalenes **4** and **6**[8] as yellow powder and **9** as reddish crystals in poor to moderate yields. Novel TTF **4** could be prepared in much better yield by protecting the thione **3** with 3,4-dihydropyran to give the protected thione **3a**. Coupling of thione **3a** gave the protected TTF **4a** which could be conveniently deprotected to afford **4**. TTFs **4** and **6** showed intermolecular hydrogen bonding as detected by IR spectoscopy dilution studies.



Scheme 3

Thione **10** was prepared by following a method similar to that used for thione **5** and converted to **11** by treating with mercuric acetate and acetic acid in chloroform, in 70% yield (Scheme 4). Thione **13** was prepared by the direct reaction of zincate salt **2** with propargyl bromide in acetone under nitrogen at 0°C. It is interesting to note that crude **13** when chromatographed on silica-gel using petroleum ether (40-60°)-ethyl-acetate (95:5) as an eluent, afforded, orange-yellow needle shaped crystals of **13** (without any recrystallization) which were of X-ray quality. Although the synthesis of **13** has been claimed by Nakamura *et.al.*[23], a detailed description of the synthetic procedure and analytical data for **13** have not been reported.



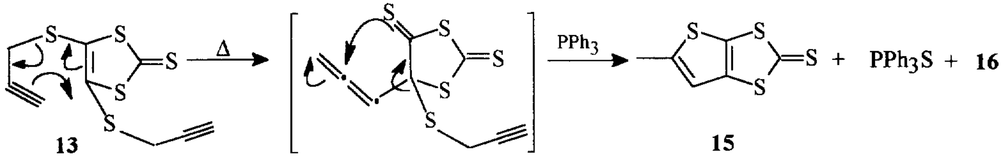
Reaction conditions: i. (±) 2, 3-dibromopropionitrile ii. Mercuric acetate/acetic acid; iii. $(EtO)_3P$, reflux, 3 h iv. Propargyl bromide, 0°C, 1 h; v. Ph_3P, benzene, 9 h, reflux; vi. Na, EtOH vii. (+) 2,3-dibromopropanol viii. $(EtO)_3P$, reflux, 6 h

Scheme 4

Compound **13** is an orange-yellow crystalline low melting solid and can be stored for long time at room temperature. The structure was further confirmed by both NMR and X-ray crystallography. However, its solution deposits a shiny black thin film on the surface of the container and presumably the polymeric product is insoluble in all common organic solvents. The IR spectrum of the product exhibits bands identical with thione **13**. Our attempts to synthesise the oxo derivative of **13** using mercuric acetate and acetic acid were unsuccessful.

All attempts to couple thiones/ketones **10**, **11** and **13** to obtain the corresponding TTF derivatives **12** and **14** were unsuccessful. The coupling agents used were $(MeO)_3P$, $(EtO)_3P$, and $Co_2(CO)_8$. In all cases, intractable black materials were obtained. The TTF **12** could, however, be synthesised by the non-coupling tetrathiolate route[24] (Scheme 4). Although the product gave a satisfactory elemental analysis, IR and CV, due to poor solubility of **12**, it could not be purified further and characterised. The crude product did not give a satisfactory ^1H NMR and mass spectra. Attempts to synthesise TTF **14** by the non-coupling tetrathiolate route were again unsuccessful and led to the isolation of unidentifiable mixtures. However, this methodology when applied to synthesise TTF **4** again yielded TTF **6** *via* epoxide mediated cyclization (Scheme 4). The coupling reaction of **13** under milder conditions i.e., in the presence of PPh_3 in refluxing benzene, afforded the novel rearranged thione **15** in 23% yield. Initially elemental analysis and ^1H NMR served to identify the compound. Unambiguous proof for the structure of **15** was later obtained from single crystal X-ray crystallographic data. A side-product formed in this reaction is Ph_3PS. Formation of Ph_3PS was confirmed by comparing melting point, ^1H NMR and elemental analysis with an authentic sample. Interestingly the mass spectrum of the crude sample of **15** showed an additional peak (m/z 344) corresponding to the TTF derivative **16**. Self coupling of the thione **15** in presence of trimethyl phosphite afforded **16** (probably a mixture of *cis* and *trans* isomers) in low yield. Although simple dithiophenetetrathiafulvalenes[14-17] are known, to our knowledge, **16** is the first substituted thiophene fused tetrathiafulvalene.

A probable mechanism for the formation of **15** *via* Thio-Claisen rearrangement involving an allenic intermediate is proposed and is shown in Scheme 5.[25] It is interesting to note that **15** was not formed only on refluxing the thione **13** in benzene/toluene without using triphenyl phosphine thus confirming the crucial role played by triphenyl phosphine in abstracting the sulphur atom from the allenic intermediate. The thione **15** then appears to undergo coupling reaction with PPh_3 yielding traces of TTF **16**.



Scheme 5

Crystal Structures of Compounds 5, 13 and 15. Although the single crystal X-ray structure of **5** has been recently reported,[8] our structure determination gave a better R-value (0.029).[20] The -OH group is thermally disordered and has shown two positions with site occupation factors of 0.7 and 0.3. The molecular structure of **13** is shown in Figure 1. The five membered ring is almost planar. The maximum deviation from the least squares plane defined by the dithiole ring atoms is 0.049(7) Å.[26] The two propargyl chains in thione do not elongate parallel to each other like other alkylthio derivatives.[27] The molecular structure of **15** is shown in Figure 2. The sulphur atom S(4) and carbon atom C(4) are thermally disordered and have shown two positions [(S4), (S4')] and [(C4), (C4')] with site occupation factors of 0.6 and 0.4. Both the five membered rings, i.e., dithiole ring and thiophene ring are almost planar.

The electrochemical redox behaviour of the donors **4**, **6**, **9**, **12** and **16** has been studied by cyclic voltammetry and results are summarised in Table 1. Each donor shows two single-electron, reversible redox waves. The donor strength of **4**, **12** and **16** are similar to that of the BEDT-TTF. However, oxidation potentials of the donors **6** and **9** were slightly higher than that of BEDT-TTF. The donors **4**, **6** and **9** were reacted with the acceptors I_2, $CuCl_2$, and $HgCl_2$ to yield the corresponding charge-transfer complexes. The complexes are poorly conducting and their conductivities fall in the range of 10^{-5}-10^{-7} S cm^{-1} at room temperature. The ESR spectra of all the charge-transfer complexes showed a symmetric signal. The observed g-values are nearly equal to the free electron value, suggesting that the signal was due to an unpaired electron on donors. The ESR data of $CuCl_2$ complexes indicate the absence of the Cu^{II} moiety. The copper atoms in these complexes are in diamagnetic Cu^{I} state and the symmetric signal observed is due to the unpaired electron on donors.

Table 1. Cyclic voltammetric data[a]

Compound	$E_1^{1/2}$ V	$E_2^{1/2}$ V	$\Delta E^{1/2}$V
BEDT-TTF	0.455	0.875	0.420
4	0.470	0.840	0.370
6	0.525	0.895	0.370
9	0.522	0.895	0.373
12	0.470	0.835	0.365
16[b]	0.443	0.872	0.429

[a] recorded *verses* SCE, Pt electrode, scan rate 100 mVs^{-1}, 5 x 10^{-4} mol dm^{-3} compound, 0.1mol dm^{-3} $Bu_4N^+PF_6$ in CH_2Cl_2.

[b] recorded *verses* Ag/AgCl

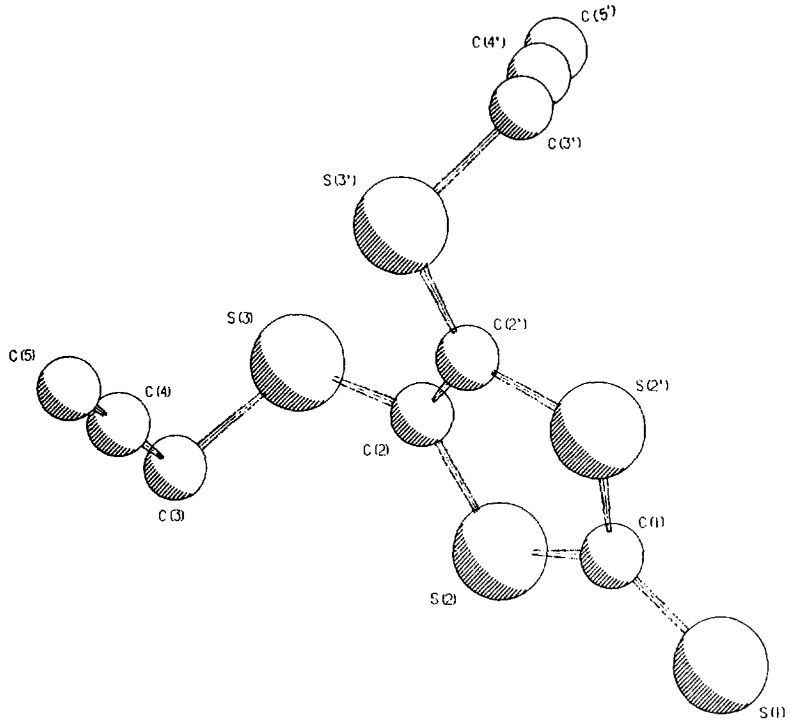


Figure 1. X-Ray molecular structure of **13** and crystallographic numbering scheme
Selected bond lengths. C(1) - S(1) 1.637(2) C(1) - S(2) 1.726(3); C(2) - S(2) 1.746(2); C(2) - S(3) 1.744(2); C(3) - S(3) 1.823(3); C(1) - S(2') 1.738(2); C(2') - S(2') 1.748)2); C(2') - S(3') 1.748(2); C(3') - S(3') 1.823(3); C(2') - C(2) 1.349(3); C(4) - C(5) 1.165(5); C(4') - C(3') 1.452(4); C(5') - C(4') 1.159 (4)Å

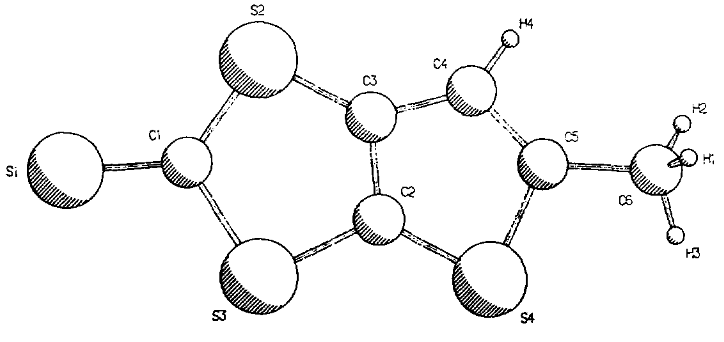


Figure 2. X-Ray molecular structure of compound **15** and crystallographic numbering scheme
Selected bond lengths. C(1) - S(1) 1.631(7); C(1) - S(2) 1.678(8); C(3) - S(2) 1.682(9); C(3) - C(4) 1.39(2); C(4) - C(5) 1.38(2); C(5) - C(6) - 1.51(1); C(2) - S(4) 1.681(8); C(5) - S(4) 1.720(1) Å **Significant intermolecular** S...S. **interactions**. S(1)...S(2) = 3.4383 Å [0.5-x, 0.5+y, 0.5+z], S(2)...S(1) = 3.4383 Å [0.5-x, 0.5+y, 0.5+z], S(4')...S(4) = 3.5101 Å [-x, -y, 0.5+z], S(4')...S(3) = 3.564 Å [0.5-x, 0.5+y, 0.5+z], S(4)...S(4') = 3.5110 Å [-x, -y, 0.5+z].

Conclusion. The attempted synthesis of **3** *via in situ* generated $Na_2C_3S_5$ synthon leads to the epoxide mediated formation of the rearranged product **5**. Interestingly, the chlorination of both **3** and **5** leads to formation of **7** and **8** *via* a cyclic episulphonium ion intermediate. The facile conversion of seven membered exocyclic ring to a six membered ring and *vice versa* is noteworthy. Reaction of **13** with Ph_3P leads to the novel thione **15** and traces of its TTF **16** *via* Thio-Claisen rearrangement. The self coupling of thione **15** affords the new thiophene annulated TTF **16** in low yield. The tetrathiolate route has proved to be efficient in the synthesis of hydroxy and cyano functionalised BEDT-TTFs **6** and **12**. The charge-transfer complexes derived from donors **4**, **6** and **9** were insulators at room temperature.

EXPERIMENTAL

General. Melting points were recorded with a VEEGO melting point apparatus and are uncorrected. Elemental analysis were performed on a Carlo-Erba elemental analyser model 1106. IR spectra were recorded on Nicolet Impact 400 FT-IR spectrometer; samples were either embedded in KBr discs, (neat, if liquids between KBr plates). UV-VIS spectra were recorded on a Shimadzu UV-260 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz instrument operating at 299.9486 MHz for proton and 75.4293 MHz for the carbon nucleus. Chemical shifts, given in ppm, are relative to tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a JEOL D-300 mass instrument, operating at 70 eV. Solid state ESR spectra were recorded on a Varian E-112 ESR spectrometer using tetracyanoethylene as g-marker at room temperature. 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. Cyclic voltammetry (CV) experiments were performed on Bio-Analytical Systems (BAS) instrument which consists of one-compartment cell with platinum working and counter electrodes and a standard calomel electrode (SCE, reference electrode). All solutions were purged with argon or nitrogen and retained under the inert atmosphere while the CV data were recorded. Solvents were dried according to literature methods. All other reagents were reagent grade and used as supplied, unless otherwise stated. The compounds **1** and **2** were prepared following the literature procedure.[18, 19]

4,5-(1-Hydroxypropylenedithio)-1,3-dithiole-2-thione (3).

To a solution of the zinc salt **2** (9.41 g, 10 mmol) in warm acetone (50 mL) was added a solution of (±) 2,3-dibromopropanol (6.537 g, 30 mmol) in acetone (10 mL). The solution was heated for 1 h and concentrated by evaporating the solvent. The viscous liquid thus obtained was stirred and heated for 3 h at 70-80° C. During this period the pink-red colour of the reactants turned brownish-yellow. The residue was allowed to cool to room temperature, dissolved in dichloromethane and treated with charcoal. The filtrate was concentrated and chromatographed on a silica gel column. Elution with petroleum ether-ethyl acetate (20:80) gave the title compound **3** as yellow crystals, (2.5 g, 50%); mp 83°C (Found: C, 28.27; H, 2.13. $C_6H_6S_5O$ requires C, 28.34; H, 2.36%); ν (KBr) 1070 (C=S) cm^{-1}; λ_{max} (CH_2Cl_2) 406, 274, 229 nm; δ_H (DMSO-d_6) 5.40 (1H, OH, t), 3.90 (1H, CH, m), 3.73 (1H, m), 3.60 (1H, m), 3.39 (2H, m); δ_C (DMSO-d_6) 207.46(C=S), 125.46, 123.20, 63.26, 46.69, 31.69; m/z (EI) 254 (M^+, 100%).

Bis(1-hydroxy-2,3-propylenedithio)tetrathiafulvalene (4).

Method A. Thione **3** (1.0 g, 3.9 mmol) was suspended in triethyl phosphite (15 mL) and heated with stirring at 130-140° C for 6 h. The resulting reddish yellow solution was allowed to come to room temperature. Triethyl phosphite was removed under reduced pressure and the residue was chromatographed on a silica gel column eluting with light petroleum and ethyl acetate (50:50) to afford compound **4** (0.045 g, 5%) as yellow solid material.

Method B. 4, 5-(1-Tetrahydroypyranopropylenedithio)-1,3-dithiole-2-thione (3a). To the thione 3 (1.92 g, 7.59 mmol) dissolved in THF (30 mL) was added rapidly 3,4-dihydro-2-H-pyran (0.672 g, 8 mmol) and a catalytic amount of ceric ammonium nitrate (0.010 g). The reaction mixture was stirred at room temperature for 2 h after which the solvent was evaporated. The residue was dissolved in dichloromethane (100 mL) and washed thrice with water (50 mL). Work up and chromatographic purification petroleum ether (60-80°)-ethylacetate (80:20) yielded compound **3a** as a yellow viscous liquid (1.15 g, 45%) δ_H($CDCl_3$) 4.65 (m, 1H), 3.91 (m, 1H), 3.83(m, 1H), 3.56 (1H, m), 3.35 (m, 2H), 1.76(m, 2H), 1.56 (m, 6H); m/z (EI) 338 ($M^{+\cdot}$, 80 %).

Bis(1-tetrahydropyrano-2,3-propylenedithio)tetrathiafulvalene (4a).

The protected thione **3a** (1 g, 2.95 mmol) was suspended in triethyl phosphite (15 mL) and heated with stirring at 120-130°C for 2 h. The solution turned reddish. The triethyl phosphite was removed under reduced pressure and the residue was chromatographed on a silica gel column eluting with light petroleum (60-80°) and ethylacetate (80:20) to afford compound **4a** (0.243 g, 27%) as red crystalline material, mp 110°C (Found C, 43.05; H, 4.69 $C_{22}H_{28}S_8O_4$ requires C, 43.13; H, 4.57%); δ_H($CDCl_3$) 4.63 (m, 2H), 3.8 (m, 4H), 3.55 m, 2H), 3.23 (m, 4H), 1.70 (m, 4 H), 1.58 (m, 12H).

Deprotection of compound 4a.

Compound **4a** (0.145 g, 0.236 mmol) was treated with (CH_3COOH, THF and H_2O in the ratio of (4:2:1) and refluxed for 6 h, while the progress was followed by TLC. After completion of the reaction, solvent was evaporated and the residue was dissolved in $CHCl_3$, washed twice with water (100 ml), $NaHCO_3$ (5 %) and brine. Workup and purification of the residue yielded compound **4** as an yellow product (0.066 g, 63 %), mp 140°C; (Found: C, 32.50, H, 2.96 $C_{12}H_{12}S_8O_2$ requires C, 32.43, H, 2.70 %); δ_H (DMSO-d_6) 5.31 (2H, t, OH), 3.78 (2H, m), 3.68 (2H, m), 3.55 (2H, m), 3.29 (4H, m); ν (KBr) 3300 (OH, br), 1092 (C-O) cm^{-1}'; m/z (EI) 444 ($M^{+\cdot}$, 60%).

4,5-(2-Hydroxypropylenedithio)-1,3-dithiole-2-thione (5).[8]

To a solution of freshly generated sodium salt of 4,5-dimercapto-1,3-dithiole-2-thione **1** (4.84 g, 10 mmol) in absolute ethanol (100 mL) under an inert atmosphere was added a solution of (±) 2,3-dibromopropanol (4.35 g, 10 mmol) in ethanol (20 mL) dropwise over a period of 10 min with stirring. The reaction mixture was stirred for additional 1 h at room temperature. The orange-yellow precipitate was filtered off, washed with ethanol and dried in *vacuo* (4.0 g, 80%). Recrystallization from chloroform-ethanol (1:1) with charcoal as decolourising agent gave orange-yellow crystals of **5** (2.4 g, 50 %); mp 187-188° C (lit.[8] 188-189° C) (Found: C, 28.54; H, 2.44. $C_6H_6S_5O$ requires C, 28.34; H, 2.36%); ν (KBr) 1070 cm^{-1} (C=S); λ_{max} (CH_2Cl_2) 405, 273, 229 nm; δ_H (DMSO-d_6) 5.70 (1H, d, J=5.0 Hz), 4.02 (1H, m), 3.00 (2H, m), 2.67 (2H, m); δ_C (DMSO-d_6) 210.17 (C=S), 140.23 (C=C), 73.88, 71.91, 38.56, 36.68; m/z (EI) 254 ($M^{+\cdot}$,100%).

Bis(2-hydroxy-1,3-propylenedithio)tetrathiafulvalene (6).[8]

Method A. The thione **5** (1.0 g, 3.9 mmol) was suspended in triethyl phosphite (20 mL) and heated with stirring at 110-130° C for 2 h. The suspension changes from yellow to red-yellow colour during this period. Triethyl phosphite was removed under reduced pressure and the resulting residue was chromatographed on a silica gel column eluting with methanol-dichloromethane (5:95) to afford product **6** (0.06 g, 7%) as yellow crystalline material.

Method B. 2,3,6,7-Tetrakis(2'-cyanoethylthio)tetrathiafulvalene[24] **17** (0.521 g, 0.96 mmol) was suspended in anhydrous degassed ethanol (30 mL) under inert atmosphere and a solution of Na (0.19 g, 8 mmol) in ethanol (10 mL) was added. After stirring at room temperature for 4 h, a solution of 2,3-dibromopropanol in 10 mL of ethanol was added dropwise and left for stirring overnight. The yellow precipitate formed was washed with ethanol, filtered and dried under *vacuo* to afford TTF **6** in good yields (0.15 g, 35%); mp 238-240° C (decomp.), [lit.[8] >230° C (decomp.)]; (Found: C, 32.51; H, 2.76 $C_{12}H_{12}S_8O_2$ requires C, 32.43; H, 2.70%); λ_{max} (CH_2Cl_2) 333.4, 307, 267 and 228 nm; ν (KBr) 3000-3300 (b) (OH), 1098 (C-O) cm^{-1}; δ_H (DMSO-d_6) 5.7 (1H, d, J=4.8 Hz), 5.6 (1H, d, J=4.3 Hz), 3.9 (2H, m), 2.92 (4H, m), 2.4 (4H, m); m/z (EI) 444 ($M^{+\cdot}$, 23%).

4,5-(1-Chloropropylenedithio)-1,3-dithiole-2-thione (7).

To a solution of thione **5** (1.70 g, 3.76 mmol) in anhydrous CH_2Cl_2 (500 mL) containing pyridine (2 mL) at 0° C was added a solution of freshly distilled thionyl chloride (1.59 g, 6.7 mmol) in CH_2Cl_2 (20 mL) dropwise over a period of 30 min. The mixture was stirred for 2 h at the same temperature and further refluxed for 3 h. During this period the light yellow solution becomes dark yellow with the evolution of SO_2. It was cooled to room temperature and poured into water (1000 mL) with constant stirring. The organic layer was separated and washed successively with 5% aqueous sodium hydrogen carbonate (150 mL) and brine (200 mL) followed by 10% aqueous $CaCl_2$ solution (200 mL). The organic layer was finally washed with water and dried over anhydrous sodium sulfate. Filteration followed by concentration of the CH_2Cl_2 solution affords the crude thione (1.65g, 90%). Chromatographic separation on silica gel by eluting with petroleuum ether-ethyl acetate (90:10) gave first the thione **8** as minor product (20%) followed by title thione 7 as major yellow crystalline material (1.44 g; 79%); mp 107° C. (Found: C, 26.12; H, 1.88 $C_6H_5S_5Cl$ requires C, 26.42; H, 1.83%); ν (KBr) 1070 cm^{-1} (C=S); λ_{max} (CH_2Cl_2) 404, 273, 229 nm; δ_H ($CDCl_3$) 3.95 (1H, q), 3.90 (1H, m) 3.8 (1H, m), 3.54 (1H, m), 3.38 (1H, m); δ_C ($CDCl_3$) 207.26 (C=S), 121.85, 121.68, 44.41, 43.08, 31.07; m/z (EI) 272 ($M^{+\cdot}$, 82%).

4,5-(2-Chloropropylenedithio)-1,3-dithiole-2-thione (8).

Thione **3** was chlorinated as described for thione **5** followed by a similar work up gave the mixture of thiones 7 and **8**. Chromatographic seperation on silica gel by eluting with petroleum ether-ethyl acetate (90:10) gave the title thione **8** as minor product (0.3 g, 20%) and thione 7 as the major product (1.4 g, 80%); mp 118° C. ν (KBr) 1070 cm^{-1} (C=S); δ_H ($CDCl_3$ 4.45 (1H, t), 3.26 (2H, m), 1.8 (2H, m).

Bis(1-chloro-2,3-propylenedithio)tetrathiafulvalene (9).

The thione 7 (1.0 g, 3.66 mmol) was taken in a freshly distilled trimethyl phosphite (10 mL) and refluxed with stirring at 120-130° C for 1 h; the solution became orange. Trimethyl phosphite was removed under reduced pressure and chromatographic separation of the residue on a silica column eluting with light petroleum and chloroform (1:1) yielded the compound **9** (0.065 g, 7%) as a red crystalline solid, mp 152° C. (Found: C, 29.56; H, 1.98 $C_{12}H_{10}S_8Cl_2$ requires,C, 29.93; H, 2.07%); λ_{max} (CH_2Cl_2) 447, 396, 320, 230 nm; δ_H ($CDCl_3$) 3.9 (2H, q), 3.84 (2H, m), 3.74 (2H, dd), 3.44 (2H, 2dd), 3.3 (2H, 2dds); m/z 481 (EI) ($M^{+1\cdot}$, 21%).

4,5-(Propionitriledithio)-1,3-dithiole-2-thione (10).

To a solution of freshly generated **1** (4.84 g, 10 mmol) in absolute ethanol (100 mL) under an inert atmosphere was added a solution of (±)2,3-dibromopropionitrile (2.12 g, 10 mmol) in ethanol (20 mL) drop-wise over a period of 10 min. with stirring. The reaction mixture was stirred for additional 2 h at room temperature. The orange yellow crystalline precipitate was filtered off, washed with ethanol and dried in *vacuo* to yield **10** (2.6 g, 53%), mp 151° C (Found: C, 28.83; H, 1.22; N, 6.03 $C_6H_3S_5N$ requires C, 28.91; H, 1.20; N, 5.62%); ν (KBr) 2307 cm^{-1} (C≡N), 1070 cm^{-1} (C=S); λ_{max} (CH_2Cl_2) 395, 251, 230 nm; δ_H($CDCl_3$) 4.54 (t, 1H, CHCN, J=4.42 Hz), 3.57 (d, 2H, CH_2-S, J=4.42 Hz); m/z (EI) 249 ($M^{+\cdot}$, 100%).

4,5-(Propionitriledithio)-1,3-dithiole-2-one (11).

To the thione **10** (1 g, 4.0 mmol) was added glacial acetic acid (25 mL) and $Hg(OAc)_2$ (3.20 g, 10 mmol). The mixture was stirred at room temperature for 1 h and the white precipitate was filtered off, and the filtrate washed with water. After drying (Na_2SO_4) and evaporation of solvent in *vacuo,* white solid of **11** was obtained (0.65 g, 70%); mp 137-139° C (d) (Found: C, 29.98; H, 1.21; N, 5.17 $C_6H_3S_4ON$ requires C, 30.90; H, 1.28; N, 6.00%); δ_H($CDCl_3$) 4.55 (m, 1H, CHCN), 3.60 (m, 2H, CH_2-S); m/z (EI) 233 ($M^{+\cdot}$, 26 %).

Bis-(propionitriledithio)tetrathiafulvalene (12).

2,3,6,7-Tetrakis(2'-cyanoethylthio)tetrathiafulvalene **17** (0.521 g, 0.96 mmol) was suspended in anhydrous degassed ethanol (30 mL) under argon atmosphere and a solution of Na (0.19 g, 8 mmol) in ethanol (10 mL) was added. After stirring at room temperature for 4 h, a solution of (+) 2,3-dibromopropionitrile (1.06 g, 5 mmol) in ethanol (5 mL) was added dropwise and left for stirring for 6 h. The precipitate formed was filtered, washed with ethanol and chromatographed on a silica gel column. Elution with CH_2Cl_2. gave the title compound **12** as reddish brown crystalline material (0.060 g, 19 %); mp >220° C (decomp) (Found: C, 33.01; H, 2.38; N, 6.26 % $C_{12}H_6N_2S_8$ requires C, 33.17; H, 1.38: N, 6.45 %; ν (KBr) 2308 cm^{-1} (C≡N); λ_{max} (CH_2Cl_2) 396, 299.4, 235.8 nm.

4,5-Bis(propargylthio)-1,3-dithiol-2-thione (13).

To a solution of the zinc salt **2** (9.41 g, 10 mmol) in acetone was added a solution of propargyl bromide (4.76 g, 40 mmol) dropwise with continuous stirring for a period of 1 h at 0°C. The colour of the solution changed from red to yellow. The solvent was removed under reduced pressure without heating. The crude was dissolved in chloroform and washed with water. The organic layer was separated and dried over anhydrous sodium sulfate and chromatographed on silica gel. Elution of the yellow band from column with petroleum ether-ethyl acetate (95:5) gave orange-yellow needle shaped crystals of X-ray quality. (3.29 g, 60%); mp 54-55° C (Found: C, 39.74; H, 2.23. $C_9H_6S_5$ requires C, 39.41; H, 2.18%); ν (KBr) (C=S) 1070 cm^{-1}; λ_{max} (CH_2Cl_2) 3765, 266, 230 nm; δH ($CDCl_3$) 3.60 (d, 4H, ≡CCH_2, J=2.6 Hz), 2.40 (t, 2H, HC≡C-, J=2.6 Hz,); δ_C ($CDCl_3$) 210.69 (C=S), 137.5 (C=C), 77.88 (≡C-), 74.08 (HC≡), 24.87 (-CH S); m/z (EI) 274 ($M^{+\cdot}$, 92%).

Attempted synthesis of bis(dipropargyldithio)tetrathiafulvalene (14).

Thione **13** (0.70 g, 2.55 mmol) and triphenyl phosphine (2.79 g, 10.65 mmol) dissolved in anhydrous benzene (40 mL) were refluxed and stirred for 9 h to give a red-brown coloured solution and a black-brown precipitate. The reaction mixture was filtered off and the precipitate was washed with benzene. The combined filtrate and the washings were concentrated under reduced pressure to give an oily residue which was chromatographed on a silica column eluting with petroleum ether (40-60° C). Initial fractions collected (400 mL) yielded unreacted PPh_3 (1.55 g, 55.45%), next three fractions (100 mL, 200 mL, 200 mL) yielded crude **15** (along with traces of **16**). Recrystallization from CH_2Cl_2-hexane (2:1) yielded pure **15** (0.12 g, 23 %) as yellow crystalline material, mp 154-155° C. (Found: C, 34.76; H, 1.85 $C_6H_4S_4$ requires C, 35.29; H, 1.96%); ν (KBr) 1060 cm^{-1} (C=S); λ_{max} (CH_2Cl_2) 385, 276, 235 nm; δ_H ($CDCl_3$) 6.75 (s. 1H, CH); 2.57 (s, 3H, CH_3); δ_C($CDCl_3$) 214.57 (C=S), 137.98 (C=C), 146.11 (C-CH_3), 118.13(CH). 16.05 (CH_3); m/z (EI) 204 ($M^{+\cdot}$, 100%), 344 (25%). After collecting all the fractions having compound **15**, the column was eluted with ethylacetate-petroleum ether (5:95). An orange-yellow band which moved rapidly down the column was collected to yield $Ph_3P{=}S$ as light yellow needles (0.175 g); mp160° C. The black-brown precipitate obtained above has shown high melting point and was found to be insoluble in all common organic solvents. It showed the characteristic ν (C=S) band at 1060 cm^{-1}.

Photochemical reaction of Bis-(propargylthio)-1,3-dithiole-2-thione with $(EtO)_3P$.

A mixture of thione **13** (1 g, 3.64 mmol) and triethyl phosphite (0.60 g, 3.64 mmol) in a two-neck flask fitted with water condenser and nitrogen-inlet was diluted with benzene (5 mL). The reaction mixture was irradiated with a 100 Watt general electric bulb at a distance of 5 cm from the flask for 24 h. Benzene was removed under reduced pressure and the orange-red viscous liquid thus obtained was chromatographed [eluent, petroleum ether (60-80°)-CH_2Cl_2 (10:1)] to only give the starting thione in 50% yield.

Attempted Coupling with $Co_2(CO)_8$.

To a solution of **13** (2.0 g, 7.2 mmol) in benzene (50 mL) at 40°C under N_2 atmosphere was added dicobalt octacarbonyl (1.20 g, 3.50 mmol). The solution immediately turned dark brown with evolution of CO and formation of a black precipitate. After refluxing for 6 h the solution was filtered to remove the black solid which was washed with a further portion of dry benzene. The combined benzene solutions were treated with charcoal, filtered, concentrated to dryness. The crude was chromatographed on silica gel (60-120 mesh) by eluting with petroleum ether (60-80°) to afford the starting material (1.2 g, 60%). Attempts to carry out the coupling of **13** with neat $(EtO)_3P$ at 120°C or in benzene at 80°C gave only interactable materials.

5, 5'-Dimethyl-$\Delta^{2,2'}$-bithieno[2,3-d]-1,3-dithiole (16).

Thione **15** (0.30 g, 1.47 mmol) was heated to reflux under nitrogen atmosphere in 6 ml of freshly distilled trimethyl phosphite. After a few minutes, the thione dissolved in trimethyl phosphite resulting in a dark red solution. The heating was continued for 6 h. After refrigeration (0°C), reddish crystalline **16** (0.036 g, 14 %) was obtained and recrystallized from CH_2Cl_2-Hexane (1:1), mp 210-212° C (d); Found C, 41.43; H, 2.28 $C_{12}H_8S_6$ requires C, 41.86; H, 2.32%); δ_H ($CDCl_3$) 6.54 (q, 2H); 2.47 (d, 6H, CH_3, J = 1.09 Hz); m/z (EI) 344 ($M^{+\cdot}$, 100 %).

Charge-Transfer complexes. The complexes were synthesised by mixing equimolar solutions of donors and acceptors in dichloromethane (for compound **9**) or methanol/acetonitrile (for compound **6**).

Complexation of 6 and $HgCl_2$. (**6**)$(HgCl_3)_2$. 52% λ_{max} (DMSO) 336.4, 270.2, 244.8, 237.0 221.2 nm; (Found: C, 14.33; H, 1.45; requires C, 14.61; H, 1.21; corresponding to the formulation of $C_{12}H_{12}S_8O_2$ $2HgCl_3$; $\sigma_{r.t}$ = 0.1 x 10^{-5} S cm^{-1} ESR g = 2.0027.

Complexation of 6 and $CuCl_2$. $(\mathbf{6})_{1/3}$ $(CuCl_2)$. 42% λ_{max} (DMSO) 335.6, 310, 262, 232 nm; (Found: C, 29.83; H, 2.55; requires C, 29.47; H, 2.45; corresponding to the formulation of $(C_{12}H_{18}O_2)_{1/3}$ $(CuCl_2)$; $\sigma_{r.t}$ = 2.35 x 10^{-5} S cm^{-1}; ESR g = 2.0032.

Complexation of 9 and $HgCl_3$. (**9**)$(HgCl_3)$ 46 % λ_{max} (DMSO) 576, 523, 326, 249 nm; (Found: C, 18.56; H, 1.35; requires C, 19.19; H, 1.33; corresponding to the formulation of $C_{12}H_{10}S_8C_{12}.HgCl_3$; $\sigma_{r.t}$ = 0.5 x 10^{-6} S cm^{-1}; ESR g = 2.00277.

Complexation of 9 and I_2 (**9**)(I_3). 37% λ_{max} (DMSO) 362, 332, 292, 258 nm; (Found: C, 16.46; H, 1.10; requires C, 16.73; H, 1.16; corresponding to the formulation of $C_{12}H_{10}S_8Cl_2.I_3$; $\sigma_{r.t.}$ = 3.85 x 10^{-5} S cm^{-1}; ESR g = 2.0056.

Crystal Data for Compound 13. $C_9H_6S_5$, M = 274.47, monoclinic, space group $P2_1/c$, a = 8.6488(7), b = 18.4020(2), c= 7.403(1) Å, β = 94.504(9)°, U = 1174.6(2) $Å^3$, Z = 4, D_c = 1.552 g cm^{-3}, F(000) = 560, (Mo-Kα) λ = 0.7107 Å, μ(Mo-Kα) = 1.12 mm^{-1}, T = 288 K, R = 0.033, R_w = 0.034, $(\Delta\rho)_{max.}$ = 0.440 $eÅ^{-3}$, $(\Delta\rho)_{min.}$ = -0.238 $eÅ^{-3}$

Crystal Data for Compound 15. $C_6H_4S_4$, M = 204.35, orthorhombic, space group $Pna2_1$, a = 13.25(3), b = 6.542(2), c= 9.304(2)Å, U = 806.5(5) $Å^3$, Z = 4, D_c = 1.6832 g cm^{-3}, F(000) = 416, (Mo-Kα) λ = 0.7107 Å, μ(Mo-Kα) = 1.05 mm^{-1}, T = 288 K, R = 0.047, R_w = 0.072, $(\Delta\rho)_{max.}$ = 0.390 e$Å^{-3}$, $(\Delta\rho)_{min.}$ = 0.00 e$Å^{-3}$ The structues were solved by a direct method using SHELX-76, SHELX-86, SHELXL-93 programs.[28]

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