# A Novel Tetrathiafulvalene Building Block

Jan Oskar Jeppesen,[a] Kazuo Takimiya,[a] Niels Thorup,[b] Jan Becher*[a]

[a]Department of Chemistry, University of Odense, Campusvej 55, DK-5230 Odense M, Denmark
Fax + 45(66)158780; E-mail: jbe@chem.ou.dk

[b]Department of Chemistry, Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark

*Received 19 August 1998; revised 30 November 1998*

**Abstract:** Efficient synthesis of a novel tetrathiafulvalene building block, 2,3-bis(2-cyanoethylthio)-6,7-bis(thiocyanatomethyl)tetrathiafulvalene **(7)** useful for stepwise and asymmetrical bis-functionalization is reported.

**Key words:** tetrathiafulvalene building block, orthogonal sets of protection groups, stepwise and asymmetrical bis-functionalization, thiocyanatomethyl, bromomethyl

Among sulfur-containing heterocycles the tetrathiafulvalenes have been intensively studied during the past two decades.[1] The tetrathiafulvalene moiety has been extensively modified in the search of new donor molecules suitable for the formation of low dimensional organic metals.[2] Furthermore, there has been an increasing interest in incorporating tetrathiafulvalenes into macrocyclic and supramolecular structures.[3,4] From this point of view the selective functionalization of tetrathiafulvalenes is a problem, because tetrathiafulvalene has a $D_{2h}$ symmetry with four identical potential attachment sites (Figure 1, **a**).

Versatile tetrathiafulvalene building blocks have been developed in recent years, and many problems concerning the selective functionalization of tetrathiafulvalene have been solved.[5–8] Tetrakis(2-cyanoethylthio)tetrathiafulvalene[5] is a useful tetrafunctionalized tetrathiafulvalene building block of type **a** (Figure 1). The four cyanoethyl thiolate protecting groups are readily deprotected when treated with 4.5 equivalents of cesium hydroxide monohydrate, and the resulting thiolates can subsequently be realkylated. In addition it has been shown that selective and stepwise deprotection of the cyanoethyl thiolate protecting groups is possible, by treatment with one equivalent of cesium hydroxide monohydrate.[4,9] When tetrakis(2-cyanoethylthio)tetrathiafulvalene is treated with 2.0 equivalents of cesium hydroxide monohydrate, symmetrical/pseudo-symmetrical deprotection takes place exclusively to produce a *cis*/*trans* mixture of type **b**/**c** bis-thiolates, i.e. no asymmetrical bis-deprotection (type **d**) is formed.[4,9]

Although the discovery of the cyanoethyl thiolate protecting group and the methodology for selective deprotection/realkylation have revolutionized the possibilities for incorporation of tetrathiafulvalene into macrocyclic and supramolecular structures, no preformed tetrafunctionalized tetrathiafulvalene building block of type **d** has so far been presented. A perfect type **d** building block should possess two orthogonal sets of protection groups.[10] Each set should contain two identical protection groups, hence it is possible to functionalize the tetrathiafulvalene moiety regioselectively in the 6- and 7-position (see Figure 1 **d**) in one synthetic step, followed by a functionalization of the tetrathiafulvalene moiety in the 2- and 3-position in the next step.

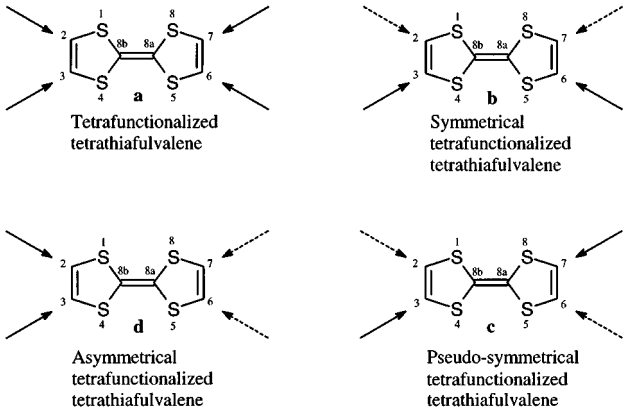



**Figure 1** Symmetry properties of substituted tetrathiafulvalenes

We report here the synthesis of a versatile tetrafunctionalized tetrathiafulvalene of type **d**, having two thiolate groups in the 2- and 3-positions protected by the conventional cyanoethyl group,[5,6,9] whereas the tetrathiafulvalene is functionalized through two thiocyanatomethyl groups in the 6- and 7-positions. The two thiocyanatomethyl groups can be deprotected with sodium borohydride in a mixture of THF and ethanol to generate the reactive 2,3-bis(2-cyanoethylthio)tetrathiafulvalene-6,7-bis(methylthiolate) (**7b**) (Figure 2), without interfering with the cyanoethyl protected thiolate groups.

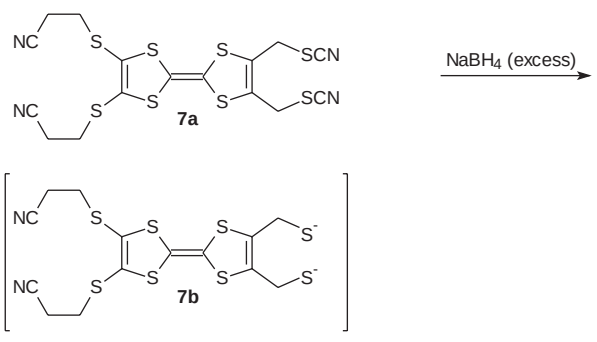
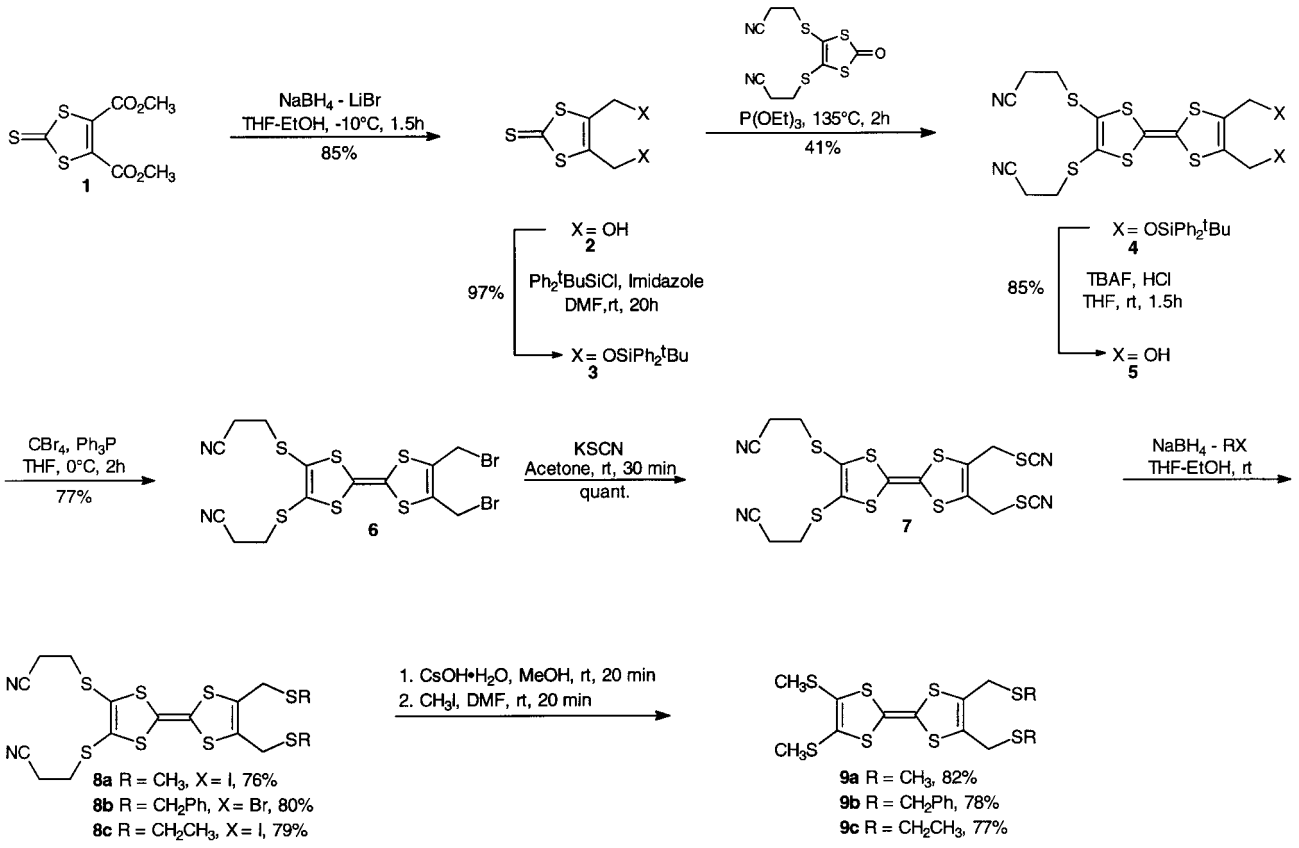



**Figure 2** Reductive deprotection of thiocyanate protection groups




**Scheme 1**

The key starting material in our synthesis is the 4,5-bis(hydroxymethyl)-1,3-dithiole-2-thione **2**, which was obtained by modification of the procedure reported by Fox and coworkers.[11] The reported procedure for reduction of 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione[12] **(1)** with sodium borohydride in the presence of lithium chloride was not suitable for scale-up in our hands. However, by using sodium borohydride in the presence of lithium bromide in a mixture of THF and ethanol at –10 °C, the reduction of **1** proceeded smoothly in 85% yield to give the desired dialcohol **2** in multigram quantities.

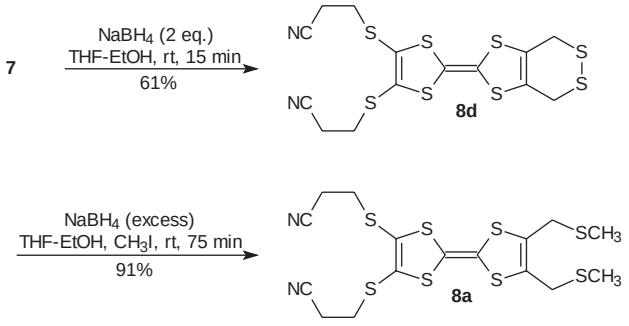
Next the two hydroxy groups in 4,5-bis(hydroxymethyl)-1,3-dithiole-2-thione **(2)** was protected as the *tert*-butyldiphenylsilyl ethers[13] using *tert*-butyldiphenylchlorosilane in DMF in the presence of imidazole, affording **3** in almost quantitative yield.

The bis-protected dialcohol **3** was then cross-coupled with an excess (2.8 equiv) of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one[5] in neat triethyl phosphite to give the asymmetric tetrathiafulvalene **4** in 41% yield. Deprotection of the two *tert*-butyldiphenylsilyl protecting groups with tetrabutylammonium fluoride (TBAF) in THF afforded 2,3-bis(2-cyanoethylthio)-6,7-bis(hydroxymethyl)tetrathiafulvalene **(5)** in 85% yield. Conversion of dialcohol **5** to the useful 2,3-bis(2-cyanoethylthio)-6,7-bis(bromomethyl)tetrathiafulvalene **(6)** posed a challenging problem.[14] The bromination was carried out in THF using carbon tetrabromide and triphenyl phosphine yielding **6** as orange needles in good yield. It is important that the starting dialcohol **5** is pure and the solvent is absolutely dry, otherwise byproducts are formed. Compound **6** is a reactive bis-electrophile, due to the pseudo-benzylic position of the two bromine atoms, which makes **6** unstable under ambient conditions. Elemental analyses and spectral data for compound **6** were all consistent with the assigned structure. The high reactivity of **6** is seen in the reaction with potassium thiocyanate, which converts **6** quantitatively to 2,3-bis(2-cyanoethylthio)-6,7-bis(thio-cyanatomethyl)-tetrathiafulvalene **(7)** in < 5 minutes. Although bis(thiocyanatomethyl)aromatic/heteroaromatic compounds are useful for the preparation of the corresponding thiolates,[15] no analog in the tetrathiafulvalene series has, to our knowledge, been described.

To study the potential of **7** as a type **d** building block, the following regioselective deprotection and realkylation reactions were carried out. Treatment of **7** with excess sodium borohydride in THF/ethanol afforded the reactive 2,3-bis(2-cyanoethylthio)tetrathiafulvalene-6,7-bis(methylthiolate) **(7b)** (Figure 2) which was trapped in situ with different electrophiles to give *S*-alkylated tetrathiafulvalenes **8a–c** in 76–80% yields. Subsequently the remaining two cyanoethyl thiolate protecting groups in **8a–c** were deprotected using 2.2 equivalents of cesium hydroxide monohydrate followed by addition of iodomethane affording

the corresponding 2,3-bis(methylthio)tetrathiafulvalenes **9a–c** in 77–82% yields after column chromatography.[16]

Furthermore, treatment of **7** with 2 equivalents of sodium borohydride and quenching the reaction mixture with saturated ammonium chloride after 15 minutes, followed by column chromatography gave 2,3-bis(2-cyanoethylthio)-6,7-bis(2,3-dithiabutane-1,4-diyl)tetrathiafulvalene **(8d)** in 61% yield. This type of tetrathiafulvalene derivatives are of considerable current interrest due to its peripheral *S*-position isomerism with ethylenedithiotetrathiafulvalene.[17–19]




**Scheme 2**

The disufide **8d** could be further reduced with excess sodium borohydride to give **7b** which was trapped in situ with iodomethane affording **8a** in 91% yield. These results strongly indicate that the disulfide **8d** is an intermediate in the generation of the bis-thiolate **7b**.[20]

Single crystals of **9c** were obtained by careful recrystallization from chloroform/methanol, and its structure was determined by X-ray crystallography. As shown in Figures 3 and 4, the central tetrathiafulvalene framework of **9c** is essentially planar. The asymmetric unit is half a molecule as a two-fold rotation axis passes through the central C1–C2 bond.

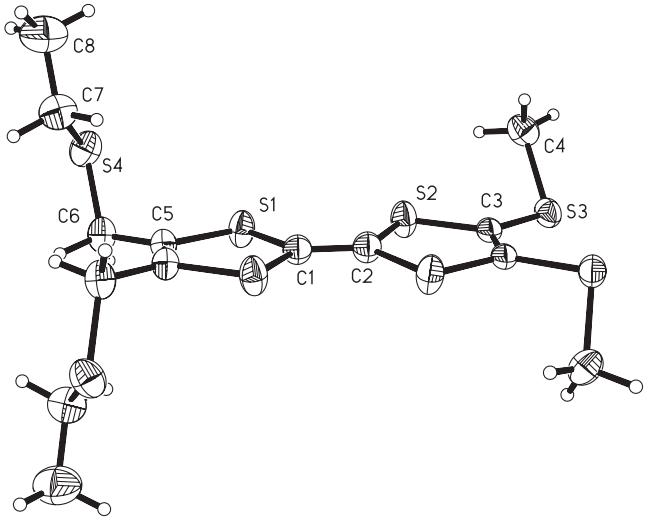



**Figure 3** Molecular structure of **9c**. Displacement ellipsoids are drawn at the 50% level

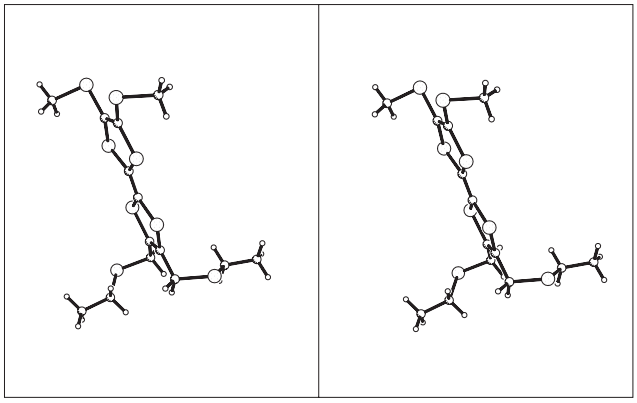


**Figure 4** Stereo drawing of the molecular structure of **9c**

In conclusion, we have developed an effective synthesis of 2,3-bis(2-cyanoethylthio)-6,7-bis(thiocyanatomethyl)-tetrathiafulvalene **(7)** possessing two orthogonal sets of thiolate protecting groups and demonstrated that it fulfills the requirement for an asymmetrical tetrafunctionalized tetrathiafulvalene of type **d**. Thus **7** is the first example of a type **d** tetrathiafulvalene building block.

All reactions involving tetrathiafulvalenes were carried out under an atmosphere of dry $N_2$. THF was distilled from Na/benzophenone immediately prior to use, MeOH and EtOH was distilled from Mg. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 d before use, while acetone was dried over $CaSO_4$ (Drierite). LiBr was dried overnight at approx. 200 °C in vacuo. All reagents were standard grade and used as received unless otherwise stated. Analytical TLC was performed on Merck DC-Alufolien Kieselgel 60 F254 0.2 mm thickness precoated TLC plates, while column chromatography was performed using Merck Kieselgel 60 (0.040–0.063 mm, 230–400 mesh ASTM). Melting points were determined on a Büchi melting point apparatus and are uncorrected. Microanalyses were performed at the Microanalytical Laboratory, University of Copenhagen, or the Atlantic Microlab, inc., Atlanta, Georgia. $^1$H NMR spectra were recorded on a Gemini-300BB instrument at 300 MHz using the deuterated solvent as lock and TMS or the residual solvent as internal standard. $^{13}$C NMR spectra were recorded at 75 MHz using Broad Band Decoupling. Electron Impact Ionisation Mass Spectrometry (EIMS) was performed on a Varian MAT 311A instrument and Plasma Desorption Mass Spectrometry (PDMS) was performed on a Bio-Ion 20K time of flight instrument from Applied Biosystem on the basis of 5.000.000 fission events. IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Cyclic Voltammetry (CV) was carried out on an Autolab/PGSTAT 10 instrument using $CH_2Cl_2$ as the solvent employing $Bu_4NPF_6$ (0.10 M) as supporting electrolyte, with a sweep rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl.

**4,5-Bis(hydroxymethyl)-1,3-dithiole-2-thione (2)**

To a well stirred solution of **1**[12] (15.0 g, 59.9 mmol) and dry LiBr (10.4 g, 120 mmol) in anhyd THF (120 mL) and anhyd EtOH (60 mL) at –15 to –10 °C was slowly added powdered $NaBH_4$[21] (4.80 g, 127 mmol) in portions over 20 min. An exothermic reaction took place and temperature should be kept under –10 °C for further 30 min. Then $H_2O$ (600 mL, 0 °C) was added and then dil HCl (4 N) was carefully added until the evolution of $H_2$ gas ceased. The mixture was extracted with EtOAc (8 × 80 mL), and the extract was dried ($MgSO_4$). Evaporation of the solvent gave an yellow oily

residue which was redissolved in $CH_2Cl_2$/EtOAc (2:1, 50 mL) and filtered through a short column (6 cm silica gel, 10 cm Ø). The column was first eluted with $CH_2Cl_2$/EtOAc (2:1, approx. 1 L). The first yellow fraction contained trace amount of the starting material and the mono alcohol. Next the desired dialcohol **2** (Rf 0.2, $CH_2Cl_2$/EtOAc, 1:1) was eluted with $CH_2Cl_2$/EtOAc (1:1) until the solution was colourless (approx. 2 L). The second fraction was concentrated in vacuo to give yellow crystals of **2**; yield: 9.93 g (85%). The product was sufficiently pure for further reactions, but can be recrystallized from EtOAc/petroleum ether (bp 60–80 °C) to give pale yellow crystals; mp 88–89 °C (Lit[11] mp 87–88 °C).

**4,5-Bis(*tert*-butyldiphenylsiloxymethyl)-1,3-dithiole-2-thione (3)**

To a solution of **2** (3.20 g, 16.5 mmol) in anhyd DMF (200 mL) was first added *tert*-butyldiphenylchlorosilane (13.5 mL, 14.3 g, 52.0 mmol) in one portion followed by imidazole (24.0 g, 353 mmol). The yellow solution was stirred overnight at r.t., whereupon the yellow orange solution was diluted with $CH_2Cl_2$ (400 mL). The combined organic phase were washed with 4 N HCl (3 × 300 mL), $H_2O$ (2 × 300 mL), dried ($MgSO_4$) and the solvent was evaporated. The resulting yellow residue was redissolved in $CH_2Cl_2$ (15 mL) and subjected to column chromatography (600 mL silica gel, 6 cm Ø, eluent: $CH_2Cl_2$). The broad yellow band (Rf 0.8) was collected and evaporation of the solvent in vacuo afforded initially **3** as an yellow oil. Leaving the product in vacuum overnight afforded **3** as an analytically pure yellow solid; yield: 10.7 g (97%); mp 104–105.5 °C.

$^1$H NMR ($CDCl_3$/TMS): δ = 1.00 (s, 18 H) , 4.27 (s, 4 H), 7.34 (m, 12 H), 7.55 (m, 8 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 18.99, 26.45, 59.36, 128.00, 130.21, 132.06, 135.49, 140.40, 213.18.

MS(EI): m/z (%) = 670 ($M^+$, 9), 237 (75), 199 (45), 197 (55), 161 (85), 135 (100).

IR (KBr): ν = 3071, 3050, 3015, 2958, 2931, 1727, 1428, 1263, 1114, 1071 $cm^{-1}$.

Anal. $C_{37}H_{42}O_2S_3Si_2$ (671.1): calcd C 66.22, H 6.31; found C 65.85, H 6.58.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(*tert*-butyldiphenylsiloxymethyl)tetrathiafulvalene (4)**

Compound **3** (6.00 g, 8.94 mmol) and 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one[5] (7.20 g, 24.9 mmol) were suspended in distilled $P(OEt)_3$ (50 mL) under $N_2$ in a 250 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, and the suspension was heated on an oil bath at 135 °C, causing dissolution within 5 min, and leaving a red reaction mixture. After 10 min a orange precipitate of tetrakis(2-cyanoethylthio)tetrathiafulvalene was formed. The orange red suspension was stirred for 2 h, cooled to r.t. Addition of MeOH (50 mL) yielded an orange solid,[22] which was filtered and washed with MeOH (3 × 20 mL). The combined filtrate was concentrated in vacuo and the resulting red oil was purified by column chromatography (700 mL silica gel, 6 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 9:1). The broad red band (Rf 0.4) was collected and concentrated to give crude **4** as a red oil (3.69 g), which was redissolved in $CH_2Cl_2$ (10 mL) and rechromatographed (500 mL silica gel, 6 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 9:1). The broad red band was collected and the solvent evaporated to give a red semisolid, which was repeatedly dissolved in $CH_2Cl_2$ (3 × 100 mL) and concentrated to give analytically pure **4** as a red semisolid; yield: 3.37 g (41%).

$^1$H NMR ($CDCl_3$/TMS): δ = 1.00 (s, 18 H), 2.75 (t, 4 H, J = 7.1 Hz), 3.10 (t, 4 H, J = 7.1 Hz), 4.10 (s, 4 H), 7.35 (m, 12 H), 7.56 (m, 8 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 18.72, 19.04, 26.50, 31.14, 59.44, 99.97, 102.21, 117.53, 127.85, 128.19, 129.99, 130.35, 132.49, 135.54.

MS(EI): m/z (%) = 910 ($M^+$, 2.5), 199 (100).

IR (KBr): ν = 3069, 3046, 3014, 2953, 2929, 2250 (CN), 1471, 1427, 1263, 1113 $cm^{-1}$.

Anal. $C_{46}H_{50}N_2O_2S_6Si_2$ (911.4): calcd C 60.62, H 5.53, N 3.07; found C 60.45, H 5.51, N 3.01.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.54 V, 0.96 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(hydroxymethyl)tetrathiafulvalene (5)**

Compound **4** (2.90 g, 3.18 mmol) was dissolved in anhyd THF (50 mL) under $N_2$ in a 250 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a septum. 4 N HCl (1.65 mL, 6.60 mmol) was added by means of a syringe to the orange red solution in one portion. TBAF (9.20 mL of a 1.0 M solution in THF, 9.20 mmol) was added dropwise to the mixture using a syringe (10 min). After stirring for an additional 1.5 h the colour darkened and the solvent was evaporated in vacuo at 25 °C. The resulting red oil was dissolved in EtOAc (300 mL), washed with acid free $H_2O$ (4 × 150 mL), and dried ($Na_2SO_4$).[23] Concentration in vacuo (T < 30 °C) gave an orange solid, which was recrystallized from propan-2-ol (85 mL) to give **5** as thin orange needles; yield: 1.18 g (85%); mp 139.5–140 °C.

$^1$H NMR (DMSO-$d_6$/TMS): δ = 2.85 (t, 4 H, J = 6.7 Hz), 3.12 (t, 4 H, J = 6.7 Hz), 4.23 (d, 4 H, J = 5.2 Hz), 5.50 (t, 2 H, J = 5.2 Hz).

$^{13}$C NMR (DMSO-$d_6$/TMS): δ = 18.22, 30.85, 56.62, 102.95, 115.25, 118.99, 127.77, 131.72.

MS(EI): m/z (%) = 434 ($M^+$,1.1), 172 (21), 100 (27), 54 (100), 45 (43).

IR (KBr): ν = 3435 (OH), 2923, 2254 $cm^{-1}$ (CN).

Anal. $C_{14}H_{14}N_2O_2S_6$ (434.6): calcd C 38.69, H 3.25, N 6.45; found C 38.83, H 3.20, N 6.32.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.51 V, 0.85 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(bromomethyl)tetrathiafulvalene (6)**

Compound **5** (0.49 g, 1.13 mmol) was dissolved in anhyd THF (15 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet. The orange solution was degassed ($N_2$, 5 min) and cooled (0 °C) before $CBr_4$ (1.12 g, 3.38 mmol) was added. Then $Ph_3P$ (0.89 g, 3.39 mmol) was added in one portion and the orange solution was stirred for 2 h at 0 °C, during this time a white precipitate was formed. The solvent was evaporated in vacuo at 25 °C and the orange oily residue was redissolved in $CH_2Cl_2$/(EtOAc/cyclohexane, 1:2) (10 mL, 7:3) and purified by column chromatography (200 mL silica gel, 4 cm Ø, eluent: EtOAc/cyclohexane, 1:2). The orange band (Rf 0.3) was collected and concentrated (T < 30 °C) to give **6** as analytically pure orange needles;[24] yield: 0.49 g (77%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **6** as orange red plates; mp 106–106.5 °C (dec).

$^1$H NMR ($CDCl_3$/TMS): δ = 2.75 (t, 4 H, J = 7.1 Hz), 3.09 (t, 4 H, J = 7.1 Hz), 4.21 (s, 4 H).

PDMS: m/z (%) =

561.8 ($M^+$ + 4,69); calcd[25] for $C_{14}H_{12}{}^{81}Br_2N_2S_6$, 561.8.

559.8 ($M^+$ + 2,93); calcd[25] for $C_{14}H_{12}{}^{79}Br_{81}BrN_2S_6$, 559.8.

557.8 ($M^+$, 38); calcd[25] for $C_{14}H_{12}{}^{79}Br_2N_2S_6$, 557.8.

400.0 ($M^+$ – 2 Br, 100); calcd[25] for $C_{14}H_{12}N_2S_6$, 399.9.

IR (KBr): ν = 2954, 2927, 2251 (CN), 1636, 1590, 1417, 1205 $cm^{-1}$.

Anal. $C_{14}H_{12}Br_2N_2S_6$ (560.4): calcd C 30.00, H 2.16, Br 28.52, N 5.00, S 34.32; found C 30.16, H 2.15, Br 28.57, N 4.92, S 34.26.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.70 V, 1.09 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(thiocyanatomethyl)tetrathiafulvalene (7)**

Compound **6** (0.49 g, 0.87 mmol) was dissolved in acetone (25 mL) in a 250 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet. KSCN (1.76 g, 18.1 mmol) was added in one portion to the orange solution. After stirring for 30 min at r.t., the solvent was removed in vacuo. The orange solid residue was dissolved in $CH_2Cl_2$ (250 mL), washed with $H_2O$ (4 × 150 mL) and dried ($MgSO_4$). Evaporation of the solvent gave **7** as an orange solid; yield: 0.44 g (quant); mp 120–122 °C.

$^1$H NMR (DMSO-$d_6$/TMS): δ = 2.89 (t, 4 H, J = 6.8 Hz), 3.16 (t, 4 H, J = 6.8 Hz), 4.46 (s, 4 H).

$^{13}$C NMR (DMSO-$d_6$/TMS): δ = 18.18, 30.47, 30.95, 107.45, 110.26, 112,54, 119.01, 128.02, 130.57.

PDMS: m/z (%) =

516.6 ($M^+$, 71); calcd[25] for $C_{16}H_{12}N_4S_8$, 516.8.

400.5 ($M^+$ – 2 SCN, 100); calcd[25] for $C_{14}H_{12}N_2S_6$, 400.6.

IR (KBr): ν = 2928, 2250 (CN), 2153 (SCN), 1417 $cm^{-1}$.

Anal. $C_{16}H_{12}N_4S_8$ (516.8): calcd C 37.19, H 2.34, N 10.84; found C 37.56 H 2.38, N 10.45.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.74 V, 1.04 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(methylthiomethyl)tetrathiafulvalene (8a)**

Method A: Compound **7** (0.29 g, 0.56 mmol) was dissolved in a mixture of anhyd THF (20 mL) and anhyd EtOH (10 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet and cooled (0 °C) before MeI (1.0 mL, 2.28 g, 16 mmol) was added. Then powdered $NaBH_4$ (0.10 g, 2.64 mmol) was added in one portion at 0 °C, causing gas evolution. The mixture was stirred at 0 °C for further 10 min, causing the initially orange red reaction mixture to become orange. The solution was allowed to come to r.t. and stirred for 20 min followed by addition of powdered $NaBH_4$ (0.10 g, 2.64 mmol) (gas evolution), whereupon the orange reaction mixture was stirred for 2 h at r.t. and then purged with $N_2$ for 20 min (evaporating the excess of MeI). The mixture was then poured into ice containing aq sat. $NH_4Cl$ solution (70 mL), and extracted with $CH_2Cl_2$ (2 × 125 mL). The combined orange red extracts were washed with $H_2O$ (2 × 125 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the resulting orange solid purified by column chromatography (200 mL silica gel, 4 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 9:1). The orange band (Rf 0.25) was collected and concentrated to give **8a** as an analytically pure orange powder; yield: 0.21 g (76%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **8a** as fine orange needles; mp 118–119 °C.

Method B: Compound **8d** (0.10 g, 0.22 mmol) was dissolved in a mixture of anhyd THF (10 mL) and anhyd EtOH (5 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet and cooled (0 °C) before MeI (0.4 mL, 0.91 g, 6.4 mmol) was added. Then powdered $NaBH_4$ (0.033 g, 0.87 mmol) was added in one portion at 0 °C, causing gas evolution, whereupon the reaction mixture was allowed to come to r.t. and stirred for 30 min followed by addition of powdered $NaBH_4$ (0.033 g, 0.87 mmol) (gas evolution). The orange reaction mixture was stirred for further 45 min at r.t. and then purged with $N_2$ for 20 min (evaporating the excess of MeI). The mixture was then poured into ice containing sat. aq $NH_4Cl$ solution (50 mL), and extracted with $CH_2Cl_2$ (2 × 60 mL). The combined orange red extracts were washed with $H_2O$ (2 × 75 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the resulting orange solid purified by column chromatography (150 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 9:1). The orange band (Rf 0.25) was collected and concentrated to give *8a* as a pure orange powder; yield: 0.097 g (91%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **8a** as fine orange needles. The analytical data of **8a** obtained by both Methods A and B were identical.

$^1$H NMR ($CDCl_3$/TMS): δ = 2.15 (s, 6 H), 2.74 (t, 4 H, J = 7.2 Hz), 3.09 (t, 4 H, J = 7.2 Hz), 3.46 (s, 4 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 15.32, 18.77, 30.99, 31.16, 104.18, 115.62, 117.51, 128.15, 129.77.

MS(EI): m/z (%) = 494 ($M^+$, 48), 400 (45), 54 (83), 47 (58), 45 (100) .

IR (KBr): ν = 2952, 2918, 2249 (CN), 1631, 1598, 1412 $cm^{-1}$.

Anal. $C_{16}H_{18}N_2S_8$ (494.8): calcd C 38.84, H 3.67, N 5.66, S 51.83; found C 38.78, H 3.69, N 5.56, S 51.77.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.58 V, 0.99 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(benzylthiomethyl)tetrathiafulvalene (8b)**

Compound **7** (0.19 g, 0.37 mmol) was dissolved in a mixture of anhyd THF (10 mL) and anhyd EtOH (5 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet and cooled (0 °C) before benzyl bromide (0.10 mL, 0.14 g, 0.84 mmol) was added. Then powdered $NaBH_4$ (0.056 g, 1.48 mmol) was added in one portion at 0 °C. The solution was allowed to come to r.t. and stirred for 60 min. The mixture was then poured into ice containing sat. aq $NH_4Cl$ solution (50 mL), and extracted with $CH_2Cl_2$ (150 mL). The orange red extract was washed with $H_2O$ (2 × 100 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the resulting orange solid purified by column chromatography (150 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$). The orange band (Rf 0.25) was collected and concentrated to give **8b** as an analytically pure orange powder; yield: 0.19 g (80%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **8b** as fine orange needles; mp 112.5–113 °C.

$^1$H NMR ($CDCl_3$/TMS): δ = 2.75 (t, 4 H, J = 7.1 Hz), 3.09 (t, 4 H, J = 7.1 Hz), 3.09 (s, 4 H), 3.70 (s, 4 H), 7.28 (m, 10 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 18.78, 28.18, 31.16, 36.13, 104.08, 115.62, 117.50, 127.44, 128.15, 128.71, 128.95, 129.56, 137.02.

MS(EI): m/z (%) = 646 ($M^+$, 0.11), 91 (100).

IR (KBr): ν = 3059, 3026, 2917, 2250 (CN), 1631, 1601, 1493, 1452, 1413 $cm^{-1}$.

Anal. $C_{28}H_{26}N_2S_8$ (647.0): calcd C 51.98, H 4.05, N 4.33, S 39.64; found C 52.02, H 4.06, N 4.38, S 39.53.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.55 V, 0.94 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(ethylthiomethyl)tetrathiafulvalene (8c)**

Compound **7** (0.20 g, 0.39 mmol) was dissolved in a mixture of anhyd THF (10 mL) and anhyd EtOH (5 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet and cooled (0 °C) before EtI (0.07 mL, 0.14 g, 0.88 mmol) was added. Then powdered $NaBH_4$ (0.059 g, 1.56 mmol) was added in one portion at 0 °C. The solution was allowed to come to r.t. and stirred for 45 min. The mixture was then poured into ice containing sat. aq $NH_4Cl$ solution (50 mL), and extracted with $CH_2Cl_2$ (150 mL). The orange red extract was washed with $H_2O$ (3 × 100 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the resulting orange solid purified by column chromatog-

raphy (100 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$). The orange band (Rf 0.2) was collected and concentrated to give **8c** as an analytically pure orange powder; yield: 0.16 g (79%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **8c** as fine orange needles; mp 103.5–104 °C.

$^1$H NMR ($CDCl_3$/TMS): δ = 1.29 (t, 6 H, J = 7.4 Hz), 2.59 (q, 4 H, J = 7.4 Hz), 2.74 (t, 4 H, J = 7.0 Hz), 3.08 (t, 4 H, J = 7.0 Hz), 3.49 (s, 4 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 14.28, 18.76, 26.00, 28.87, 31.15, 103.93, 115.80, 117.49, 128.12, 129.72.

MS(EI): m/z (%) = 522 ($M^+$, 31), 400 (29), 172 (30), 87 (47), 76 (62), 54 (77), 45 (97), 32 (100).

IR (KBr): ν = 2965, 2924, 2868, 2251 (CN), 1631, 1598, 1422, 1376 $cm^{-1}$.

Anal. $C_{18}H_{22}N_2S_8$ (522.9): calcd C 41.35, H 4.24, N 5.36, S 49.05; found C 41.34, H 4.13, N 5.27, S 49.09.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.54 V, 0.95 V.

**2,3-Bis(2-cyanoethylthio)-6,7-bis(2,3-dithiabutane-1,4-diyl)-tetrathiafulvalene (8d)**

Compound **7** (0.24 g, 0.46 mmol) was dissolved in a mixture of anhyd THF (10 mL) and anhyd EtOH (5 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and a $N_2$ inlet. Powdered $NaBH_4$ (0.035 g, 0.092 mmol) was added in one portion. The solution was stirred for 15 min whereupon addition of sat. aq $NH_4Cl$ solution (50 mL) yielded an orange solid, which was filtered and washed with $H_2O$ (3 × 10 mL). The orange solid was dried in vacuo and purified by column chromatography (100 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$). The orange band (Rf 0.3) was collected and concentrated to give **8d** as analytically pure red orange needles; yield: 0.13 g (61%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **8d** as fine orange needles; mp 177–178 °C.

$^1$H NMR (DMSO-$d_6$/TMS): δ = 2.87 (t, 4 H, J = 6.8 Hz), 3.15 (t, 4 H, J = 6.8 Hz), 3.72 (s, 4 H).

13C NMR (DMSO-$d_6$/TMS): δ = 18.16, 29.75, 30.87, 105.92, 109.60, 118.97, 123.24, 127.89.

MS(EI): m/z (%) = 464 (5, $M^+$), 430 (9), 400 (13), 54 (100).

IR (KBr): ν = 2927, 2252 (CN), 1635, 1416, 1396 $cm^{-1}$.

Anal. $C_{14}H_{12}N_2S_8$ (464.7): calcd C 36.18, H 2.60, N 6.03, S 55.19; found C 36.23, H 2.48, N 5.99, S 55.08.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.62 V, 1.02 V.

**2,3-Bis(methylthio)-6,7-bis(methylthiomethyl)tetrathiafulvalene (9a)**

Compound **8a** (0.16 g, 0.32 mmol) was dissolved in anhyd DMF (25 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and purged with $N_2$ (20 min.). A solution of CsOH•$H_2O$ (0.12 g, 0.71 mmol) in anhyd MeOH (5 mL) was added over a period of 5 min. The mixture was stirred for 20 min, causing the initially orange solution to become redish brown. MeI (0.60 mL, 1.37 g, 9.6 mmol) was added in one portion, causing a momentary colour change to orange. The mixture was stirred for 20 min and then purged with $N_2$ (20 min.). The solvent was removed in vacuo and the resulting orange residue dissolved in $CH_2Cl_2$ (150 mL) and washed with $H_2O$ (4×100 mL). After drying ($MgSO_4$) and evaporation of the solvent, the resulting orange product was purified by column chromatography (150 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 1:1). The orange band (Rf 0.4) was collected and concentrated to give **9a** as an analytically pure yellow orange powder; yield: 0.11 g (82%). Recrystallization from $CH_2Cl_2$/petroleum ether (bp 60–80 °C) gave **9a** as yellow needles; mp 112–112.5 °C

$^1$H NMR ($CDCl_3$/TMS): δ = 2.14 (s, 6 H), 2.42 (s, 6 H), 3.45 (s, 4 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 15.22, 19.03, 30.94, 107.17, 111.98, 127.51, 129.57.

MS(EI): m/z (%) = 416 (100, $M^+$), 322 (92), 172 (29).

IR (KBr): ν = 2952, 2918, 1630, 1599, 1421 $cm^{-1}$.

Anal. $C_{12}H_{16}S_8$ (416.7): calcd C 34.59, H 3.87, S 61.54; found C 34.49, H 3.87, S 61.58.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.47 V, 0.88 V.

**2,3-Bis(methylthio)-6,7-bis(benzylthiomethyl)tetrathiafulvalene (9b)**

Compound **8b** (0.15 g, 0.23 mmol) was dissolved in anhyd DMF (20 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and purged with $N_2$ (20 min). A solution of CsOH•$H_2O$ (0.086 g, 0.51 mmol) in anhyd MeOH (5 mL) was added over a period of 5 min. The mixture was stirred for 20 min., causing the initially orange solution to become redish brown. MeI (0.40 mL, 0.91 g, 6.4 mmol) was added in one portion, causing a momentary colour change to orange. The mixture was stirred for 20 min and then purged with $N_2$ (20 min). The solvent was removed in vacuo and the resulting orange residue dissolved in $CH_2Cl_2$ (150 mL) and washed with $H_2O$ (4 × 100 mL). After drying ($MgSO_4$) and evaporation of the solvent, the resulting orange product was purified by column chromatography (150 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 1:1). The orange band (Rf 0.3) was collected and concentrated to give **9b** as an orange oil; yield: 0.10 g (78%).

$^1$H NMR ($CDCl_3$/TMS): δ = 2.43 (s, 6 H), 3.08 (s, 4 H), 3.69 (s, 4 H), 7.28 (m, 10 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 19.08, 28.22, 36.07, 107.20, 112.16, 127.37, 127.60, 128.67, 128.96, 129.44, 137.14.

MS(EI): m/z (%) = 568 ($M^+$, 14), 354 (18), 322 (17), 91 (100).

IR (KBr): ν = 3059, 3026, 2917, 1600, 1493, 1453, 1420 $cm^{-1}$.

Anal. $C_{24}H_{24}S_8$ (568.9): calcd C 50.67, H 4.25, S 45.08; found C 51.07, H 4.39, S 44.59.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.44 V, 0.84 V.

**2,3-Bis(methylthio)-6,7-bis(ethylthiomethyl)tetrathiafulvalene (9c)**

Compound **9b** (0.11 g, 0.21 mmol) was dissolved in anhyd DMF (20 mL) in a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer and purged with $N_2$ (20 min). A solution of CsOH•$H_2O$ (0.082 g, 0.49 mmol) in anhyd MeOH (5 mL) was added over a period of 5 min. The mixture was stirred for 20 min, causing the initially orange solution to become redish brown. MeI (0.40 mL, 0.91 g, 6.4 mmol) was added in one portion, causing a momentary colour change to orange. The mixture was stirred for 20 min and then purged with $N_2$ (20 min). The solvent was removed in vacuo and the resulting orange residue dissolved in $CH_2Cl_2$ (150 mL) and washed with $H_2O$ (4 × 100 mL). After drying ($MgSO_4$) and evaporation of the solvent, the resulting orange product was purified by column chromatography (100 mL silica gel, 3 cm Ø, eluent: $CH_2Cl_2$/cyclohexane, 1:1). The orange band (Rf 0.5) was collected and concentrated to give **9c** as an orange powder; yield: 0.072 g (77%). Recrystallization from $CHCl_3$/MeOH gave **9c** as red needles; mp 103.5–104.5 °C.

$^1$H NMR ($CDCl_3$/TMS): δ = 1.28 (t, 6 H, J = 7.4 Hz), 2.42 (s, 6 H), 2.58 (q, 4 H, J = 7.4 Hz), 3.48 (s, 4 H).

$^{13}$C NMR ($CDCl_3$/TMS): δ = 14.28, 19.05, 25.92, 28.88, 106.99, 112.23, 127.56, 129.57.

MS(EI): m/z (%) = 444 ($M^+$, 100), 398 (37), 322 (95), 276 (39).

IR (KBr): ν = 2959, 2920, 2867, 1630, 1599, 1452, 1423, 1375 $cm^{-1}$.

Anal. $C_{14}H_{20}S_8$ (444.8): calcd C 37.81, H 4.53, S 57.66; found C 37.60, H 4.42, S 57.41.

CV ($CH_2Cl_2$, vs. Ag/AgCl): $E_{½}$ = 0.44 V, 0.85 V.

**Crystallographic Data for Compound 9c**

$C_{14}H_{20}S_8$, M = 444.8, Crystal size 0.30 × 0.16 × 0.10 mm, hexagonal, *a* = 11.7402(2) Å, *b* = 11.7402(2) Å, *c* = 12.661(3) Å, α = 90°, β = 90°, γ = 120°, V = 1511.3(5) $Å^3$, space group $P_{62}$, *Z* = 3, $D_c$ = 1.466 g cm–3, *F*(000) = 696, Graphite monochromated MoKα radiation, λ = 0.71073 Å, μ = 0.879 $mm^{-1}$, T = 120 K. The intensities of 16224 reflections were measured on a Siemens SMART CCD diffractometer to $\theta_{max}$ = 26.35°, and were merged to 2065 unique reflections ($R_{int}$ = 0.026). Structure solution, refinement and analysis of the structure, and production of crystallographic illustrations were carried out using the programs SHELXS97,26 SHELXL97,27 PLATON28 and SHELXTL.29 The refinement using 103 parameters converged at R = 0.0288 (for $F_o > 4_\sigma(Fo)$). Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

## Acknowledgement

We thank University of Odense for a Ph.D. scholarship to J.O.J. and the Danish Research Academy for a post doctoral fellowship to K.T., as well as helpful discussions with Prof. P. Hudhomme, Université d'Angers.

## References

(1) For reviews, see:
Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Reports* **1987**, *7*, 155.
Schukat, G.; Fanghänel, E. *ibid* **1993**, *14*, 245.
(2) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355.
(3) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41.
(4) Becher, J.; Li, Z.-T.; Blanchard, P.; Svenstrup, N.; Lau, J.; Nielsen, M. B.; Leriche, P. *Pure & Appl. Chem.* **1997**, *69*, 465.
(5) Svenstrup; N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809.
(6) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1995**, 407.
(7) Garin, J.; Orduna, J.; Uriel, J.; Moore, A. J.; Bryce, M. R; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489.
(8) Garin, J. *Adv. Heterocycl. Chem.* **1995**, *62*, 249.
(9) Simonsen, K. B.; Becher, J. *Synlett* **1997**, 1211.
(10) For definition of orthogonal sets, see:
Barany, G.; Merrifield, R. B. *J. Am Chem. Soc.* **1977**, *99*, 7363.
Barany, G.; Albericio, F. J. *ibid* **1985**, *107*, 4936.
(11) Fox, A. F.; Pan, H. *J. Org. Chem.* **1994,** *59*, 6519.
(12) 4,5-Bis(methoxycarbonyl)-1,3-dithiole-2-thione **(1)** is available in a one-step reaction between ethylene trithiocarbonate and dimethyl acetylendicarboxylate, see:
Easton, D. B. J.; Leaver, D. *J. Chem. Soc., Chem. Commun.* **1965**, 585.
O'Connor, B. R.; Jones, F. N. *J. Org. Chem.* **1970**, *35*, 219.
(13) Previous results have shown that an primary alcohol functionality is unable to survive the standard trialkyl phosphite coupling, whereas the *tert*-butyldiphenylsilyl alcohol protecting group is able to withstand the standard coupling conditions, see:
Marshallsay, G. J; Bryce, M. R.; Cooke, G.; Jørgensen, T.; Becher, J.; Reynolds, C. D.; Wood, S. *Tetrahedron* **1993**, 49, 6849.
Marshallsay, G. J, Hansen, T. K.; Moore, A. J.; Bryce, M. R.; Becher, J. *Synthesis* **1995**, 926.
A tetrathiafulvalene bearing a secondary alcohol functionality has been produced by a trialkyl phosphite coupling in reasonable yield, see:
Ozturk, T.; Rice, C.R.; Wallis, J.D. *J. Mater Chem* **1995**, *5*, 1553.
(14) 6,7-Bis(bromomethyl)-2,3-bis(methylthio)tetrathiafulvalene is to our knowledge the only example of a tetrathiafulvalene bearing two vicinal bromomethyl groups, so far described in the literature. 6,7-Bis(bromomethyl)-2,3-bis(methylthio)-tetrathiafulvalene was prepared by treatment of the corresponding 6,7-bis(hydroxymethyl)-2,3-bis(methylthio)tetrathiafulvalene with phosphorus tribromide and have been used as a diene precursor in a [4+2] Diels–Alder cycloaddition with $C_{60}$, see:
Boulle, C.; Rabreau, J. M.; Hudhomme, P.; Cariou, M.; Jubault, M.; Gorgues, A.; Orduna, J.; Garin, J. *Tetrahedron Letters* **1997**, *38*, 3909.
(15) Richter, R.; Ulrich, H. *The Chemistry of Cyanates and Their Thio Derivatives*, Patai, S., Ed.; John Wiley & Sons: New York, 1977; Vol. 2, Chapter 17.
Breitenbach, J.; Boosfeld, J.; Vögtle, F. *Comprehensive Supramolecular Chemistry*, Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D., Vögtle, F.: Lehn, J.-L., Eds.; Pergamon: 1996, Vol. 2, Chapter 2.
(16) It was not possible to deprotect the cyanoethyl thiolate protecting groups in presence of the thiocyanatomethyl groups, using the standard deprotection technique (i.e. first treatment of **7** with 2.2 equivalents of $CsOH•H_2O$ followed by addition of MeI) nor by addition of 2.2 equivalents of $CsOH•H_2O$ to a mixture of **7** and MeI.
(17) Hudhomme, P.; Blanchard, P.; Sallé, M.; Moustarder, S. L.; Riou, A.; Jubault, M.; Gorgues, A.; Duguay, G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 878.
(18) Durand, C.; Hudhomme, P.; Duguay, G.; Jubault, M.; Gorgues, A. *J. Chem. Soc., Chem. Commun.* **1998**, 361.
(19) Attempt to deprotect the remaining two cyanoethyl thiolate protecting groups in **8d** followed by addition of iodomethane failed, probably due to the unstability of the disulfide moiety.
(20) It was not possible to isolate the bis-thiol [i.e $(RS)_2TTF(CH_2SH)_2$] by addition of excess $NaBH_4$ to **7** in THF/EtOH (2:1) followed by addition of deoxygenated water and pH adjustment (pH = 7).
(21) Fresh $NaBH_4$ should be used.
(22) The orange solid exclusively contains tetrakis(2-cyanoethylthio)tetrathiafulvalene (TLC and PDMS).
(23) If the organic phase darkens under aquous work up, the following procedure was applied. The organic phase was concentrated to approximately 50 mL and filtered through a short column (4 cm silica gel, 10 cm Ø). The column was first eluted with $CH_2Cl_2$ (300 mL). The first fraction contained a colourless impurity (TLC, $R_f$ 0.8, eluent EtOAc). Next the desired dialcohol **5** ($R_f$ 0.4, eluent EtOAc) was eluted with EtOAc until the solution was colourless (ca 2 L). This fraction contains trace of the above colourless impurity. Evaporation of the solvent in vacuo (T < 30 °C) gave a orange solid. Recrystallization from propan-2-ol (85 mL) gave the product **5** as thin orange needles with a slight decrease in the yield (81%).
(24) Compound **6** is unstable and darkens after a few days when exposed to air, and should be converted to **7** as rapidly as possible. **6** reacted fast with $H_2O$. $^1H$ NMR spectroscopy of **6**

in DMSO-$d_6$ showed that the $H_2O$ signal (which normally appears in spectra recorded in commercial DMSO-$d_6$) disappeared very fast.
(25) The calculated values are based on the exact mass for compound **6** and for the molecular mass for compound **7**.
(26) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(27) Sheldrick, G. M. *SHELXL97. Program for the Refinement of Crystal Structures*, 1997, University of Göttingen, Germany.
(28) Spek, A .L. *Acta Crystallogr.* **1990**, *A46*, C-34.
(29) Sheldrick, G. M. *SHELXTL. Structure Determination Programs. Version 5.10.*, 1997, Bruker (formerly Siemens) Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA.

Article Identifier:
1437-210X,E;1999,0,05,0803,0810,ftx,en;P04698SS.pdf