Supporting Information

A family of unsymmetrical hydroxyl-substituted BEDT-TTF donors: syntheses, structures and preliminary thin film studies

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Preparation of donor H1

6-Hydroxy-6,7-dihydro-5H-1,3-dithiolo[4,5-b]-1,4-dithiepine-2-thione (3)

Following a modified literature procedure.[1] 1,3-Dibromo-2-propanol (3.20 g, 95%, 14.0 mmol) was added to a solution of the tetraethylammonium salt of *bis*(2-thioxo-1,3-dithiolo-4,5-dithio)zincate salt (5.00 g, 7.00 mmol) in dry MeCN (60 mL), and the mixture refluxed under nitrogen for 16 h. After cooling to room temperature, the mixture was filtered and the yellow crystalline solid collected was dissolved in hot THF. The combined solution was decolourised by heating with active carbon for 10 min and filtered. The cold filtrate was concentrated and acetone was added to precipitate a solid which was collected, washed with DCM and dried *in vacuo* to give **3** as a bright yellow crystalline solid (2.46 g, 69%). δ_H (300 MHz, $(CD_3)_2SO$): 5.69 (1H, d, J = 4.8 Hz, O*H*), 4.05 (1H, m, 6-*H*), 3.04 (2H, dd, J = 14.1, 2.7 Hz, 5-,7-H_α), 2.66 (2H, dd, J = 14.1, 9.3 Hz, 5-,7-H_β); δ_C (75 MHz, $(CD_3)_2SO$): 210.67 (2-*C*), 140.36 (3a-,8a-*C*), 72.94 (6-*C*), 38.45 (5,7-*C*)).

6-Acetoxy-6,7-dihydro-5H-1,3-dithiolo[4,5-b]-1,4-dithiepine-2-thione (4)

Thione **3** (0.90 g, 3.78 mmol) was dissolved in dry pyridine (10ml) under nitrogen and cooled to 0°C. A solution of acetic anhydride (0.39 g, 3.78 mmol) in dry pyridine (5 ml) was added, and the mixture was stirred at RT for 24 h. DCM (50 ml) and water (30 ml) were added to the mixture, and the organic phase was separated and washed sequentially with HCl (1M) (3×80 ml), water (2×50 ml) and finally brine (50 ml). After drying over $MgSO_4$, removal of solvent afforded **4** as yellow solid (0.96 g, 91.6%), m.p. 143-145°C. δ_H (300 MHz, $CDCl_3$): 5.33 (1H, m, 6-*H*), 3.11 (2H, dd, J = 14.4, 2.7 Hz, 5-,7-H_α), 2.78 (2H, dd, J = 14.4, 9.3 Hz, 5-,7-H_β), 2.14 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 210.30 (2-*C*), 169.70 (*C*=O), 139.62 (3a-,8a-*C*), 74.11 (6-*C*), 36.29 (5-,7-*C*), 21.22 (*C*H_3); ν_{max} (cm^{-1}, KBr): 2108 (w), 1730 (vs), 1411 (w), 1363(m), 1319 (w), 1223 (vs), 1113 (w), 1066 (vs), 1012 (s), 962 (m), 901 (m), 862 9w), 824 (w), 602 (w), 503 (w), 459 (w); *m/z* (EI^+): 296 ($[M]^+$, 100%); *HRMS* (EI^+): found $[M]^+$ 295.91309, $C_8H_8O_2S_5$ requires 295.91279.

6-Acetoxy-6,7-dihydro-5H-1,3-dithiolo[4,5-b]-1,4-dithiepine-2-one (5)

Glacial acetic acid (15 ml) and then mercury(II) acetate (6.90 g, 22.0 mmol) were added to a solution of thione **4** (2.58 g, 8.71 mmol) in chloroform (30ml), and this was stirred overnight at room temperature. The mixture was filtered, water (40 ml) was added to the filtrate and the mixture neutralized with saturated $NaHCO_3$ solution. The organic layer was separated and dried over $MgSO_4$. Evaporation of solvent yielded **5** as a cream solid (1.70g, 69.6%), m.p. 112-114˚C. δ_H (300 MHz, $CDCl_3$): 5.31 (1H, m, 6-*C*), 3.04 (2H, dd, J = 14.4, 2.7 Hz, 5-,7-H_α), 2.78 (2H, dd, J = 14.4, 9.3 Hz, 5-,7-H_β), 2.13 (3H, s, CH_3); δ_C (75 MHz): 188.50 (2-*C*), 169.61 (CH_3CO), 129.92 (3a-,8a-*C*), 73.81 (6-*C*), 36.02 (5-,7-*C*), 21.31 (CH_3); ν_{max} (cm^{-1}, KBr): 2116 (w), 1738 (s), 1720 (sh), 1664 (vs), 1612 (s), 1421 (w), 1365 (s), 1321 (w), 1228 (vs), 1113 (m), 1014 (s), 959 (m), 891 (s), 825 (m), 754 (m), 729 (w), 642 (w), 600 (w), 548 (w), 496 (w), 465 (w); *m/z* (EI^+): 280 ($[M]^+$, 50%); *HRMS* (EI^+): found $[M]^+$ 279.93575, $C_8H_8O_3S_4$ requires 279.93564.

(2-Acetoxypropylene-1,3-dithio)(ethylenedithio)tetrathiafulvalene (7)

A suspension of oxo compound **5** (0.70 g, 2.50 mmol) and unsubstituted thione **6** (1.12 g, 5.00 mmol) in dry triethyl phosphite (5 ml) was heated to 90°C under nitrogen for 16 h. The mixture was cooled to room temperature and hexane (10 mL) was added to facilitate further precipitation. The solid was collected and washed with hexane (5 mL). The crude product was purified by flash chromatography on silica (hexane:CH_2Cl_2 1:2) to give first BEDT-TTF and then the title compound **7** as an orange-yellow solid (0.75g, 65.8%), m.p. 185-187˚C. δ_H (300 MHz, $CDCl_3$): 5.24 (1H, m, 2-*H*), 3.31 (4H, s, -5'-,6'-H_2), 2.96 (2H, dd, J = 13.7, 2.1Hz, 1-,3-H_α), 2.65 (2H, dd, J = 13.7, 9.9 Hz, 1-,3-H_β), 2.11 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$): 169.48 (C=O), 130.32, 113.79, 113.29 & 111.66 (6 x sp^2C), 77.22 (2-*C*), 36.04 (1-,3-*C*), 30.16 *(-*CH_2CH_2*-),* 21.06 (CH_3); ν_{max} (cm^{-1}, KBr): 2964 (w), 2920 (w), 1740 (s), 1417 (w), 1292 (w), 1230 (vs), 1109 (w), 1014 (m), 957 (w), 889 (w), 771 (w), 648 (w), 505 (w); *m/z*: (EI^+) 456 ($[M]^+$, 50%); *HRMS*: (EI) found $[M]^+$ 455.85995, $C_{13}H_{12}O_2S_8$ requires 455.86031. Further elution afforded the homo coupled *cis* and *trans* isomers of *bis*(2-acetoxypropylene-1,3-dithio)tetrathiafulvalene **8** as an orange solid (70 mg, 5.3%), m.p. 270-273 °C (dec); δ_H: (300 MHz, $CDCl_3$): 5.22 (m, 2H, 2-,2′-*H*), 2.94 (4H, dd, J = 14.4, 2.7 Hz, 1-,1′-,3-,3′-H_α), 2.66 (4H, m, 1-,1′-,3-,3′-H_β), 2.11 & 2.10 (6H, 2 × CH_3); δ_C: (75 MHz, $CDCl_3$): 169.60 & 169.49 (*C*=O, 2 isomers), 130.30 & 112.42 (6 ×

sp^2*C*), 79.91 (2-,2′-*C*), 36.12 & 36.00 (1-,1′-, 3-,3'-*C,* 2 isomers), 21.11 (2 × *C*H$_3$); ν_{max} (cm^{-1}, KBr): 2968 (w), 2920 (w), 1740 (vs), 1423 (w), 1403 (w), 1369 (m), 1232 (vs), 1111 (w), 1020 (s), 960 (m), 903 (m), 770 (w), 646 (w), 501 (w); *m/z*: (FAB$^+$) 528 ([M]$^+$, 100%); *HRMS*: (FAB) found [M]$^+$ 527.88348, $C_{16}H_{16}O_4S_8$ requires 527.88144.

Ethylenedithio)(2-hydroxypropylene-1,3 dithio) tetrathia-fulvalene (H1)

A solution of protected donor **7** (0.55 g, 1.21 mmol) in THF (30 mL) and 6M HCl solution (6.5 mL) was stirred under nitrogen for 40 h. The solution was neutralized by the addition of solid $NaHCO_3$. The organic layer was collected, washed with brine and dried over $MgSO_4$. Removal of solvent yielded **H1** as an orange-yellow solid (0.48 g, 96%), m.p. 227-230°C(dec). δ_H (600 MHz, DMSO-d$_6$): 5.62 (1H, d, *J* = 3.6 Hz, O*H*), 3.96 (1H, m, 2-*H*), 3.41 (4H, s, 5'-,6'--H_2), 2.96 (2H, dd, *J* =14.4, 2.4 Hz, 1-,3-H_α), 2.46 (2H, dd, *J* =13.2, 9.6 Hz, 1-,3-H_β); δ_C (150 MHz, DMSO-d$_6$): 129.88, 113.26, 109.18 (6 × sp^2-*C*), 73.50 (2-C), 38.58 (1-,3-C), 29.99 (-CH_2CH_2-); ν_{max} (cm^{-1}, KBr): 3547 (s), 3392 (w), 3313 (w), 2958 (w), 2910 (w), 1728 (w), 1645 (w), 1551 (w), 1412 (m), 1290 (w), 1165 (m), 1057 (w), 1013 (vs), 918 (w), 889 (m), 770 (m), 743 (m), 507 (w), 463 (w). *m/z*: (EI$^+$) 414 ([M]$^+$, 100%); *HRMS*: (EI) found [M]$^+$ 413.85016, $C_{11}H_{10}OS_8$ requires 413.84975. Elem. Anal. found C: 32.76, H: 2.50%; $C_{11}H_{10}OS_8$ requires C:31.88, H: 2.41%.

Preparation of donor H2

(4a*R*,7a*S*)-6,6-Bis(hydroxymethyl)-5,6,7,7a-tetrahydro-4aH-cyclopenta[b][1,3]dithiolo[4,5-e][1,4]dithiine-2-thione (10).

A suspension of trithione **9** (2.60 g, 13.3 mmol) and 3,3-bis(hydroxymethyl)cyclopent-1-ene(1.30 g, 10.2 mmol) in toluene (50 ml) was refluxed for 17 h under nitrogen. After cooling to room temperature the reaction mixture was filtered, and the solid residue was washed thoroughly with acetone/THF (1:1). Combined washings and filtrate were decolourised with active carbon by heating for 15 min. The mixture was filtered and the filtrate evaporated to yield a yellow solid, which was purified by chromatography on silica. Impurities were eluted with hexane:ethyl acetate (1:8), and then the product was eluted with THF/hexane (3:1). Recrystallization from THF/hexane gave **10** as a yellow solid (2.18 g, 66%), m.p.168-169°C; δ_H (300 MHz, DMSO-d$_6$): 4.69 (2H, t, *J* = 5.1Hz, 2 × O*H*), 4.10 (2H, m, 2 × 4a-,7a-*H*), 3.27 (4H, m, 2 × 6-CH_2OH), 2.00

(2H, m, 5-,7-H_α), & 1.70 (2H, m, 5-,7-H_β); δ_C (75 MHz, DMSO-d_6,): 210.01 (2-*C*), 133.10 (3a-,8a-*C*), 65.71 & 64.82 (2× 6-*C*H_2OH), 52.20 (4a-,7a-*C*), 49.74 (6-*C*), 37.46 (*C*H_2, 5-,7-*C*); ν_{max} (cm^{-1}, KBr): 3344 (s, sh), 3280 (vs, br), 2951 (sh), 2920 (m), 2870 (m), 1481 (m), 1429 (m), 1238 (w), 1213 (w), 1109 (w), 1055 (vs), 1026 (s), 905 (m), 797 (w), 721 (m), 675 (w), 588 (m), 513 (w), 478 (w), 449 (w); *m/z*: (FAB) 325 ($[M+H]^+$, 100%); *HRMS*: (FAB) found $[M]^+$ 323.94487, $C_{10}H_{12}O_2S_5$ requires 323.94409.

(4a*R*,7a*S*)-6,6-Bis(acetoxymethyl)-5,6,7,7a-tetrahydro-4aH-cyclopenta[b][1,3]dithiolo[4,5-e][1,4]dithiine-2-thione (11)

Thione **10** (1.40 g, 4.32 mmol) was dissolved in dry pyridine (15 ml) under nitrogen, the solution cooled to 0 °C, after which time a solution of acetic anhydride (0.88 g, 8.64 mmol) in dry pyridine (5 ml) was added and the mixture stirred at RT for 24 h under nitrogen. The mixture was partitioned between DCM (100 ml) and water (60 ml). The organic layer was separated and washed sequentially with HCl (1M) (3×60 ml) and water (2×80 ml), and dried over $MgSO_4$. Removal of solvent afforded **11** as a thick yellow oil which solidified upon storing at RT (2.67 g, 99.6%), m.p. 98-100°C. δ_H (300 MHz, $CDCl_3$): 4.08 (2H, s) & 3.98 (2H, s) (2 × 6–CH_2O), 3.94 (2H, m, 4a-,7a-*H*), 2.19 (2H, m, 5-,7-H_α), 2.11 (6H, s, 2 × CH_3), 1.93 (2H, m, 5-,7-H_β); δ_C (75 MHz, $CDCl_3$): 209.58 (2-*C*), 170.90 (2 × *C*=O), 132.91 (3a-,8a-*C*), 67.41 & 66.18 (2 × 6-*C*H_2O), 51.80 (4a-,7a-*C*), 45.89 (6-*C*), 38.21 (5-,7-*C*), 21.02 (2 × *C*H_3); ν_{max} (cm^{-1}, KBr): 2937 (m), 2885 (m), 1739 (vs), 1460 (m), 1435 (m), 1383 (s), 1362 (m), 1223 (vs), 1053 (vs), 920 (m), 887 (m), 787 (w), 638 (w), 602 (w), 528 (w), 507 (w), 422 (w); *m/z*: (FAB) 408 ($[M]^+$, 100%); *HRMS*: (FAB) found $[M]^+$ 407.96253, $C_{14}H_{16}O_4S_5$ requires 407.96522.

(4a*R*,7a*S*)-6,6-Bis(acetoxymethyl)-5,6,7,7a-tetrahydro-4aH-cyclopenta[b][1,3]dithiolo[4,5-e][1,4]dithiine-2-one (12)

Glacial acetic acid (13 ml) followed by mercury(II) acetate (4.94 g, 15.5 mmol) were added to a solution of thione **11** (2.53 g, 6.20 mmol) in chloroform (40 ml) and the mixture stirred for 3 hat RT. The mixture was filtered, water (50 ml) added to the filtrate and the mixture neutralized with saturated $NaHCO_3$ solution. The organic layer was separated and dried over $MgSO_4$. Removal of solvent yielded **12** as a light yellow oil which solidified upon storing at RT (2.10 g, 86%), m.p.

80-81˚C. δ_H (300 MHz, $CDCl_3$): 4.08 (2H, s) & 3.99 (2H, s) (2 × 6-CH_2O), 4.03 (2H, m, 4a-,7a-*H*), 2.21 (2H, m, 5-,7-H_α), 2.12 (6H, s, 2 × CH_3), 1.93 (2H, m, 5-,7-H_β); δ_C (75 MHz, $CDCl_3$): 189.61 (2-*C*), 170.89 (2 × *C*=O), 124.51 (3a-,8a-*C*), 67.38 & 66.01 (2 × *C*H_2O), 52.89 (4a-,7a-*C*), 45.90 (6-*C*), 38.21 (5-,7-*C*), 21.00 (2 ×*C*H_3); ν_{max} (cm^{-1}, KBr): 2958 (m), 2920 (w), 2858 (w), 1734 (vs), 1655 (s), 1610 (s), 1468 (m), 1375 (m), 1234 (vs), 1095 (w), 1040 (s), 903 (w), 881 (m), 800 (m), 746 (w), 675 (w), 638 (w), 550 (w), 498 (w); *m/z*: (EI^+) 392 ($[M]^+$, 30%); *HRMS*: (EI) found $[M]^+$ 391.98834, $C_{14}H_{16}O_5S_4$ requires 391.98806.

(*cis*-4,4-bis(acetoxymethyl)cyclopenta-1,2-dithio)(ethylene-dithio)-tetrathiafulvalene (13)

A suspension of oxo compound **12** (1.72 g, 4.40 mmol) and unsubstituted thione **6** (1.98 g, 8.80 mmol) in dry triethyl phosphite (6 mL) was heated to 90°C under nitrogen for 16 h. The mixture was cooled to RT and hexane (40 mL) was added to facilitate further precipitation. The solid was collected by filtration and washed with hexane (5 mL). The residue obtained was purified by a flash chromatography on silica eluting with CH_2Cl_2 to give **13** as an orange crystalline solid (1.31 g, 52.3%), m.p. 168-170 ˚C. δ_H (300 MHz, $CDCl_3$): 4.06 (2H, s), & 3.97 (2H, s) (2 × 4”-CH_2O), 3.92 (2H, m, 1”,2”-*H*),3.33 (4H, s, 5’-,6’-H_2), 2.15 (2H, m, 3”-,5”-H_α), 2.10 (3H, s) & 2.09 (3H, s) (2 × CH_3), 1.86 (2H, m, 3”-,5”-H_β); δ_C (75 MHz, $CDCl_3$): 171.01 (2 × *C*=O), 124.51, 113.78, 112.56 & 112.13 (6 x sp^2*C*), 67.40 & 65.88 (2 × 4”- *C*H_2O), 52.31 (1”-,2”-*C*), 46.18 (4”-*C*), 38.43 (3”-,5”-*C*), 30.15 (*5’-,6’-C*), 20.81 (2 ×*C*H_3); ν_{max} (cm^{-1}, KBr): 2947 (w), 2924 (w), 2854 (w), 1732 (vs), 1433 (w), 1367 (m), 1236 (vs), 1038 (s), 987 (w), 912 (w), 889 (w), 768 (w), 679 (w), 606 (w), 449 (w); *m/z*: (FAB) 568 ($[M]^+$, 100%); *HRMS*: (FAB) found $[M]^+$ 567.91530, $C_{19}H_{20}O_4S_8$ requires 567.91274.

(*cis*-4,4-Bis(hydroxymethyl)cyclopenta-1,2-dithio)(ethylene-dithio)tetrathiafulvalene (H2)

A solution of the *bis*(acetyl) protected donor **13** (1.17 g, 2.06 mmol) in THF (50 mL) and 6M HCl solution (22 mL) was stirred under N_2 for 43 h. THF (80 mL) was added and the mixture was neutralized by the addition of solid $NaHCO_3$. The organic layer was collected and dried over $MgSO_4$. The crude product was purified by chromatography on silica firstly eluted with THF: hexane (3:2) to remove side products, followed by THF to elute **H2**. Further product was obtained by thorough extraction of silica from the top of the column with THF, evaporation and

washing the solid with CH_2Cl_2. **H2** was obtained as a yellow solid. (0.65g, 65%), m.p: 211-213 °C (dec.). δ_H (600 MHz, DMSO-d_6): 4.67 (2H, s, 2 × O*H*), 4.01 (2H, m, 2 × 1",2"-*H*), 3.41 (4H, s, 5'-,6'-H_2), 3.28 (2H, s) & 3.25 (2H, s) (2 × 4"-CH_2O), 1.95 (2H, m, 3"-,5"-H_α), 1.61 (2H, m, 3"-,5"-H_β); δ_C (150 MHz): 123.01, 113.22, 111.70 & 111.38 (6 × sp^2*C*), 65.90 & 64.52 (2 × 4"-*C*H_2O), 52.14 (1"-,2"-*C*), 49.87 (4"-*C*), 37.74 (3"-,5"-*C*), 29.95 (5'-,6'-H_2); ν_{max} (cm^{-1}, KBr): 3305 (vs, br), 2918 (m), 2868 (m), 1645 (w), 1551 (w), 1439 (m), 1406 (m), 1284 (m), 1255 (w), 1198 (m), 1146 (w), 1088 (w), 1041 (vs), 1018 (vs), 908 (m), 771 (m), 679 (w), 577 (w), 473 (w); *m/z*: (FAB) 484 ($[M]^+$, 60%); *m/z*: (EI^+) 484 ($[M]^+$, 10%); *HRMS*: (EI) found $[M]^+$ 483.89134, $C_{15}H_{16}O_2S_8$ requires 483.89161; Elem. Anal. found C: 36.38, H: 3.13%; $C_{15}H_{16}O_2S_8.0.25CH_2Cl_2$ requires C: 36.22, H: 3.27%.

Preparation of donor H3

(+/-) (1'*R*,5*R*)- and (1'*R*,5*S*)-5-(1'-Hydroxybutyl)-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (14)

A suspension of trithione **9** (2.50 g, 12.7mmol) and (+/-)-hex-1-en-3-ol (2.10 g, 21.0 mmol) in toluene (80 ml) was refluxed for 24 h under nitrogen. After cooling to RT the reaction mixture was filtered, and the dark residue was washed with DCM and acetone. Combined washings and filtrate were decolourised with active carbon by heating for 15 min, the mixture filtered and the filtrate concentrated to give a dark oil residue. The residue was purified by flash chromatography on silica (hexane:ethyl acetate 3:1) to furnish **14** as a thick yellow oil (2.66 g, 71%). ^{1}H NMR showed the product was a mixture of diastereomers with estimated ratio 65:35. δ_H (300 MHz, $CDCl_3$): 3.92 (1H, m, 1'-C*H*), 3.77 (0.35H, m, 5-*H*), 3.62 (0.65H, m, 5-*H*), 3.43-3.27 (2H, m, 6-H_2), 2.08 (0.35H, d, *J* = 5.3Hz, O*H*), 2.01 (0.65H, d, *J* = 5.3Hz, O*H*), 1.80-1.50 (4H, m, 2'-,3'-H_2), 1.00 (0.65×3H, t, *J* = 7.1Hz, CH_3), 0.99 (0.35×3H, t, *J* = 7.1 Hz, CH_3). *m/z*: (FAB) 297 ($[M+H]^+$, 100%). *HRMS*: (FAB) found $[M]^+$ 295.94457, $C_9H_{12}OS_5$ requires 295.94918.

(+/-) (1'*R*,5*R*)- and (1'*R*,5*S*)-5-(1'-acetoxybutyl)-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (15)

Thione **14** (2.12 g, 7.16 mmol) was dissolved in dry pyridine (20 ml) and the solution was cooled to 0 °C. A solution of acetic anhydride (0.94 g, 9.20 mmol) in dry pyridine (5 ml) was added, and the mixture was heated at 70 °C for 24 h under nitrogen. Afternoon cooling to RT, water (50 ml)

was added to the mixture, and it was extracted with DCM (3×40 ml). The organic phase was separated and washed sequentially with HCl (1M) (3×60ml) and water (2×50 ml), and dried over $MgSO_4$. Removal of the solvent afforded **15** as a dark brown oil (2.09 g, 86.4%). ^{1}H NMR showed the product was a mixture of diastereomers with estimated ratio 65:35. δ_H (300 MHz, $CDCl_3$): 5.25 (0.35H, q, *J* = 6.2Hz, 1'-*H*), 5.17 (0.65H q, *J* = 6.2Hz, 1'-*H*), 3.83 (1H, m, 5-*H*), 3.35 (1H, m, 6-H_α), 3.20 (1H, m, 6-H_β), 2.11 (3H, s, CH_3CO), 1.70 (2H, m, 2'-H_2), 1.37 (2H m, 3'-H_2), 0.95 (3H, t, *J* = 7.3Hz, 4'-H_3); δ_C (75 MHz, $CDCl_3$): 208.10 & 208.00 (*C*=S), 170.27 & 170.14 (*C*=O), 124.51, 124.05, 123.36 & 123.13 (3a-,7a-*C,* 2 isomers), 73.31 & 73.25 (1′-*C*), 48.68 & 47.95 (5-*C*), 33.76 (2′-CH_2), 32.27& 31.40 (6-*C*), 20.89 (CH_3CO), 18.52 & 18.34 (3'-CH_2), 13.84 & 13.78 (4′-CH_3); ν_{max} (cm^{-1}, neat): 2958 (m), 2932 (m), 2871 (w), 1741 (s), 1490 (m), 1462 (w), 1427 (w), 1371 (m), 1227 (s), 1118 (w), 1063 (vs), 1024 (s), 949 (w), 892 (w), 833 (w), 786 (w), 740 (w), 606 (w), 514 (w), 446 (w); *m/z*: (EI$^+$) 338 ([M]$^+$, 30%); *HRMS* (EI) found [M] $^+$ 337.95912, $C_{11}H_{14}O_2S_5$ requires 337.95974.

(+/-) (1'*R*,5*R*)- and (1'*R*,5*S*)-5-(1'-Acetoxybutyl)-[1,3]dithiolo [4,5-*b*][1,4]dithiin -2-one (16)

Glacial acetic acid (6 ml) followed by mercury(II) acetate (4.70 g, 14.8 mmol) were added to a solution of thione **15** (2.00 g, 5.91 mmol) in chloroform (30 ml). The mixture was stirred for 3 h at RT and then filtered. Water (40 ml) was added to the filtrate, the mixture was neutralized with saturated $NaHCO_3$ solution, and the organic layer separated and dried over $MgSO_4$. Removal of solvent yielded **16** as a yellow oil (1.62 g, 85%). ^{1}H NMR showed the product was a mixture of diastereomers with estimated ratios of 65:35. δ_H (300 MHz, $CDCl_3$): 5.27 (0.35H, q, *J* = 6.2Hz, 1'-*H*), 5.20 (0.65H, q, *J* = 6.2Hz, 1'-*H*), 3.88 (1H, m, 5-*H*), 3.41 (1H, m, 6-H_α), 3.20 (1H, m, 6-H_β), 2.12 (3H, s, CH_3CO), 1.69 (2H, m, 2'-H_2), 1.38 (2H, m, 3′-H_2), 0.95 (3H, t, *J*=7.3Hz, 4′-H_3); δ_C (75 MHz, $CDCl_3$): 188.87 & 188.78 (2-*C*), 170.28 & 170.15 (O=*C*Me), 115.14,114.78,114.21 & 114.00 (3a-,7a-*C*, 2 isomers), 73.53 & 73.44 (1'-*C*), 50.36 & 49.72 (5-*C*), 33.76 & 33.41 (2'-CH_2), 32.49 (6-*C*), 20.87 (CH_3CO), 18.52 & 18.31 (3′-CH_2), 13.81 & 13.76 (4′-H_3); ν_{max} (cm^{-1}, neat): 2960 (m), 2934 (m), 2872 (w), 1743 (s), 1680 (s), 1631 (m), 1510 (w), 1429 (w), 1372 (m), 1227 (s), 1119 (w), 1024 (m), 949 (w), 892 (m), 833 (w), 767 (w), 606 (w), 554 (w), 465 (w); *m/z*: (EI$^+$) 322 ([M] $^+$, 50%); *HRMS*: (EI) found [M] $^+$ 321.98271, $C_{11}H_{14}O_3S_4$ requires 321.98259.

(+/-) (1''*R*,5*R*)- and (1''*R*,5*S*) (1''-Acetoxybutyl) *bis*(ethylenedithio)tetrathiafulvalene (17)

A suspension of oxo compound **16** (1.54 g, 4.78 mmol) and unsubstituted thione **6** (2.13 g, 9.56 mmol) in dry triethyl phosphite (7 ml) was heated to 90 ^{o}C under nitrogen for 24 h. The mixture was cooled to RT and triethyl phosphite was removed by distillation under reduced pressure. The residue was purified by flash chromatography on silica (hexane:DCM 1:1) to give **17** as an orange solid (1.34 g, 56 %). ^{1}H NMR showed the product was a mixture of diastereomers with estimated ratio 65:35. m.p. 78-80°C; δ_{H} (300 MHz, $CDCl_3$): 5.20 (0.35H, q, J = 6.1 Hz, 1′′-*H*), 5.15 (0.65H, q, J = 6.1 Hz, , 1′′-*H*), 3.79 (1H, m, 5-*H*), 3.31 (4H, s, 5′-,6′-H_2), 3.20 (1H, m, 6-H_α), 3.08 (1H, m, 6-H_β), 2.11 (3H, s, CH_3CO), 1.73 (2H, m, 2′′-H_2), 1.37 (2H, m, 3′′-H_2), 0.96 (3H, t, J = 7.3Hz, 4''-H_3); δ_{C} (75 MHz): 170.34 & 170.18 (*C*=O), 115.60, 115.22, 114.99 & 113.84 (6 x sp^2*C*), 73.68 & 73.63 (1′′-*C*), 49.49 & 48.78 (5-*C*), 33.89 & 33.81 (2′′-*C*), 32.95 & 32.22 (6-*C*), 30.20 (5′-,6′-*C*), 20.94 (*C*H_3CO), 18.57 & 18.36 (3′′-*C*), 13.84 & 13.79 (4′′-*C*); ν_{max} (cm^{-1}, KBr): 2954 (w), 2922 (w), 2866 (w), 1738 (s), 1458 (w), 1410 (w), 1367 (m), 1227 (vs), 1120 (w), 1020 (m), 887 (w), 770 (m), 635 (w), 606 (w), 490 (w); *m/z*: (FAB$^+$) 498 ([M]$^+$, 100%); *HRMS*: (FAB) found [M]$^+$ 497.90754, $C_{16}H_{18}O_2S_8$ requires 497.90726.

(+/-) (1''*R*,5*R*)- and (1''*R*,5*S*)-(1''-Hydroxybutyl) *bis*(ethylenedithio)tetrathiafulvalene (H3)

A solution of ester **17** (1.30 g, 2.61 mmol) in THF (30 mL) and 6M HCl solution (16 mL) was stirred under nitrogen for 40 h. The solution was neutralized by the addition of solid $NaHCO_3$. The organic layer was collected, washed with brine and dried over $MgSO_4$. Removal of solvent yielded a sticky residue, which was purified by flash chromatography on silica (hexane:CH_2Cl_2 1:1) to afford a sticky orange solid. Recrystallisation from CH_2Cl_2/hexane gave **H3** as an orange solid (0.77g, 65%), m.p: 101-103 $^{\circ}$C; ^{1}H NMR showed the product was a mixture of diastereomers with estimated ratio 4:1. δ_{H} (300 MHz, $CDCl_3$): 3.85 (1H, m, 1′′-H), 3.67 (0.2H, m, 5-*H*), 3.54 (0.8H, m, 5-*H*), 3.29 (4H, m, 5′-,6,6′-H_2), 2.11 (0.2H, d, J = 5.4Hz, O*H*), 2.00 (0.8H, d, J = 3.6 Hz, O*H*), 1.58 (4H, m, 2′′-,3′′-H_2), 0.95 (3H, t, J = 7.0 Hz, 4′-H_3); δ_{C} (75 MHz, $CDCl_3$): 115.05, 114.35, 113.87, 111.89 (6 × sp^2*C*), 72.41 & 72.25 (1′′-*C*), 52.77 & 50.25 (5-*C*), 36.76 & 36.56 (2′′-*C*), 33.18 & 31.54 (6-*C*), 30.20 (5′-,6′-*C*), 18.92 & 18.83 (3′′-*C*), 13.97 & 13.95 (4′′-*C*); ν_{max} (cm^{-1}, KBr): 3402 (br), 3334 (br, sh), 2951 (s), 2918 (s), 2864 (m), 1655

(w), 1514 (w), 1456 (w), 1408 (m), 1282 (m), 1223 (w), 1115 (m), 1066 (m), 1020 (m), 1003 (m), 908 (s), 847 (w), 770 (s), 592 (w), 503 (w), 449 (w); *m/z*: (FAB) 456 ($[M]^+$, 100%); Elem. Anal. Found C: 36.89, H: 3.54%; $C_{14}H_{16}OS_8$ requires C: 36.84, H: 3.51%.

S2 – Tables of Bond Lengths and Angles

Selected bond lengths and angles for (H1)

Bond	Length (Å)	Bond	Length (Å)
S(1)-C(3)	1.745(2)	S(1)-C(1)	1.809(3)
S(2)-C(4)	1.752(2)	S(2)-C(2)	1.806(3)
S(3)-C(5)	1.758(2)	S(3)-C(3)	1.761(2)
S(4)-C(5)	1.7607(19)	S(4)-C(4)	1.776(2)
S(5)-C(6)	1.7571(19)	S(5)-C(7)	1.7609(19)
S(6)-C(6)	1.7578(19)	S(6)-C(8)	1.7611(19)
S(7)-C(7)	1.7492(19)	S(7)-C(9)	1.817(3)
S(8)-C(8)	1.7489(19)	S(8)-C(11)	1.821(2)
S(21)-C(23)	1.744(2)	S(21)-C(21A)	1.793(6)
S(21)-C(21)	1.794(3)	S(22)-C(24)	1.752(2)
S(22)-C(22A)	1.787(6)	S(22)-C(22)	1.798(3)
S(23)-C(25)	1.7483(19)	S(23)-C(23)	1.762(2)
S(24)-C(25)	1.7599(19)	S(24)-C(24)	1.762(2)
S(25)-C(27)	1.760(2)	S(25)-C(26)	1.7638(18)
S(26)-C(26)	1.7543(19)	S(26)-C(28)	1.7657(19)
S(27)-C(27)	1.7496(19)	S(27)-C(29)	1.812(2)
S(28)-C(28)	1.751(2)	S(28)-C(31)	1.816(2)
O(1)-C(10)	1.421(3)	O(2)-C(30)	1.415(2)
C(1)-C(2)	1.517(5)	C(3)-C(4)	1.345(3)
C(5)-C(6)	1.345(3)	C(7)-C(8)	1.341(3)
C(9)-C(10)	1.524(4)	C(10)-C(11)	1.522(3)
C(21)-C(22)	1.514(4)	C(21A)-C(22A)	1.513(7)
C(23)-C(24)	1.347(3)	C(25)-C(26)	1.347(3)
C(27)-C(28)	1.350(3)	C(29)-C(30)	1.519(3)
C(30)-C(31)	1.525(3)		
Bond	**Angle (°)**	**Bond**	**Angle (°)**

C(3)-S(1)-C(1)	102.87(13)	C(3)-S(1)-C(1A)	96.9(5)
C(1)-S(1)-C(1A)	29.2(4)	C(4)-S(2)-C(2)	97.91(13)
C(4)-S(2)-C(2A)	102.6(4)	C(2)-S(2)-C(2A)	21.7(4)
C(5)-S(3)-C(3)	93.59(9)	C(5)-S(4)-C(4)	92.95(9)
C(6)-S(5)-C(7)	94.42(9)	C(6)-S(6)-C(8)	94.21(9)
C(7)-S(7)-C(9)	103.41(11)	C(8)-S(8)-C(11)	103.68(11)
C(23)-S(21)-C(21A)	98.0(6)	C(23)-S(21)-C(21)	101.41(11)
C(21A)-S(21)-C(21)	29.2(5)	C(24)-S(22)-C(22A)	101.9(6)
C(24)-S(22)-C(22)	101.07(12)	C(22A)-S(22)-C(22)	24.4(5)
C(25)-S(23)-C(23)	93.97(9)	C(25)-S(24)-C(24)	94.05(9)
C(27)-S(25)-C(26)	94.33(9)	C(26)-S(26)-C(28)	94.17(9)
C(27)-S(27)-C(29)	103.44(9)	C(28)-S(28)-C(31)	103.74(9)
C(2)-C(1)-S(1)	114.0(3)	C(1)-C(2)-S(2)	114.0(3)
C(4)-C(3)-S(1)	130.01(16)	C(4)-C(3)-S(3)	116.69(15)
S(1)-C(3)-S(3)	113.04(12)	C(3)-C(4)-S(2)	126.87(16)
C(3)-C(4)-S(4)	117.06(15)	S(2)-C(4)-S(4)	115.56(12)
C(6)-C(5)-S(3)	120.86(15)	C(6)-C(5)-S(4)	125.55(15)
S(3)-C(5)-S(4)	113.58(10)	C(5)-C(6)-S(5)	121.03(15)
C(5)-C(6)-S(6)	125.08(15)	S(5)-C(6)-S(6)	113.79(10)
C(8)-C(7)-S(7)	127.11(15)	C(8)-C(7)-S(5)	116.66(14)
S(7)-C(7)-S(5)	116.15(11)	C(7)-C(8)-S(8)	125.79(15)
C(7)-C(8)-S(6)	117.47(14)	S(8)-C(8)-S(6)	116.74(11)
C(10)-C(9)-S(7)	116.54(16)	O(1)-C(10)-C(11)	112.0(2)
O(1)-C(10)-C(9)	109.0(2)	C(11)-C(10)-C(9)	115.09(18)
C(10)-C(11)-S(8)	116.91(17)	C(22)-C(21)-S(21)	114.0(2)
C(21)-C(22)-S(22)	114.5(2)	C(22A)-C(21A)-S(21)	115.2(10)
C(21A)-C(22A)-S(22)	110.7(9)	C(24)-C(23)-S(21)	129.02(15)
C(24)-C(23)-S(23)	117.41(15)	S(21)-C(23)-S(23)	113.52(11)
C(23)-C(24)-S(22)	128.20(16)	C(23)-C(24)-S(24)	116.72(15)
S(22)-C(24)-S(24)	114.98(11)	C(26)-C(25)-S(23)	122.73(15)
C(26)-C(25)-S(24)	122.79(15)	S(23)-C(25)-S(24)	114.47(11)
C(25)-C(26)-S(26)	123.34(14)	C(25)-C(26)-S(25)	123.34(15)
S(26)-C(26)-S(25)	113.30(10)	C(28)-C(27)-S(27)	126.82(15)
C(28)-C(27)-S(25)	116.76(15)	S(27)-C(27)-S(25)	116.42(11)

C(27)-C(28)-S(28)	126.35(15)	C(27)-C(28)-S(26)	116.78(15)
S(28)-C(28)-S(26)	116.87(11)	C(30)-C(29)-S(27)	116.72(14)
O(2)-C(30)-C(29)	110.00(16)	O(2)-C(30)-C(31)	112.22(16)
C(29)-C(30)-C(31)	114.90(17)	C(30)-C(31)-S(28)	117.66(14)
C(2A)-C(1A)-S(1)	110.6(8)	C(1A)-C(2A)-S(2)	117.6(8)

Selected bond lengths and angles for (H2)

Bond	**Length (Å)**	**Bond**	**Length (Å)**
S1-C1	1.798(9)	O1-H1	0.90(5)
S1-C3	1.747(8)	O2-H2	0.91(6)
S2-C2	1.801(9)	C1-C2	1.515(13)
S2-C4	1.739(8)	C3-C4	1.354(11)
S3-C3	1.761(8)	C5-C6	1.338(10)
S3-C5	1.760(8)	C7-C8	1.337(11)
S3-C5	1.760(8)	C9-C11	1.526(10)
S4-C5	1.756(8)	C9-C10	1.535(10)
S5-C6	1.758(8)	C10-C12	1.547(10)
S5-C7	1.756(8)	C11-C13	1.555(11)
S6-C6	1.756(8)	C11-C13	1.555(11)
S6-C8	1.769(7)	C13-C15	1.522(10)
S7-C7	1.750(7)	C13-C14	1.522(11)
S7-C9	1.854(8)	O1-C14	1.424(9)
S8-C8	1.738(8)	O2-C15	1.444(9)
S8-C10	1.819(7)		
Bond	**Angle (°)**	**Bond**	**Angle (°)**
C1-S1-C3	102.0(4)	S6-C8-C7	116.4(6)
C2-S2-C4	99.6(4)	S8-C8-C7	122.6(6)
C3-S3-C5	94.7(4)	S7-C9-C10	116.1(5)
C4-S4-C5	95.1(4)	C10-C9-C11	105.3(6)
C6-S5-C7	93.6(3)	S7-C9-C11	110.1(5)
C6-S6-C8	94.0(4)	S8-C10-C12	108.5(5)
C7-S7-C9	103.6(3)	C9-C10-C12	104.3(6)
C8 -S8-C10	96.9(4)	S8-C10-C9	114.0(5)

C14-O1-H1	121(6)	C9-C11-C13	103.8(5)
C15-O2-H2	113(6)	C10-C12-C13	108.1(6)
S1-C1-C2	113.9(6)	C11-C13-C12	103.8(6)
S2-C2-C1	112.3(7)	C12-C13-C14	109.0(6)
S3-C3-C4	117.3(6)	C12-C13-C15	112.5(6)
S1-C3-S3	114.4(4)	C14-C13-C15	111.3(6)
S1-C3-C4	128.3(6)	C11-C13-C15	110.0(6)
S4-C4-C3	116.5(6)	C11-C13-C14	110.0(6)
S2-C4-C3	128.3(6)	O1-C14-C13	114.1(6)
S2-C4-S4	115.0(4)	O2-C15-C13	110.9(6)
S3-C5-C6	122.8(6)	S5 -C6-C5	123.0(6)
S4-C5-C6	123.2(6)	S7-C7-C8	123.6(6)
S3-C5-S4	113.9(4)	S5 -C7-S7	118.0(4)
S6-C6-C5	122.3(6)	S5 -C7-C8	118.4(6)
S5-C6-S6	114.6(4)	S6 -C8-S8	120.5(5)

Selected bond lengths and angles for (13)

Bond	**Length (Å)**	**Bond**	**Length (Å)**
S(1)-C(3)	1.7528(15)	S(1)-C(1)	1.8071(16)
S(2)-C(4)	1.7482(15)	S(2)-C(2)	1.8081(17)
S(3)-C(5)	1.7559(15)	S(3)-C(3)	1.7654(15)
S(4)-C(5)	1.7534(15)	S(4)-C(4)	1.7584(15)
S(5)-C(7A)	1.67(3)	S(5)-C(7)	1.7544(17)
S(5)-C(6)	1.7639(15)	S(6)-C(8)	1.7485(16)
S(6)-C(6)	1.7647(15)	S(6)-C(8A)	1.79(3)
S(7)-C(7)	1.7420(17)	S(7)-C(9)	1.8418(17)
S(8)-C(8)	1.7385(17)	S(8)-C(10)	1.8396(17)
O(1)-C(15)	1.3446(19)	O(1)-C(14)	1.458(2)
O(2)-C(15)	1.203(2)	O(3)-C(18)	1.3404(19)
O(3)-C(17)	1.4476(19)	O(4)-C(18)	1.203(2)
C(1)-C(2)	1.519(2)	C(3)-C(4)	1.345(2)
C(5)-C(6)	1.348(2)	C(7)-C(8)	1.345(2)
C(9)-C(11)	1.547(2)	C(9)-C(10)	1.549(2)

C(10)-C(13)	1.554(2)	C(11)-C(12)	1.539(2)
C(11)-C(9A)	1.69(3)	C(12)-C(14)	1.522(2)
C(12)-C(17)	1.524(2)	C(12)-C(13)	1.548(2)
C(13)-C(10A)	1.67(3)	C(15)-C(16)	1.496(2)
C(18)-C(19)	1.497(2)	S(7A)-C(7A)	1.79(3)
S(7A)-C(9A)	1.80(3)	S(8A)-C(8A)	1.75(3)
S(8A)-C(10A)	1.76(3)	C(7A)-C(8A)	1.34(5)
C(9A)-C(10A)	1.61(4)		
Bond	**Angle (°)**	**Bond**	**Angle (°)**
C(3)-S(1)-C(1)	102.11(7)	C(4)-S(2)-C(2)	99.20(7)
C(5)-S(3)-C(3)	95.10(7)	C(5)-S(4)-C(4)	94.93(7)
C(7A)-S(5)-C(7)	18.4(10)	C(7A)-S(5)-C(6)	95.2(11)
C(7)-S(5)-C(6)	94.07(7)	C(8)-S(6)-C(6)	94.36(7)
C(8)-S(6)-C(8A)	17.8(10)	C(6)-S(6)-C(8A)	91.8(11)
C(7)-S(7)-C(9)	99.30(8)	C(8)-S(8)-C(10)	100.94(8)
C(15)-O(1)-C(14)	115.10(13)	C(18)-O(3)-C(17)	116.04(13)
C(2)-C(1)-S(1)	113.70(11)	C(1)-C(2)-S(2)	112.05(11)
C(4)-C(3)-S(1)	128.67(12)	C(4)-C(3)-S(3)	116.84(11)
S(1)-C(3)-S(3)	114.47(8)	C(3)-C(4)-S(2)	128.14(12)
C(3)-C(4)-S(4)	117.85(11)	S(2)-C(4)-S(4)	114.00(9)
C(6)-C(5)-S(4)	122.43(12)	C(6)-C(5)-S(3)	122.29(12)
S(4)-C(5)-S(3)	115.25(8)	C(5)-C(6)-S(5)	122.92(12)
C(5)-C(6)-S(6)	121.69(12)	S(5)-C(6)-S(6)	115.23(8)
C(8)-C(7)-S(7)	121.99(13)	C(8)-C(7)-S(5)	117.79(13)
S(7)-C(7)-S(5)	120.16(10)	C(7)-C(8)-S(8)	121.24(13)
C(7)-C(8)-S(6)	117.79(13)	S(8)-C(8)-S(6)	120.95(10)
C(11)-C(9)-C(10)	105.65(13)	C(11)-C(9)-S(7)	108.92(11)
C(10)-C(9)-S(7)	115.54(11)	C(9)-C(10)-C(13)	106.29(13)
C(9)-C(10)-S(8)	116.65(11)	C(13)-C(10)-S(8)	107.66(11)
C(12)-C(11)-C(9)	106.95(13)	C(12)-C(11)-C(9A)	89.8(9)
C(9)-C(11)-C(9A)	40.0(9)	C(14)-C(12)-C(17)	112.52(14)
C(14)-C(12)-C(11)	112.64(13)	C(17)-C(12)-C(11)	112.36(13)
C(14)-C(12)-C(13)	107.27(13)	C(17)-C(12)-C(13)	109.01(13)
C(11)-C(12)-C(13)	102.36(13)	C(12)-C(13)-C(10)	106.99(13)

C(12)-C(13)-C(10A)	88.1(9)	C(10)-C(13)-C(10A)	40.2(9)
O(1)-C(14)-C(12)	109.41(13)	O(2)-C(15)-O(1)	122.88(16)
O(2)-C(15)-C(16)	124.94(16)	O(1)-C(15)-C(16)	112.17(14)
O(3)-C(17)-C(12)	109.09(13)	O(4)-C(18)-O(3)	123.55(15)
O(4)-C(18)-C(19)	125.87(15)	O(3)-C(18)-C(19)	110.57(14)
C(7A)-S(7A)-C(9A)	98.4(13)	C(8A)-S(8A)-C(10A)	100.7(14)
C(8A)-C(7A)-S(5)	119(3)	C(8A)-C(7A)-S(7A)	121(2)
S(5)-C(7A)-S(7A)	119.7(19)	C(7A)-C(8A)-S(8A)	122(2)
C(7A)-C(8A)-S(6)	118(2)	S(8A)-C(8A)-S(6)	120.2(18)
C(10A)-C(9A)-C(11)	100.8(16)	C(10A)-C(9A)-S(7A)	116.1(17)
C(11)-C(9A)-S(7A)	98.7(13)	C(9A)-C(10A)-C(13)	106.6(17)
C(9A)-C(10A)-S(8A)	116.1(17)	C(13)-C(10A)-S(8A)	98.9(13)

Selected bond lengths and angles for (18)

Bond	**Length (Å)**	**Bond**	**Length (Å)**
S(11)-C(14)	1.747(10)	S(11)-C(13)	1.809(16)
S(12)-C(15)	1.746(10)	S(12)-C(11)	1.813(11)
S(13)-C(16)	1.721(9)	S(13)-C(14)	1.732(11)
S(14)-C(16)	1.713(9)	S(14)-C(15)	1.735(9)
S(15)-C(17)	1.727(9)	S(15)-C(18)	1.742(9)
S(16)-C(17)	1.728(9)	S(16)-C(19)	1.737(9)
S(17)-C(18)	1.739(9)	S(17)-C(21)	1.790(12)
S(18)-C(19)	1.731(10)	S(18)-C(20)	1.877(15)
O(1)-C(12)	1.380(17)	O(1)-H(1)	0.8200
C(11)-C(12)	1.533(15)	C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700	C(12)-C(13)	1.508(18)
C(12)-H(12)	0.9800	C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700	C(14)-C(15)	1.361(13)
C(16)-C(17)	1.387(14)	C(18)-C(19)	1.359(13)
C(20)-C(21)	1.423(19)	C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700	C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700	I(1)-I(1)#1	2.8377(18)
I(3A)-I(3A)#2	2.951(10)	I(3B)-I(4)	2.833(7)

I(3C)-I(4)#2	2.587(8)	I(3D)-I(4)	2.625(13)
I(3D)-I(3D)#2	3.14(2)	I(4)-I(4)#3	2.016(10)
I(4)-I(3C)#2	2.587(8)		
Bond	**Angle (°)**	**Bond**	**Angle (°)**
C(14)-S(11)-C(13)	101.1(6)	C(15)-S(12)-C(11)	101.7(5)
C(16)-S(13)-C(14)	95.3(5)	C(16)-S(14)-C(15)	96.1(5)
C(17)-S(15)-C(18)	96.1(4)	C(17)-S(16)-C(19)	95.8(4)
C(18)-S(17)-C(21)	101.2(5)	C(19)-S(18)-C(20)	98.0(6)
C(12)-O(1)-H(1)	109.5	C(12)-C(11)-S(12)	116.0(8)
C(12)-C(11)-H(11A)	108.3	S(12)-C(11)-H(11A)	108.3
C(12)-C(11)-H(11B)	108.3	S(12)-C(11)-H(11B)	108.3
H(11A)-C(11)-H(11B)	107.4	O(1)-C(12)-C(13)	108.8(12)
O(1)-C(12)-C(11)	110.1(12)	C(13)-C(12)-C(11)	112.9(10)
O(1)-C(12)-H(12)	108.3	C(13)-C(12)-H(12)	108.3
C(11)-C(12)-H(12)	108.3	C(12)-C(13)-S(11)	116.0(11)
C(12)-C(13)-H(13A)	108.3	S(11)-C(13)-H(13A)	108.3
C(12)-C(13)-H(13B)	108.3	S(11)-C(13)-H(13B)	108.3
H(13A)-C(13)-H(13B)	107.4	C(15)-C(14)-S(13)	117.2(8)
C(15)-C(14)-S(11)	126.3(8)	S(13)-C(14)-S(11)	116.4(6)
C(14)-C(15)-S(14)	115.7(8)	C(14)-C(15)-S(12)	125.7(8)
S(14)-C(15)-S(12)	118.6(5)	C(17)-C(16)-S(14)	122.9(7)
C(17)-C(16)-S(13)	121.4(7)	S(14)-C(16)-S(13)	115.7(6)
C(16)-C(17)-S(15)	122.6(7)	C(16)-C(17)-S(16)	122.4(7)
S(15)-C(17)-S(16)	115.0(6)	C(19)-C(18)-S(17)	129.9(8)
C(19)-C(18)-S(15)	116.1(7)	S(17)-C(18)-S(15)	113.9(5)
C(18)-C(19)-S(18)	127.2(7)	C(18)-C(19)-S(16)	117.0(7)
S(18)-C(19)-S(16)	115.8(5)	C(21)-C(20)-S(18)	112.3(11)
C(21)-C(20)-H(20A)	109.1	S(18)-C(20)-H(20A)	109.1
C(21)-C(20)-H(20B)	109.1	S(18)-C(20)-H(20B)	109.1
H(20A)-C(20)-H(20B)	107.9	C(20)-C(21)-S(17)	118.8(10)
C(20)-C(21)-H(21A)	107.6	S(17)-C(21)-H(21A)	107.6
C(20)-C(21)-H(21B)	107.6	S(17)-C(21)-H(21B)	107.6
H(21A)-C(21)-H(21B)	107.1	I(4)-I(3D)-I(3D)#2	86.2(5)
I(4)#3-I(4)-I(3C)#2	155.8(3)	I(4)#3-I(4)-I(3D)	137.4(4)

I(4)#3-I(4)-I(3B)	126.8(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x,-y+1,-z #3 -x+1,-y+1,-z

Selected bond lengths and angles for (19)

Bond	Length (Å)	Bond	Length (Å)
I(1)-C(12)#1	2.56(2)	I(1)-I(2)	2.9028(17)
I(2)-I(3)	2.9187(17)	I(4)-I(7)	1.053(18)
I(4)-I(5)	2.906(7)	I(4)-I(5)#2	2.906(7)
I(6)-I(7)	2.56(4)	I(6)-I(8)#2	2.68(4)
I(6)-I(8)	2.68(4)	I(5)-I(9)	1.54(3)
I(5)-I(9)#3	2.36(3)	I(5)-I(5)#3	2.993(12)
I(8)-I(8)#2	1.84(6)	I(9)-I(5)#3	2.36(3)
I(9)-I(9)#3	2.63(6)	S(12)-C(2)	1.75(2)
S(12)-C(4)	1.757(14)	S(11)-C(3)	1.733(15)
S(11)-C(1)	1.81(3)	C(1)-C(2)	1.46(3)
C(1)-C(13)	1.498(10)	C(1)-H(1)	1.0000
C(2)-C(14)	1.499(10)	C(2)-H(2)	1.0000
C(13)-O(14)	1.381(10)	C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900	O(14)-O(14)#4	1.3(2)
C(14)-O(15)	1.381(10)	C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900	S(13)-C(5)	1.715(14)
S(13)-C(3)	1.745(15)	S(14)-C(5)	1.733(13)
S(14)-C(4)	1.746(15)	S(15)-C(6)	1.717(12)
S(15)-C(7)	1.751(16)	S(16)-C(6)	1.723(13)
S(16)-C(8)	1.737(15)	C(3)-C(4)	1.324(18)
C(5)-C(6)	1.373(19)	C(7)-C(8)	1.34(2)
C(7)-S(17)	1.753(15)	C(8)-S(18)	1.742(16)
S(17)-C(9)	1.777(17)	S(18)-C(10)	1.793(18)
C(9)-C(10)	1.47(3)	C(9)-C(12)	1.500(10)
C(9)-H(9)	1.0000	C(10)-C(11)	1.501(10)
C(10)-H(10)	1.0000	C(11)-O(12)	1.381(10)
C(11)-H(11A)	0.9900	C(11)-H(11B)	0.9900
C(12)-O(13)	1.381(10)	C(12)-I(1)#5	2.56(2)

C(12)-H(12A)	0.9900	C(12)-H(12B)	0.9900
S(21)-C(22)	1.706(16)	S(21)-C(21)	1.719(14)
S(22)-C(23)	1.723(15)	S(22)-C(21)	1.728(14)
C(21)-C(21)#6	1.36(3)	C(22)-C(23)	1.361(19)
C(22)-S(23)	1.745(14)	C(23)-S(24)	1.750(15)
S(24)-C(25)	1.784(19)	S(23)-C(24)	1.792(17)
C(25)-C(24)	1.47(3)	C(25)-C(27)	1.501(10)
C(25)-H(25)	1.0000	C(24)-C(26)	1.497(10)
C(24)-H(24)	1.0000	C(27)-O(28)	1.380(10)
C(27)-H(27A)	0.9900	C(27)-H(27B)	0.9900
C(26)-O(27)	1.382(10)	C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900		
Bond	**Angle (°)**	**Bond**	**Angle (°)**
C(12)#1-I(1)-I(2)	85.8(16)	I(1)-I(2)-I(3)	175.87(4)
I(7)-I(4)-I(5)	123.96(14)	I(7)-I(4)-I(5)#2	123.95(14)
I(5)-I(4)-I(5)#2	112.1(3)	I(7)-I(6)-I(8)#2	159.9(6)
I(7)-I(6)-I(8)	159.9(6)	I(8)#2-I(6)-I(8)	40.1(12)
I(4)-I(7)-I(6)	180.000(11)	I(9)-I(5)-I(9)#3	82.0(14)
I(9)-I(5)-I(4)	129.2(13)	I(9)#3-I(5)-I(4)	148.9(10)
I(9)-I(5)-I(5)#3	51.4(12)	I(9)#3-I(5)-I(5)#3	30.6(8)
I(4)-I(5)-I(5)#3	179.0(3)	I(8)#2-I(8)-I(6)	69.9(6)
I(5)-I(9)-I(5)#3	98.0(14)	I(5)-I(9)-I(9)#3	62.7(14)
I(5)#3-I(9)-I(9)#3	35.4(10)	C(2)-S(12)-C(4)	96.6(9)
C(3)-S(11)-C(1)	101.9(10)	C(2)-C(1)-C(13)	109(2)
C(2)-C(1)-S(11)	118(2)	C(13)-C(1)-S(11)	104.1(18)
C(2)-C(1)-H(1)	108.4	C(13)-C(1)-H(1)	108.4
S(11)-C(1)-H(1)	108.4	C(1)-C(2)-C(14)	109(2)
C(1)-C(2)-S(12)	112.6(17)	C(14)-C(2)-S(12)	105.9(17)
C(1)-C(2)-H(2)	109.9	C(14)-C(2)-H(2)	109.9
S(12)-C(2)-H(2)	109.9	O(14)-C(13)-C(1)	105.5(15)
O(14)-C(13)-H(13A)	110.6	C(1)-C(13)-H(13A)	110.6
O(14)-C(13)-H(13B)	110.6	C(1)-C(13)-H(13B)	110.6
H(13A)-C(13)-H(13B)	108.8	O(14)#4-O(14)-C(13)	141(6)
O(15)-C(14)-C(2)	104.9(15)	O(15)-C(14)-H(14A)	110.8

C(2)-C(14)-H(14A)	110.8	O(15)-C(14)-H(14B)	110.8
C(2)-C(14)-H(14B)	110.8	H(14A)-C(14)-H(14B)	108.8
C(5)-S(13)-C(3)	95.5(7)	C(5)-S(14)-C(4)	94.7(7)
C(6)-S(15)-C(7)	95.3(7)	C(6)-S(16)-C(8)	96.0(7)
C(4)-C(3)-S(11)	127.8(12)	C(4)-C(3)-S(13)	116.7(11)
S(11)-C(3)-S(13)	115.6(8)	C(3)-C(4)-S(14)	117.5(11)
C(3)-C(4)-S(12)	126.4(12)	S(14)-C(4)-S(12)	115.8(7)
C(6)-C(5)-S(13)	122.5(10)	C(6)-C(5)-S(14)	122.0(10)
S(13)-C(5)-S(14)	115.4(9)	C(5)-C(6)-S(15)	122.2(10)
C(5)-C(6)-S(16)	122.4(10)	S(15)-C(6)-S(16)	115.4(8)
C(8)-C(7)-S(15)	116.9(12)	C(8)-C(7)-S(17)	127.8(13)
S(15)-C(7)-S(17)	115.3(9)	C(7)-C(8)-S(16)	116.4(12)
C(7)-C(8)-S(18)	127.5(12)	S(16)-C(8)-S(18)	116.0(8)
C(7)-S(17)-C(9)	97.0(10)	C(8)-S(18)-C(10)	105.2(10)
C(10)-C(9)-C(12)	108(2)	C(10)-C(9)-S(17)	118.9(18)
C(12)-C(9)-S(17)	104.5(15)	C(10)-C(9)-H(9)	108.4
C(12)-C(9)-H(9)	108.4	S(17)-C(9)-H(9)	108.4
C(9)-C(10)-C(11)	108(2)	C(9)-C(10)-S(18)	114.9(18)
C(11)-C(10)-S(18)	103.3(15)	C(9)-C(10)-H(10)	110.2
C(11)-C(10)-H(10)	110.2	S(18)-C(10)-H(10)	110.2
O(12)-C(11)-C(10)	105.0(15)	O(12)-C(11)-H(11A)	110.7
C(10)-C(11)-H(11A)	110.7	O(12)-C(11)-H(11B)	110.7
C(10)-C(11)-H(11B)	110.7	H(11A)-C(11)-H(11B)	108.8
O(13)-C(12)-C(9)	104.9(15)	O(13)-C(12)-I(1)#5	92(8)
C(9)-C(12)-I(1)#5	157(2)	O(13)-C(12)-H(12A)	110.8
C(9)-C(12)-H(12A)	110.8	I(1)#5-C(12)-H(12A)	48.0
O(13)-C(12)-H(12B)	110.8	C(9)-C(12)-H(12B)	110.8
I(1)#5-C(12)-H(12B)	75.7	H(12A)-C(12)-H(12B)	108.8
C(22)-S(21)-C(21)	95.8(7)	C(23)-S(22)-C(21)	95.9(7)
C(21)#6-C(21)-S(21)	123.2(14)	C(21)#6-C(21)-S(22)	122.0(14)
S(21)-C(21)-S(22)	114.8(8)	C(23)-C(22)-S(21)	117.6(11)
C(23)-C(22)-S(23)	129.0(12)	S(21)-C(22)-S(23)	113.4(8)
C(22)-C(23)-S(22)	115.8(11)	C(22)-C(23)-S(24)	127.5(12)
S(22)-C(23)-S(24)	116.6(9)	C(23)-S(24)-C(25)	100.0(12)

C(22)-S(23)-C(24)	103.2(10)	C(24)-C(25)-C(27)	108(2)
C(24)-C(25)-S(24)	118(2)	C(27)-C(25)-S(24)	103.9(15)
C(24)-C(25)-H(25)	108.8	C(27)-C(25)-H(25)	108.8
S(24)-C(25)-H(25)	108.8	C(25)-C(24)-C(26)	106.9(19)
C(25)-C(24)-S(23)	116.8(19)	C(26)-C(24)-S(23)	105.6(15)
C(25)-C(24)-H(24)	109.1	C(26)-C(24)-H(24)	109.1
S(23)-C(24)-H(24)	109.1	O(28)-C(27)-C(25)	105.0(15)
O(28)-C(27)-H(27A)	110.7	C(25)-C(27)-H(27A)	110.7
O(28)-C(27)-H(27B)	110.7	C(25)-C(27)-H(27B)	110.7
H(27A)-C(27)-H(27B)	108.8	O(27)-C(26)-C(24)	104.2(15)
O(27)-C(26)-H(26A)	110.9	C(24)-C(26)-H(26A)	110.9
O(27)-C(26)-H(26B)	110.9	C(24)-C(26)-H(26B)	110.9
H(26A)-C(26)-H(26B)	108.9		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,z #2 -x+2,y,-z+1/2 #3 -x+3/2,-y+1/2,-z+1/2

#4 -x+1,y,-z-1/2 #5 x+1/2,-y+3/2,z #6 -x+2,-y+1,-z

S3 - References

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