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Synthesis and photoreactivity of aryl substituted 4,5-dithienyl[1,3]dithiol-2-ones

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ABSTRACT

UV irradiation of hitherto unknown 4,5-bis-benzo[*b*]thiophen-3-yl-[1,3]dithiol-2-one gave 3-(3-benzo[*b*]thienyl)-thieno[3,4-c]benzo[*e*][1,2]dithiine by loss of carbon monoxide and rearrangement, whereas 4,5-bis-(2-bromo-phenyl)-[1,3]dithiol-2-one gave a polymeric material containing S–S bridges. The structures of both photoproducts were demonstrated on the basis of chemical behaviour and/or X-ray diffraction.

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1. Introduction

We recently reported the photoreactivity of 4,5-dithiophen-2and/or 3-yl[1,3]dithiol-2-ones **1a–c**, showing that after the common reaction pathway of photochemical loss of carbon monoxide, two different reaction pathways were observed, which depended on the nature of the R¹ and R² substituent. Where thiophen-3-yl substituents were present (**1a** and **1b**), the formation of thieno[3,4*c*]dithiines **2a,b** was observed, whereas with thiophen-2-yl substituents a loss of sulfur occurred followed by dimerisation to give the 1,4-dithiine **3c** (Scheme 1).¹



In order to gain further insight into the role of the substituents on the photoreactivity of dithiol-2-ones and in an attempt to increase the scope of the reaction we wished to investigate the process using other aromatic moieties. We thus report our studies on the photochemical behaviour of the benzo-fused system **6** (Scheme 2) and of the bromoaryl derivative **11** (Scheme 4).

2. Results and discussion

Compound **6** was prepared from the benzothiophen-3-carboxaldehyde **4**, which was dimerised in a benzoin condensation to give **5**. This in turn was converted into the target molecule via a threestep cyclisation process.¹ Irradiation of compound **6** gave the dithiine **7**, whose formation can be easily explained on the basis of the previously reported behaviour of thiophen-3-yl derivatives **1a** and **b**. The structure of compound **7** was supported by X-ray² diffraction analysis (Fig. 1). As expected, dithiine **7** gave the dimethyl dithioester **8** in quantitative yield by reduction with sodium borohydride followed by methylation with methyl iodide.

In analogy with our previous findings,¹ the mechanism of the reaction proceeds via loss of carbon monoxide from **6** to give a 1,2-dithioketone. This converts into an intermediate diradical, which then undergoes cyclisation, ring fragmentation and a further cyclisation to give **7** (Scheme 3).

We next prepared the dithiol-2-one **11** (Scheme 4) with brominated aromatic substituents, which we hoped might intercept the S centered radical and undergo displacement of the bromine atom and lead to a benzothiophene structure. The required substrate was prepared from 2-bromobenzaldehyde **9**, which was dimerised in a benzoin condensation to give **10**, which in turn was converted in a three stage process into the required dithiol-2-one **11** in good overall yield. With this material in hand, a solution of **11** was irradiated and on work-up, an amorphous material was obtained in 82% yield.

On analysis by ¹H NMR spectroscopy this material displayed only a very broad signal at 6.8 ppm and in its ¹³C NMR spectrum



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Scheme 2. Reagents and conditions: (a) 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (cat.), NEt₃, EtOH, Δ, 2.5 h, 48%. (b) PPh₃, CCl₄/CH₂Cl₂. (c) KS(CS)OEt, acetone. (d) HBr/AcOH, 34% from 5. (e) hv, 4.5 h, 63%. (f) NaBH₄, EtOH. (g) Mel, Na₂CO₃, rt, 87% (2 steps).



Figure 1. X-ray crystal structure of compound 7.²

a series of broad signals centered at 123.0, 126.9, 129.5, 132.0, 136.0 and 136.9 ppm were observed, which were characteristic of a polymeric material. This was confirmed by ES-MS analysis as the spectrum displayed in the range 2000–4000 *m/z* several typical signal clusters with a regular distance of 298/300/302 uma, suggesting the formation of the disordered polymeric substance **12**. GPC analysis of this material (Fig. 2) confirmed this hypothesis indicating for the polymer a MW distribution in the range 1000–10,000, with a maximum around 2600 uma.

The presence of a disulfide bridge between the monomeric units was supported by the reduction of **12** with sodium borohydride, followed by methylation with methyl iodide to give the *cis*-dimethyl ether **13**. Compound **13** was also prepared from the dithioester **14**³ by treatment with LDA and methyl iodide⁴ (Scheme 4). X-ray diffraction of a crystal of **13**,⁵ obtained by slow evaporation of a chloroform/cyclohexane solution, enabled the assignment of a cis-configuration to this alkene (Fig. 3).

3. Conclusion

In conclusion, our observations confirm that loss of carbon monoxide is a general photochemical process for [1,3]dithiol-2-



Scheme 4. Reagents and conditions: (a) 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (cat.), NEt₃, EtOH, Δ , 8 h, 59%. (b) PPh₃, CCl₄/CH₂Cl₂. (c) KS(CS)OEt, acetone. (d) HBr/AcOH, 43% from **10**. (e) h ν , 4 h, 82%. (f) NaBH₄, EtOH. (g) MeI, Na₂CO₃, rt, 71% (2 steps). (h) LDA, dimethoxyethane, -78 °C. (i) rt, MeI, quantitative yield.

one, however several reaction pathways are possible, depending on the substitution pattern of the intermediates. Some polymeric materials have been previously⁶ observed during irradiation of dithiolones, but the physical (spectroscopic) and chemical characterisation of the S–S polymer **12** is, to the best of our knowledge, unprecedented.

4. Experimental

4.1. General

Melting points were determined on a Kofler hot stage. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions unless stated otherwise, on a Bruker AC 200, AC 250 or AC 500 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS). All reagents were of reagents grade and





GPC analysis of thioplymer: Eluent DMF (100°C) -polystyrene calibration Mn = 2042, Mw = 2577, PDI = 1.2620 Mn = 295, Mw = 323, PDI = 1.0949

Figure 2.

were used without purification. GC–MS analysis was carried out on a Varian Saturn (electron impact) instrument equipped with a gas chromatographic apparatus HP 5890. ESI-MS spectra were recorded with a LCQ-DECA Thermo Finnigan instrument. TLC was performed on precoated 4×6.7 silica gel 60 F₂₅₄ plates silica gel on aluminium (Aldrich) with detection by UV light. Column chromatography was carried out on silica gel (E. Merck, 0.063–0.2 mm). IR spectra were run in chloroform solution on a Bruker Tensor 27 machine, UV spectra were obtained using a Perkin–Elmer Lambda 900 spectrophotometer and molar extinction coefficient are given stated in mol⁻¹ cm⁻¹. CHN analysis was obtained using a CHNS-O EA1108 elemental analyser from Carlo Erba instruments.

4.1.1. 1,2-Bis-benzo[b]thiophen-3-yl-2-hydroxy-ethanone 5

Thianaphthene-3-carboxaldehyde **4** (5.00 g, 30.9 mmol) was dissolved in absolute ethanol (9.4 mL) and triethylamine (1.4 mL, 10 mmol) and 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (0.17 g, 0.62 mmol) was added. The reaction was heated to reflux for 2.5 h, then cooled and evaporated onto silica (15 g). This was loaded onto a column of silica (30 g preflushed with 30% dichloromethane/petrol). Initial elution with 30% dichloromethane/petrol removes a yellow impurity and the product is then obtained by gradient elution from 30% dichloromethane/petrol to 100% dichloromethane. This gave on evaporation the required compound (3.66 g), which eluted in 50%–100% dichloromethane/petrol. Recrystallisation from chloroform/petrol gave white crystals of **5** (2.39 g, 48%).

 R_{f} =0.25 (in 80% dichloromethane/petrol), mp 130 °C. δ_{H} 4.64–4.66 (1H, d, J 5.7 Hz, CHOH), 6.25–6.26 (1H, d, J 5.7 Hz, CHOH), 7.37–7.47 (4H, m, 4×CH), 7.57 (1H, m, CH), 7.83–7.84 (1H, d, J 7.9 Hz, CH),



Figure 3. X-ray crystal structure of compound 13.5

7.87 (1H, d, *J* 7.9 Hz, CH), 8.01 (1H, d, *J* 8.2 Hz, CH), 8.20 (1H, s, CH), 8.87 (1H, d, *J* 8.2 Hz, CH). $\delta_{\rm C}$ 193.2, 140.9, 139.4, 139.1, 137.2, 136.7, 134.8, 131.1, 126.6, 126.3, 125.9, 125.5, 125.0, 124.8, 123.0, 122.3, 122.2, 71.7. $\nu_{\rm max}$ (film)/cm⁻¹ 3425 (O–H), 3096 (C–H), 1664 (C=O). HRMS (ESI) [M+Na⁺]: [C₁₈H₁₂O₂S₂Na]⁺ requires 347.0176; found 347.0165. Anal. Calcd for C₁₉H₁₂O₂S₂: C, 66.64; H, 3.73. Found: C, 66.85; H, 3.33.

4.1.2. 4,5-Bis-benzo[b]thiophen-3-yl-[1,3]dithiol-2-one 6

1,2-Bis-benzo[b]thiophen-3-yl-2-hydroxy-ethanone 5 (2.39 g, 7.35 mmol) was dissolved in dichloromethane (8 mL) and carbon tetrachloride (15 mL) was added (ensuring that precipitation of 5 did not occur, if this does happen then further addition of dichloromethane is required). Triphenylphosphine (3.91 g, 14.9 mmol) was then added and the resulting solution was stirred in the dark for 16 h. The reaction was then diluted with ether (100 mL), then petrol (50 mL), which precipitates the triphenylphosphine oxide by-products and the supernatant liquid, was passed through a silica pad on a sinter funnel. The remaining yellow precipitate in the flask was redissolved in dichloromethane (10-20 mL) and precipitated again by the sequential addition of diethyl ether (100 mL) and petroleum ether (50 mL) and once again the supernatant layer was filtered through the silica pad. This process was repeated twice more and the combined filtrates were evaporated onto silica (6 g). This was loaded onto a column (20 g) and was eluted using 50% dichloromethane/petrol. The combined fractions containing a spot at $R_f=0.36$ (50% dichloromethane/petrol) were evaporated to give crude 1,2-Bis-benzo[b]thiophen-3-yl-2-chloroethanone (1.69 g, 4.93 mmol, 67%), which was of sufficient purity to be used in the next step. Partial data $\delta_{\rm H}$ 6.65 (1H, s, CHCl).

The crude chloride (1.69 g, 4.9 mmol) was dissolved in acetone (50 mL) and a solution of potassium ethyl xanthate (2.81 g, 17.6 mmol) in acetone (50–100 mL) was then added. The reaction mixture was stirred for 60 min and then diluted with diethyl ether (250 mL) and the resultant suspension filtered through a silica pad, which was washed with further diethyl ether (3×100 mL); these filtrates on evaporation gave crude dithiocarbonic acid *S*-(1,2-bisbenzo[b]thiophen-3-yl-2-oxo-ethyl) ester *O*-ethyl ester (1.94 g, ca. 92%) as a brown gum. Partial data $\delta_{\rm H}$ 7.00 (1H, s, CHS(CS)OEt).

Crude *S*-(1,2-bis-benzo[*b*]thiophen-3-yl-2-oxo-ethyl) ester *O*ethyl ester (1.94 g, 4.5 mmol) was dissolved in the minimum amount of dichloromethane (ca. 10 mL) and hydrobromic acid solution (45% in acetic acid, 20 mL) was added. The mixture was stirred vigorously for 3 h whereupon dichloromethane (100 mL) and water (300 mL) were added. The organic phase was separated and the aqueous phase extracted with dichloromethane (2×50 mL) and the combined organic fractions were washed with water (2×500 mL) and saturated sodium bicarbonate until neutral. After drying (MgSO₄) and evaporation, the crude product was purified by column chromatography in dichloromethane/petrol (gradient elution 30% to 70%) to give **6** (0.95 g, 34%) as a pale yellow crystalline solid.

*R*_{*f*}=0.23 (in 30% dichloromethane/petrol), mp 178 °C. $\delta_{\rm H}$ 7.29– 7.37 (6H, m, 6×CH), 7.77 (2H, d, *J* 7.6 Hz, CH), 7.80 (2H, d, *J* 7.9 Hz, CH). $\delta_{\rm C}$ 122.5, 122.8, 124.8, 124.8, 125.0, 126.7, 128.4, 137.1, 139.6, 190.7. IR: *ν*_{max}/cm⁻¹ 3094 (CH), 1659 (C=O). UV: $\lambda_{\rm max}$ 295 nm (log ε 4.61, *c* 1.6×10⁻⁵). HRMS (ESI) [M+Na⁺]: [C₁₉H₁₀OS₄Na]⁺ requires 404.9512; found 404.9518. Anal. Calcd for C₁₉H₁₀OS₄: C, 59.65; H, 2.63. Found: C, 59.41; H, 2.52.

4.1.3. 3-(3-Benzo[b]thienyl)-thieno[3,4-c]benzo[e][1,2]dithiine 7

A solution of 1,3-dithiol-2-one **6** (0.050 g, 0.13 mmol) in benzene (20 mL) was irradiated in an air-cooled Pyrex tube for 4.5 h with a Rayonet irradiation system Mod. MLU 18 (Applied Photophysic Ltd.) equipped with 12 lamps model 1024, emitting at 350 nm. After removal of solvent the residue was purified by column chromatography with cyclohexane to give 0.020 g (63% based on recovered **6**)

of dithiine **7** and starting material (0.015 g). Compound **7** was further purified by crystallisation from benzene to give yellow crystals.

R_f=0.60 (in 25% diethyl ether/petrol), mp 128–130 °C. $\delta_{\rm H}$ (C₆D₆) 6.85 (1H, td, *J* 8.0, 1.9 Hz, CH), 7.00 (1H, td, *J* 8.0, 1.9 Hz, CH), 7.02 (1H, s, CH), 7.05 (1H, s, CH), 7.06–7.19 (2H, m, 2×CH), 7.27 (1H, dd, *J* 8.0, 1.9 Hz, CH), 7.35 (1H, dd, *J* 8.0, 1.9 Hz, CH), 7.52 (1H, dd, *J* 8.1, 1.8 Hz, CH), 7.94 (1H, dd, *J* 8.1, 1.8 Hz, CH). $\delta_{\rm C}$ 121.6, 122.9, 123.2, 124.7, 124.9, 127.4, 127.6, 127.7, 128.1, 128.6, 129.0, 130.2, 132.1, 133.0, 135.0, 137.7, 139.4, 140.1. IR: $\nu_{\rm max}/{\rm cm^{-1}}$ 3078 (CH), 1504. UV $\lambda_{\rm max}$ 292 nm (log ε 4.19, *c* 6.8×10⁻⁵). MS (EI) *m/z* (%): 354 (100), 322 (18), 290 (22), 177 (16). HRMS (EI) [M⁺]: [C₁₈H₁₀S₄]⁺ requires 353.9665; found 353.9671. Anal. Calcd for C₁₈H₁₀S₄: C, 60.98; H, 2.84. Found: C, 61.13; H, 2.75.

4.1.4. 3-(3-(Methylthio)-4-(2-(methylthio)phenyl)thiophen-2-yl)benzo[b]thiophene **8**

A stirred solution of dithile **7** (0.010 g, 0.03 mmol) in ethanol (2 mL) was treated under nitrogen with sodium borohydride (0.004 g, 0.1 mmol) and a solution of sodium carbonate (0.003 g) in the minimum amount of water. After 30 min, methyl iodide (0.025 mL) was added and after 2 h the solvents were evaporated in vacuo and the oily residue was purified by column chromatography eluting with light petroleum/ether 3:1 (v/v) to give **8** (0.010 g, 87%) as a white solid.

 $R_{f}{=}0.66$ (in 25% ethyl ether/petrol), mp 105–107 °C (cyclohexane). $\delta_{\rm H}$ (C₆D₆) 1.67 (3H, s, Me), 2.00 (3H, s, Me), 7.02–7.25 (6H, m, 6×CH), 7.37 (1H, d, *J* 7.8 Hz, CH), 7.41 (1H, s, CH), 7.57 (1H, d, *J* 8.0 Hz, CH), 8.09 (1H, d, *J* 8.0 Hz, CH). $\delta_{\rm C}$ 15.9, 18.8, 122.7, 123.5, 123.8, 124.4, 124.4, 124.7, 124.7, 127.0, 128.6, 129.5, 130.6, 131.6, 135.5, 136.9, 138.4, 139.0, 139.8, 143.6. IR: $\nu_{\rm max}/{\rm cm}^{-1}$ 3055 (CH), 2964, 2920 (CH₃), 1435 (Ar). MS (EI) m/z (%) 384 (95), 338 (100), 323 (82). HRMS (EI) [M⁺]: [C₂₀H₁₆S₄]⁺ requires 384.0135; found 384.0131. Anal. Calcd for C₂₀H₁₆S₄: C, 62.46; H, 4.19. Found: C, 62.39; H, 4.02.

4.1.5. 1,2-Bis-(2-bromo-phenyl)-2-hydroxy-ethanone 10

2-Bromobenzaldehyde **9** (20.64 g, 111.6 mmol) was dissolved in absolute ethanol (33.8 mL) and triethylamine (4.65 mL, 33.4 mmol), and 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (6.00 g, 22.5 mmol) were added. The reaction was heated to reflux for 8 h, then cooled, diluted with water (400 mL) and extracted with dichloromethane (3×100 mL). The combined organic fractions were washed with sodium bicarbonate (saturated, 3×50 mL), dried (MgSO₄) and evaporated in vacuo to give a yellow solid, which was purified by chromatography (0–100% dichloromethane in petrol gradient 20% steps) to give **10** (12.2 g, 27.7 mmol, 59%) as a white solid.

 R_{f} =0.3 (CH₂Cl₂), mp 76–78 °C. δ_{H} 4.60 (1H, d, *J* 3.7 Hz, OH), 6.36 (1H, d, *J* 3.7 Hz, CH), 7.09–7.57 (m, 8H, 8×CH). δ_{C} 77.1, 119.5, 124.0, 126.8, 127.8, 128.8, 129.2, 130.1, 132.1, 133.0, 133.4, 136.0, 137.2, 201.2. IR: ν_{max}/cm^{-1} 3459 (OH), 2965 (CH), 1705 (C=O). HRMS (CI) [M+NH₄]: C₁₄H⁷₁₄Br₂NO₂ requires 385.9386; found 385.9386.

4.1.6. 4,5-Bis-(2-bromo-phenyl)-[1,3]dithiol-2-one 11

Benzoin **10** (1.89 g, 5.34 mmol) was dissolved in dichloromethane (15 mL) and tetrachloromethane (20 mL) and triphenylphosphine (2.8 g, 10.68 mmol) was added. The reaction mixture was stirred in the dark for 16 h, then diluted with diethyl ether (100 mL), which caused the precipitation of the phosphine oxide by-products. The supernatant liquid was decanted with filtration through a silica pad, and the precipitate left in the flask was redissolved in dichloromethane (20 mL) and precipitated again by the sequential addition of diethyl ether (100 mL) and petroleum ether (50 mL). The supernatant layer was decanted and filtered as before and this process was repeated twice more. The combined filtrates were evaporated in vacuo to give 1,2-bis-(2-bromo-phenyl)-2-chloro-ethanone (2.00 g) of sufficient purity to be used immediately in the next step. Partial data $\delta_{\rm H}$ 6.76 (1H, s, CH), 7.20–7.70 (8H, m, 8×CH). $\nu_{\rm max}/{\rm cm}^{-1}$ 3063 (CH), 1721 (C=O).

The chloride (2.0 g) was dissolved in dry acetone (10 mL) and potassium ethyl xanthate (1.20 g, 8.0 mmol) was added. After stirring for 1 h, diethyl ether (100 mL) was added and the resultant solution was filtered through a silica pad (with ether rinsing) to remove precipitated salts. Evaporation of the filtrate gave crude dithiocarbonic acid *S*-[1,2-bis-(2-bromo-phenyl)-2-oxo-ethyl] ester *O*-ethyl ester (2.2 g), which was used in the next step without further purification. Partial data $\delta_{\rm H}$ 6.95 (1H, s, CH), 7.10–7.80 (8H, m, 8×CH). $\nu_{\rm max}/{\rm cm}^{-1}$ 3060, 2979 (CH), 1710 (C=O).

The xanthate ester (2.2 g) was dissolved in dichloromethane (10 mL) and a solution of hydrobromic acid (45% in acetic acid, 20 mL) was added. The mixture was stirred vigorously for 2.5 h, whereupon dichloromethane (50 mL) and water (200 mL) were added. The organic phase was separated and the aqueous phase extracted with dichloromethane (3×25 mL). The combined organic fractions were washed with water (2×500 mL), then saturated sodium bicarbonate solution until neutral then dried (MgSO₄) and evaporated. Purification by column chromatography in dichloromethane/petrol (gradient elution 20–30%) gave **11** (0.99 g, 2.31 mmol, 43% from **10**) as white crystals.

 $R_{f}{=}0.25~(30\%$ dichloromethane in petrol), mp 147–148 °C. $\delta_{\rm H}$ 7.15 (4H, m, 4×CH), 7.38 (2H, m, 2×CH), 7.52 (2H, m, 2×CH). $\delta_{\rm C}$ 124.0, 127.4, 130.1, 130.8, 131.8, 131.9, 132.9, 190.5. IR $\nu_{\rm max}/{\rm cm}^{-1}$ 3059, 2358 (CH), 1698 (C=O), 1634 (C=C). UV: $\lambda_{\rm max}$ 266 nm (log ε 3.72, c 5.4×10⁻⁵). HRMS (CI) [M+NH⁺₄]: found 443.8721; C₁₅H²₁₉Br₂NOS₂ requires 443.8722. Anal. Calcd for C₁₅H_8Br₂OS₂: C, 42.08; H, 1.88. Found: C, 42.42; H, 1.82.

4.1.7. (Z)-1,2-Bis(2-bromo-phenyl)-1,2-bis(methylthio)ethene 13

A solution of compound 11 (0.05 g, 0.12 mmol) in anhydrous benzene (15 mL) was irradiated in a Pyrex vial with an external lamp (Hg, medium pressure, 400 W) for 4 h. Solvent was removed in vacuo and the residue was treated with acetonitrile (5 mL) to give the dithiopolymer **12** as an amorphous yellow solid (0.038 g, 81.5%). UV: λ_{max} broad band 400–200 nm, shoulder at 315 nm, for NMR spectroscopy, MS data and GPC analysis see main text. A solution of sodium carbonate (0.012 g) in water (2 mL) was added to a stirred suspension of **12** (0.032 g) in ethanol (5 mL) followed by the addition of sodium borohydride (0.014 g). After 2 h, methyl iodide (0.1 mL) was added and stirring was continued for further 2 h. The pH of the solution was adjusted to 4 with HCl (1 M) and the solution evaporated in vacuo. The solid residue was treated with chloroform (20 mL), which was washed with water (20 mL), dried (Na₂SO₄) and evaporated to give a residue, which was purified by column chromatography (10% ether in petrol) to give 13 (0.030 g, 71%) as white crystals.

 R_f =0.77, mp 127–129 °C (cyclohexane). δ_H 1.95 (6H, s, 2×SMe), 6.90–7.49 (8H, m, 8×CH). δ_C 15.2, 124.0, 127.0, 127.7, 129.1, 130.7, 132.3, 138.5. IR ν_{max}/cm^{-1} 3056 (CH), 2927, 2851 (CH₃), 1640 (C=C), 1562 (Ar). HRMS (EI) [M⁺]: [C₁₆H₁₄Br₂S₂]⁺ requires 427.8904; found 427.8909. MS (EI) m/z (%) 428/430/432 (25/50/25), 349/351 (96/ 100), 302/304 (12/12), 255 (54), 176 (21). Anal. Calcd for C₁₆H₁₄Br₂S₂: C, 44.67; H, 3.28, Br, 37.15. Found: C, 44.83; H, 3.16; Br, 37.02.

An identical product (identical mp and NMR spectra) was obtained from methyl-2-bromobenzodithioate **14**³ according to a previously reported method.⁴

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- D.; Pollucein, F. J. Org. Chem. 2005, 66, 7115-7116. 2. Crystal data for 7: C₁₈H₁₀S4, MW=354.54, monoclinic, *a*=8.0004(3), *b*=14. 0430(5), *c*=27.2128(14)Å, *β*=92.302(4)°, *V*=3054.9(2)Å³ (by least-squares refinement of 14,619 reflections), space group P_{2_1}/n , *Z*=8, *F*(000)=1456, *D_c*=1. 542 g cm⁻³, *μ* (Mo Kα) 0.613 mm⁻¹. The data were collected on a Xcalibur-3 0xford diffraction with graphite monochromated Mo Kα radiation (*λ*=0.71069 Å) in the range $-10 \le h \le 10$, $-17 \le k \le 17$, $-32 \le l \le 32$, $4.11 \le \theta \le 28.34^{\circ}$ scan range. 8795 total reflections (*R*_{int}=0.09) were collected with CCD detector at 22 °C. Multi-scan absorption correction was applied. The structure was solved by direct methods implemented in SHELX-97.⁷ Refinement was carried out by full-matrix anisotropic least-squares on *F*² for all reflections for all non-H atoms by using SHELX-97.⁶ Hydrogen atoms were geometrically located and included in the structure-factor calculations. Final refinement of 409 parameters gave *R*₁=0.049 and *wR*₂=0.106 using 4453 reflections with *l*>2*a*(*l*). Weighting scheme was $w=1/[r_0^2/(F_0^2)+0.000P^2+8.4049P]$, where $P=(F_0^2+2F_0^2)/3$. Minimum and maximum heights in last map were -0.273 and 0.269 eÅ⁻³, respectively. Atomic scattering factors, including *f* and *f'* were taken from Ref. 6. List of the fractional coordinates, bond lengths and angles, thermal parameters have been deposited at the Crystallography Data Centre, UK as supplementary material. Deposit number CCDC 695917.
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- 5. Crystal data for **13**: C₁₆H₁₄Br₂S₂, MW=430.21, monoclinic, *a*=9.584(3), *b*=13. 611(2), c=13.157(2) Å, $\beta=98.20(5)^{\circ}$, V=1715.7(11) Å³ (by least-squares refinement of 35 randomly selected and automatically centered reflections), space group $P2_1/n$, Z=4, F(000)=848, $D_c=1.666 \text{ g cm}^{-3}$, μ (Mo Ka) 4.956 mm⁻¹. The data were collected on a Siemens P4 four-circle diffractometer with graphite monochromated Mo K α radiation (λ =0.71069 Å) in the range $-1 \le h \le 11$, $-1 \le k \le 16$, $-15 \le l \le 15$, ω scan mode for $2.15 \le \theta \le 25.0^\circ$ scan range, scan width 1.1° , constant scan speed 3.0° min⁻¹. Three standard reflections measured every 97 reflections showed no variations. 3868 total reflections ($R_{int}=0.09$) were collected at 22 °C. Psi-scan absorption correction was applied. The structure was solved by direct methods implemented in SHELX-97.⁶ The refinement was carried out by full-matrix anisotropic least-squares on F^2 for all reflections for all non-H atoms by using SHELX-97.⁷ The hydrogen atoms were geometrically located and included in the structure-factor calculations. Final refinement of 203 parameters gave R_1 =0.072 and wR_2 =0.164 using 2991 reflections with $I>2\sigma(I)$. Weighting scheme was $w=1/[\sigma^2(F_0)^2+0.08P^2+2.771P]$, where $P=(F_0^2+2F_0^2)/3$. Minimum and maximum heights in last map were -0.374 and $0.404 \text{ e} \text{ Å}^{-3}$, respectively. Atomic scattering factors, including f and f' were taken from Ref. 6. List of the fractional coordinates, bond lengths and angles, thermal parameters have been deposited at the Crystallography Data Centre, UK as supplementary material. Deposit number CCDC 695916.
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