

Synthesis and Photoreactivity of 4,5-Dithienyl[1,3]dithiol-2-ones

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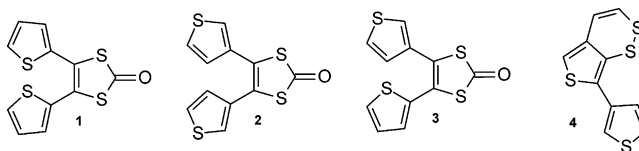
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Abstract: Whereas irradiation of 4,5-dithiophen-2-yl[1,3]-dithiol-2-one leads to the expected 2,3,5,6-tetrathiophen-2-yl-1,4-dithiine product, similar reaction of thiophen-3-yl-substituted [1,3]dithiol-2-ones leads to thieno[3,4-*c*]dithiines via a unique ring cleavage reaction.

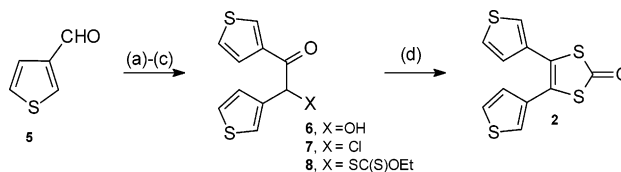
Our research on dithiophenyl[1,3]dithiol-2-ones, for example, **1** and **2**, has shown that these materials are versatile precursors for the synthesis of TTFs^{1–4} and metal dithiolenes⁵ and for the preparation of polymer films for chemical modification.⁶ More recently we reported⁷ the unique photochemical transformation of 4,5-dithiophen-3-yl[1,3]dithiol-2-one **2** to the thieno[3,4-*c*]dithiine **4** and take this opportunity to report our findings in this area of research in more detail (Scheme 1).

Preparation of Substrates. We intended to investigate the reaction of the three thiophenyl[1,3]dithiol-2-ones **1–3** as they represent all the possible substitution patterns available for the parent class of compounds. The symmetrical adducts were prepared according to our previously reported method, and details for **1** have already been reported.² The 4,5-dithiophen-3-yl[1,3]dithiol-2-one **2** was prepared similarly from thiophene-3-carboxaldehyde (**5**), which was first converted into the benzoin product **6** in 53% yield (Scheme 2). Reaction of this with triphenylphosphine and carbon tetrachloride gave the chloride **7**, which was immediately treated with

SCHEME 1

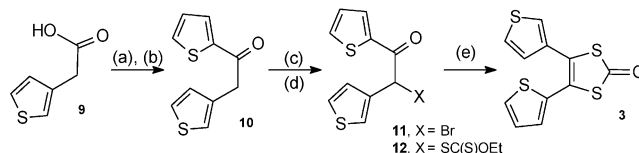


SCHEME 2^a



^a Reagents and conditions: (a) 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (cat.), NEt₃, EtOH, Δ, 2.5 h; 53%; (b) PPh₃, CCl₄/CH₂Cl₂; (c) KS(CS)OEt, acetone; (d) HBr/AcOH; 50% from **6**.

SCHEME 3^a



^a Reagents and conditions: (a) SOCl₂, Δ, 3 h; (b) thiophene, PhH, AlCl₃; 34%; (c) CuBr₂, EtOAc, Δ, 2 h; (d) KS(CS)OEt, acetone; (e) HBr/AcOH; 36% from **10**.

potassium ethyl xanthate to give **8**. Reaction of this with HBr/AcOH gave **2** in 50% overall yield from **6**.

The unsymmetrical 4-thiophen-2-yl-5-thiophen-3-yl-[1,3]dithiol-2-one **3** was prepared first by conversion of the carboxylic acid **9** to the corresponding acid chloride, which on Friedel–Crafts reaction with thiophene gave ketone **10** in 34% yield (Scheme 3). Bromination of this using CuBr₂ in EtOAc gave the bromide **11**, which was then treated with potassium ethyl xanthate to give **12**. Reaction of this with HBr/AcOH gave **3** in 36% overall yield from **10**.

Photochemistry. As previously reported,⁷ the photochemical irradiation of 4,5-dithiophen-3-yl[1,3]dithiol-2-ones **2** led to the formation of the thieno[3,4-*c*]dithiine **4** in 76% yield. A similar reaction was observed for the unsymmetrical 4-thiophen-2-yl-5-thiophen-3-yl[1,3]dithiol-2-one **3** in that the 2-thienyl-substituted thieno[3,4-*c*]dithiine **13** was again formed in 76% yield (Scheme 4). These processes both occur via a photochemical elimination of carbon monoxide from the substrate, which is followed by a ring cleavage rearrangement (vide infra), indicating a common reaction pathway for 3-thienyl-substituted systems. Structural characterization of these compounds was achieved by reduction with NaBH₄ to give the corresponding hemithioacetals **14** and **15**, the first of these giving crystals suitable for X-ray analysis.⁷ If, in a single sequence, the reduction step is followed by treatment of the crude reaction product with methyl iodide and sodium carbonate at room temperature, the methylated products **16** and **17** are formed in good yields. Heating **16** or **17** in the presence of further methyl iodide

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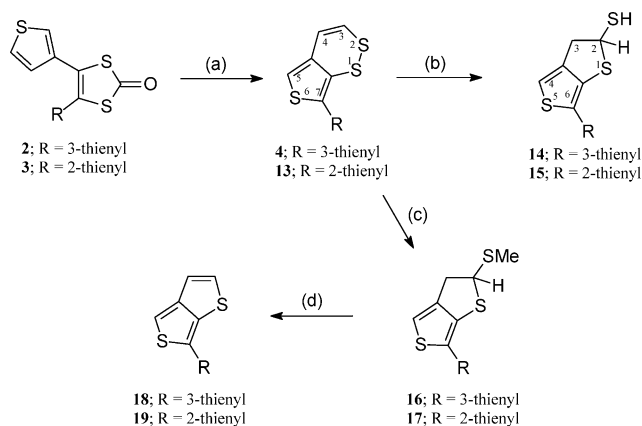
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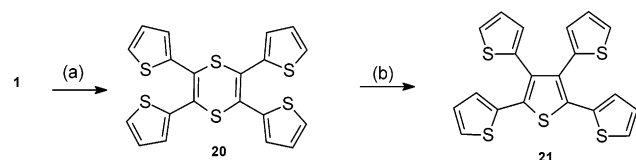
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SCHEME 4^a

^a Reagents and conditions: (a) *hν*, 6 h; **4**, 76%; **13**, 76%; (b) NaBH₄, EtOH; **14**, 65%; **15**, 78%; (c) (i) NaBH₄, EtOH; (ii) MeI, Na₂CO₃, rt; **16**, 69% from **4**; **17**, 71% from **13**; (d) MeI, Δ; **18**, 72%; **19**, 66%.

SCHEME 5^a

^a Reagents and conditions: (a) *hν*, 5 h; quantitative; (b) AcOH, H₂O₂; 75%.

and sodium carbonate leads to the formation of the thieno[3,4-*b*]thiophenes **18** and **19** in 72% and 66% yield, respectively. Thiophene **18** is a known compound,⁸ and **19** displayed very similar spectroscopic properties, thus confirming its structure.

We next investigated the irradiation of 4,5-dithiophen-2-yl[1,3]dithiol-2-one **1** and found that a considerably different process occurred. The crude reaction mixture was composed largely of a compound with *m/z* 444, which was unstable to chromatography and displayed only signals suggestive of a 2-thienyl-containing moiety. Reaction of this compound with hydrogen peroxide in acetic acid gave the known⁹ 2,3,4,5-tetrathiophen-2-ylthiophene (**21**) in 75% yield (Scheme 5). As a consequence of this we can assign the 1,4-dithiin structure **20** to be that formed from the initial photolysis. The transformation of 1,4-dithiin derivatives into thiophenes by sulfur loss has been previously described.¹⁰

A rationale for the photochemical behavior of the title compounds is illustrated in Scheme 6. The elimination of carbon monoxide^{11,12} to give the 1,2-dithioketone **22** is a common step for each system, which is confirmed by performing the reactions in the presence of Mo(CO)₆, which is able to halt the rearrangement by formation of blue Mo complexes **23**.¹¹ In the absence of this trapping

agent, the dithioketones formed from substrates **2** and **3** cyclize via the diradicals **24** to give the intermediates **25**, which undergoes ring cleavage to **26** and disulfide bond formation to give the dithiin systems **4** and **13**, respectively.

In the case of compound **1**, addition of the thioradical to a 2-thienyl ring would lead to the intermediates **27** and **28**, which are unable to undergo this ring cleavage. It is likely that if these intermediates are formed it will be in a reversible process, and the eventual fate of the dithioketone is that it undergoes dimerization with S₂ elimination¹⁰ to afford **20**.

It is apparent that there are significant differences in the reactivity of the 2-thienyl (**1**) and 3-thienyl (**2**, **3**) substituted substrates, the latter undergoing an unusual fragmentation process after the common decarbonylation step. We have illustrated that this reaction has potential in synthesis as the thieno[3,4-*c*]dithiins **4** and **13** were readily converted into the thieno[3,4-*b*]thiophenes **18** and **19** in high yield. We are currently investigating related reactions of this type and will report our findings in due course.

Experimental Section

2-Hydroxy-1,2-dithiophen-3-ylethanone (3,3'-Theonin, 6).³ 3-Thiophenecarboxaldehyde (**5**) (25 g, 223 mmol) was dissolved in absolute ethanol (67.5 mL), and triethylamine (9.3 mL, 70.3 mmol) and 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (1.2 g, 4.5 mmol) were added. The reaction was heated to reflux for 2.5 h, then cooled, diluted with water (750 mL), and extracted with dichloromethane (3 × 100 mL). The combined organic fractions were washed with sodium bicarbonate (3 × 100 mL), dried (magnesium sulfate), and evaporated in vacuo to give a pale brown solid. The solid was recrystallized from chloroform, producing white crystals of **6** (13.1 g, 53%): mp 108 °C; δ_H 4.38 (d, 1H, *J* = 5.8 Hz, OH), 5.86 (d, 1H, *J* = 5.8 Hz, CH), 7.01 (dd, 1H, *J* = 1.2, 4.9 Hz, C-H), 7.33 (m, 3H, C-H), 7.53 (dd, 1H, *J* = 0.9, 4.9 Hz, C-H), 8.06 (dd, 1H, *J* = 1.2, 2.8 Hz, C-H); δ_C 192.4 (C), 139.9 (C), 139.9 (C), 134.3 (CH), 127.3 (CH), 128.1 (CH), 126.6 (CH), 126.3 (CH), 72.9 (CH); ν_{max} 3428 (O-H), 3097 (C-H), 3018 (C-H), 1667 (C=O); MS (EI) *m/z* (rel intens) 224 (100, [M⁺]); HRMS (EI) (*m/z*) C₁₀H₈O₂S₂ [M⁺] requires 223.9966, found 223.9974. Anal. Expected: C, 53.55; H, 3.59. Found: C, 53.85; H, 3.61.

4,5-Dithiophen-3-yl[1,3]dithiol-2-one 2. 6 (5.4 g, 24.1 mmol) was dissolved in dichloromethane (25 mL) and added to a solution of triphenylphosphine (12.7 g, 48.5 mmol) in tetrachloromethane (50 mL). The reaction mixture was stirred in the dark for 18 h and then diluted with ether (100 mL), which caused the precipitation of a yellow solid. The solution was decanted with filtration through a silica pad and the yellow precipitate 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 the process was repeated twice more. After evaporation of the combined filtrates, the product was purified by column chromatography using diethyl ether/petrol (30:70, collecting pots containing *R_f* 0.2) as eluent to give **7** as a white solid (5.3 g, ca. 90%) of sufficient purity to be used immediately in the next step.

Chloride **7** (5.3 g) was dissolved in dried acetone (5 mL) and added to a solution of potassium ethyl xanthate (13.9 g, 86.8 mmol) in acetone (100 mL). The reaction mixture was stirred for 15 min and then diluted with diethyl ether (200 mL). The resultant solution was filtered through a silica pad which was washed with further diethyl ether (2 × 50 mL). These filtrates on evaporation gave crude **8** (4.5 g, ca. 63%).

Xanthate ester **8** (4.5 g) was dissolved in glacial acetic acid (15 mL), and 45% hydrobromic acid solution in acetic acid (15

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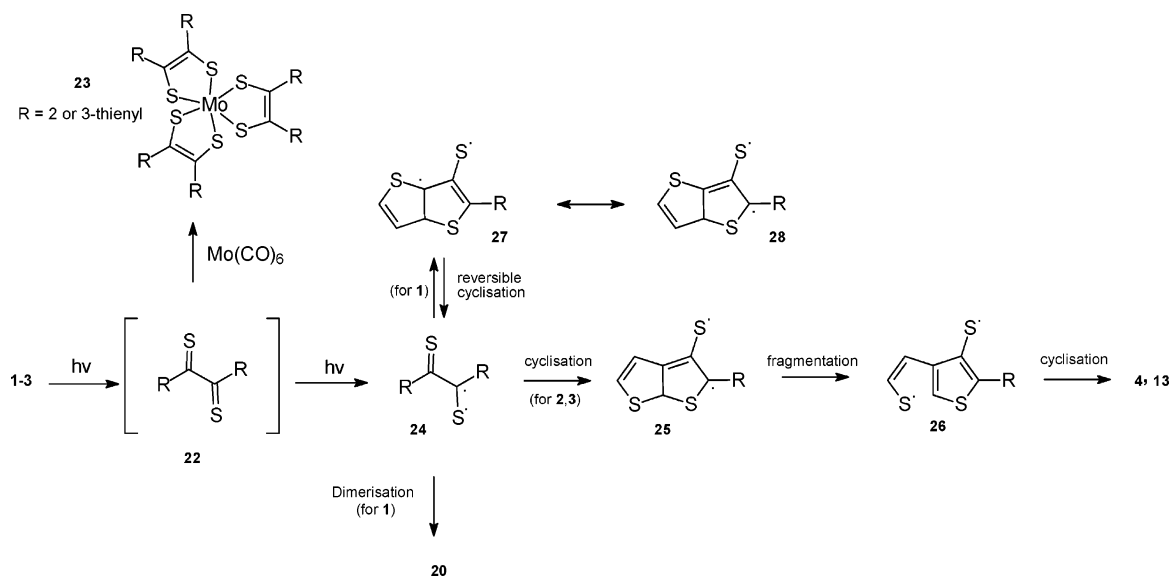
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SCHEME 6



mL) was added. The mixture was stirred vigorously for 15 min, 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), and the combined organic fractions were washed with saturated sodium bicarbonate (3×25 mL), dried (magnesium sulfate), and evaporated. The crude product was purified by column chromatography using diethyl ether/petrol (3:97, 10:90, 30:70) collecting fractions containing spots at $R_f = 0.25$ (diethyl ether/petrol, 10:90). Recrystallization from ether/hexane gave **2** (3.4 g, 50% from **6**) as needles: mp 102 °C.

δ_H 6.86 (dd, 2H, $J = 4.0, 1.2$ Hz, 2 CH), 7.24 (dd, 2H, $J = 3, 1.2$ Hz, 2 CH), 7.28 (dd, 2H, $J = 4.0, 3.0$ Hz, 2 H); δ_C 189.9 (C), 131.8 (C), 127.6 (CH), 126.5 (CH), 125.8 (CH), 123.5 (C); ν_{max} 3111 (C-H), 1659 (C=O), 1629 (C=C); MS (EI) m/z (rel intens) 282 (100, $[M^+]$); HRMS (EI) (m/z) $C_{11}H_6OS_4$ [M^+] requires 281.9302, found 281.9302.

2-Thiophen-3-yl-1-thiophen-2-ylethanone (10). 3-Thiopheneacetic acid (**9**) (5 g, 35.2 mmol) was dissolved in thionyl chloride (13.7 mL, 70.4 mmol) and heated under reflux for 3 h. After removal of the excess thionyl chloride by evaporation on a vacuum pump, thiophene (3.6 g, 42.3 mmol) and dry benzene (50 mL) were added and the solution was cooled (5 °C). Aluminum chloride (5.5 g, 42.3 mmol) was then added in small portions and the reaction stirred to room temperature overnight. The reaction mixture was then poured carefully onto a mixture of crushed ice (200 mL) and concentrated HCl (100 mL), the organic phase separated, and the aqueous layer extracted with further dichloromethane (3×50 mL). The combined extracts were dried ($MgSO_4$) and evaporated, following which column chromatography of the crude product (diethyl ether/petrol, 20:80) gave the ketone **10** (2.52 g, 34%) as an oil:

δ_H 7.77 (dd, 1H, $J = 4.0, 1.0$ Hz, CH), 7.66 (1H, dd, $J = 4.9, 0.9$ Hz, CH), 7.31 (1H, dd, $J = 4.9, 3.1$ Hz, CH), 7.19 (1H, m, CH), 7.15 (1H, dd, $J = 4.0, 4.9$ Hz, CH), 7.06, (1H, dd, $J = 4.9, 0.9$, CH), 4.24, (2H, s, CH_2); δ_C 189.9 (C), 131.9 (C), 134.1 (CH), 133.9 (C), 132.6 (CH), 128.5 (CH), 125.9 (CH), 122.94 (CH), 40.9 (CH₂); ν_{max} 3099 (C-H), 1656 (C=O) MS (CI) m/z (rel intens) 226 (100, $[M + NH_4^+]$), 209 (33, $[M + H^+]$); HRMS (CI) (m/z) $C_{10}H_8OS_2$ [$M + NH_4^+$] requires 226.0360, found 226.0356.

4-Thiophen-2-yl-5-thiophen-3-yl[1,3]dithiol-2-one 3. Ketone **10** (3.64 g, 17.5 mmol) was dissolved in dry ethyl acetate (80 mL), copper(II) bromide (8.6 g, 38.5 mmol) was added, and the mixture was then stirred while being heated at 60 °C. After 2 h the reaction was cooled and filtered through a Celite pad and the filtrate evaporated. Diethyl ether (25 mL) was then added to the crude product, followed by petroleum ether (50 mL) to precipitate any inorganic material, following which the organic

layer was decanted and filtered through a Celite pad. This process was repeated three times and the combined filtrate evaporated to give crude bromide **11** (4.3 g, ca. 85%).

Bromide **11** (4.3 g) was dissolved in dried acetone (30 mL) and added to a solution of potassium ethyl xanthate (5.6 g, 35 mmol) dissolved in dried acetone (100 mL). The reaction mixture was stirred for 15 min and then diluted with diethyl ether (200 mL). The resultant solution was filtered through a silica pad and washed with further diethyl ether (2×50 mL). Evaporation gave crude **12** (3.0 g ca. 58%).

Xanthate ester **12** (3.0 g) was dissolved in glacial acetic acid (20 mL), and 45% hydrobromic acid solution in acetic acid (20 mL) was added. The mixture was stirred vigorously for 1 h, whereupon dichloromethane (50 mL) and water (200 mL) were added. The reaction was then separated and the aqueous phase extracted with dichloromethane (3×25 mL). The combined organic fractions were washed with saturated sodium bicarbonate (3×25 mL), dried (magnesium sulfate), and evaporated. The crude product was purified by column chromatography using diethyl ether/petrol (5:95, 10:90, 30:70, collecting fractions containing R_f 0.25). Recrystallization from ether/hexane gave **3** (1.76 g, 36% from **10**): mp 95 °C;

δ_H 7.35–7.25 (m, 3H, 3 CH), 7.02–6.92 (m, 3H, 3 CH); δ_C 186.7 (C), 129.8 (C), 128.1 (C), 126.2 (CH), 125.0 (CH), 124.9 (CH), 122.4 (CH), 123.9 (CH), 123.8 (CH), 121.2 (C), 119.2 (C); ν_{max} 3105 (C-H), 1663 (C=O), 1637 (C=C); MS (CI) m/z (rel intens) 300 (100, $[M + NH_4^+]$), 282 (15, $[M^+]$); HRMS (CI) (m/z) $C_{11}H_{10}NOS_4$ [$M + NH_4^+$] requires 299.9645, found 299.9641.

7-Thiophen-3-ylthieno[3,4-c]-1,2-dithiin (4). A solution of 1,3-dithiol-2-one **2** (0.25 g, 0.89 mmol) in benzene (15 mL) was irradiated in an air-cooled Pyrex tube for 6 h with a Rayonet apparatus at 350 nm. After removal of solvent, column chromatography gave 140 mg (92%, based on recovered **1**) of crude dithiin **4** (yellow oil) and starting material (80 mg). Compound **4** was further purified (yield 76%) by preparative TLC followed by sublimation at 40 °C and 0.03 mmHg:

δ_H 6.50 (1H, dd, $J = 9.5, 0.4$ Hz, H-3), 6.92 (1H, dd, $J = 9.5, 0.5$ Hz, H-4), 7.09 (1H, dd, $J = 0.5, 0.4$ Hz, H-5), 7.39 (1H, d, $J = 1.8$ Hz, H-2'), 7.41 (1H, d, $J = 2.5$ Hz, H-4'), 7.51 (1H, dd, $J = 2.5, 1.8$ Hz, H-5'); δ_C 121.6 (C-3), 121.8 (C-5), 122.6 (C-7a), 123.5 (C-5'), 126.2, 127.4 (C-2', C-4'), 127.25 (C-4), 133.0 (C-3'), 133.5 (C-7), 136.1 (C-4a); ν_{max} (KBr) 1652. MS (EI) m/z 254 (rel intens) (M^+ , 100), 221 (32), 209 (11), 190 (14), 177 (13), 127 (16), 69 (18). Anal. Calcd for $C_{10}H_6S_4$: C, 47.21; H, 2.38. Found: C, 47.46; H, 2.02.

7-Thiophen-2-ylthieno[3,4-c]-1,2-dithiin (13). A solution of 1,3-dithiol-2-one **3** (0.050 g, 0.177 mmol) in benzene (20 mL) was irradiated in a Pyrex tube for 5 h with a Rayonet apparatus

at 350 nm. After removal of solvent, the residue was purified by preparative TLC to give dithiin **13** (26 mg, 76%, based on recovered **3**) (yellow oil, R_f 0.46, cyclohexane) and starting material (12 mg):

δ_H 6.52 (1H, dd, $J = 9.5, 0.5$ Hz, H-3), 6.92 (1H, dd, $J = 9.5, 0.5$ Hz, H-4), 7.08 (1H, t, $J = 0.5$ Hz, H-5), 7.10 (1H, dd, $J = 5.3, 4.5$ Hz, H-4'), 7.28 (1H, dd, $J = 4.5, 1.3$ Hz, H-3'), 7.38 (1H, dd, $J = 5.3, 1.3$ Hz, H-5'); δ_C 121.8 (CH), 122.0 (CH), 123.1 (C), 126.6 (CH), 126.7 (CH), 127.2 (CH), 127.5 (CH), 132.0 (C), 134.3 (C), 136.3 (C); MS (EI) m/z (rel intens) 254 (M^+ , 100), 221 (38), 209 (16), 190 (25), 177 (18), 127 (41), 69 (43); HRMS (EI) (m/z) $C_{10}H_6S_4$ [M^+] requires 253.9352, found 253.9349.

6-Thiophen-3-yl-2,3-dihydrothieno[3,4-*b*]thiophene-2-thiol (14). Sodium borohydride (0.015 g, 0.4 mmol) was added to a stirred solution of 1,2-dithiin **4** (0.03 g, 0.12 mmol) in ethanol (2 mL) under nitrogen. After 30 min the solvent was removed and the residue treated with hydrochloric acid (0.1 N). This solution was extracted with ether (3 \times 5 mL), and the combined extracts were dried (sodium sulfate) and evaporated to give **14** (0.02 g, 65%) as a white solid: mp 193–195 °C;

δ_H 2.59 (1H, exch. d, $J = 8.5$ Hz, SH), 3.06 (1H, ddd, $J = 15.6, 5.9, 1.3$ Hz, H-3), 3.50 (1H, ddd, $J = 15.6, 6.7, 1.3$ Hz, H-3'), 5.32 (1H, ddd, $J = 8.5, 6.7, 5.9$ Hz, H-2), 6.86 (1H, t, $J = 1.3$ Hz, H-4), 7.31 (2H, m, H-2', H-4'), 7.37 (1H, dd, $J = 4.7, 3.1$ Hz, H-5'); δ_C 42.26 (C-3), 54.76 (C-2), 114.48 (C-4), 120.00 (C-4'), 124.74 (C-6), 125.89, 126.35 (C-2', C-5'), 134.26 (C-3a), 134.36 (C-3'), 143.36 (C-6a); ν_{max} 1650; MS (EI) m/z (rel intens) 256 (M^+ , 71), 223 (100), 190 (57), 177 (10), 127 (11), 111 (8), 95 (10), 69 (15), 45 (17). Anal. Calcd for $C_{10}H_8S_4$: C, 46.84; H, 3.14. Found: C, 46.56; H, 3.39.

6-Thiophen-2-ylthieno[3,4-*b*]thiophene-2-thiol (15). Sodium borohydride (0.015 g, 0.4 mmol) was added to a stirred solution of 1,2-dithiin **13** (0.03 g, 0.12 mmol) in ethanol (2 mL) under nitrogen. After 30 min the solvent was removed and the residue treated with hydrochloric acid (0.1 N). This solution was extracted with ether (3 \times 5 mL), and the combined extracts were dried (sodium sulfate) and evaporated to give **15** (0.024 g, 78%) contaminated with a small amount of the corresponding disulfide derivative:

δ_H 2.59 (1H, exch. d, $J = 8.6$, SH), 3.05 (1H, ABX, $J = 15.8, 6.0, 1.2$ Hz, H-3_A), 3.50 (1H, ABX, $J = 15.8, 6.8, 1.2$ Hz, H-3_B), 5.32 (1H, ddd, $J = 8.6, 6.8, 6.0$ Hz, H-2) 6.83 (1H, t, $J = 1.2$ Hz, H-4), 7.02–7.29 (3H, m, H-3', 4', 5'); MS (EI) m/z (rel intens) 256 (M^+ , 46), 255 (21), 223 (100), 222 (96), 209 (12), 190 (62), 177 (26). Some data for the disulfide derivative: δ_H 3.34 (2H, d, $J = 4.4$ Hz, 3-H), 5.43 (1H, t, $J = 4.4$ Hz, 2-H); MS (EI) m/z (rel intens) 510 (M^+ , 2), 442 (0.5). Attempted purification of **15** led to further disulfide formation.

2-Methylsulfanyl-6-thiophen-3-yl-2,3-dihydrothieno[3,4-*b*]thiophene (16). Sodium borohydride (0.015 g, 0.4 mmol) and a solution of sodium carbonate (0.012 g, dissolved in the minimum amount of water required) were added under nitrogen to a stirred solution of **4** (0.03 g, 0.12 mmol) in ethanol (5 mL). After 30 min methyl iodide (0.1 mL) was added and the reaction stirred for 3 h at rt. After evaporation of the reaction solvent, the residue obtained was dissolved in chloroform and the resultant solution dried and evaporated to give **16** (0.022 g, 69%) as a yellow oil (R_f 0.21 in cyclohexane):

δ_H 2.23 (3H, s, SMe), 3.07 (1H, ABX, $J = 15.9, 5.4, 1.0$ Hz, H-3), 3.36 (1H, ABX, $J = 15.9, 7.3, 1.0$ Hz, H-3'), 5.30 (1H, ABX, $J = 7.3, 5.4$ Hz, H-2) 6.76 (1H, t, $J = 1.0$ Hz, H-4), 7.21–7.48 (3H, m, H-2', 4', 5'); δ_C 14.25 (SMe), 37.0 (C-3), 63.0 (C-2), 114.0 (CH), 119.9 (CH), 124.45 (C), 125.9 (CH), 126.2 (CH), 133.2 (C), 134.55 (C), 144.2 (C); MS (EI) m/z (rel intens) 270 (M^+ , 46), 223 (100), 190 (53); HRMS (EI) (m/z) $C_{11}H_{10}S_4$ [M^+] requires 269.9665, found 269.9670.

2-Methylsulfanyl-6-thiophen-2-yl-2,3-dihydrothieno[3,4-*b*]thiophene (17). Sodium borohydride (0.015 g, 0.4 mmol) and a solution of sodium carbonate (0.012 g, dissolved in the minimum amount of water required) were added under nitrogen to a stirred solution of **13** (0.03 g, 0.12 mmol) in ethanol (5 mL). After 30 min methyl iodide (0.1 mL) was added and the reaction stirred for 3 h at rt. After evaporation of the reaction solvent, the residue obtained was dissolved in chloroform and the

resultant solution dried and evaporated to give **17** (0.023 g, 71%) as a yellow oil (R_f 0.21 in cyclohexane):

δ_H 2.26 (3H, s, SMe), 3.10 (1H, ABX, $J = 15.9, 5.4, 1.0$ Hz, H-3_A), 3.39 (1H, ABX, $J = 15.9, 7.3, 1.0$ Hz, H-3_B), 5.33 (1H, dd, $J = 7.3, 5.4$ Hz, H-2), 6.79 (1H, t, $J = 1.0$ Hz, H-4), 7.04 (1H, dd, $J = 4.7, 3.6$ Hz, H-4'), 7.13 (1H, dd, $J = 3.6, 1.0$ Hz, H-3'), 7.24 (1H, dd, $J = 4.7, 1.0$ Hz, H-5'); δ_C 14.25 (SMe), 37.1 (C-3), 63.3 (C-2), 114.2 (CH), 123.55 (CH), 124.3 (CH), 125.9 (C), 127.7 (CH), 135.1 (C), 136.6 (C), 144.2 (C); MS (EI) m/z (rel intens) 270 (M^+ , 57), 223 (100), 190 (45), 177 (12); HRMS (m/z) $C_{11}H_{10}S_4$ [M^+] requires 269.9665, found 269.9668.

6-Thiophen-3-ylthieno[3,4-*b*]thiophene (18). Methyl iodide (0.2 mL) and sodium carbonate (0.1 g) were added to a stirred solution of the thioether **16** (0.050 g, 0.19 mmol) in ethanol (5 mL). The reaction mixture was heated to reflux, and further aliquots (0.1 mL) of methyl iodide were added until the starting material was consumed (TLC). The solvent was removed in vacuo and the residue purified by chromatography (silica gel eluting with cyclohexane) to give compound **18** (0.030 mg, 72%) identical (1H and ^{13}C NMR) with an authentic sample.⁸

6-Thiophen-2-ylthieno[3,4-*b*]thiophene (19). Methyl iodide (0.2 mL) and sodium carbonate (0.1 g) were added to a stirred solution of the thioether **17** (0.050 g, 0.19 mmol) in ethanol (5 mL). The reaction mixture was refluxed with further addition of methyl iodide until the starting material was consumed (TLC). Solvent was removed in vacuo and the residue purified by chromatography (silica gel eluting with cyclohexane) to give compound **19** (28 mg, 66%) as an orange oil (R_f 0.53 in cyclohexane):

δ_H (CD_3OD , 600 MHz) δ 6.98 (1H, d, $J = 5.5$, Hz, H-3), 7.13 (1H, dd, $J = 5.0, 3.6$ Hz, H-4'), 7.29 (1H, dd, $J = 3.6, 0.9$ Hz, H-3'), 7.42 (1H, s, H-4), 7.43 (1H, dd, $J = 5.0, 0.9$ Hz, H-5'), 7.52 (1H, d, $J = 5.5$ Hz, H-2); δ_C 111.6 (CH), 118.5 (CH), 124.3 (CH), 125.4 (C-H), 129.0 (CH), 133.8 (CH), 136.4 (C), 137.2 (C), 149.6 (C); MS (EI) m/z (rel intens) 222 (M^+ , 100), 190 (20), 177 (20), 145 (7); HRMS (m/z) $C_{10}H_6S_3$ [M^+] requires 221.9632, found 221.9630.

2,3,5,6-Tetrathiophen-2-yl-1,4-dithiin (20). A solution of 1,3-dithiol-2-one **1** (0.050 g, 0.177 mmol) in benzene (20 mL) was irradiated in a Pyrex tube for 5 h with a Rayonet apparatus at 350 nm. Removal of the solvent gave crude 1,4-dithiin **20** as a yellow oil in quantitative yield:

δ_H 6.96 (1H, dd, $J = 5.1, 3.7$ Hz, H-4), 7.24 (1H, dd, $J = 3.7, 1.2$ Hz, H-3), 7.32 (1H, dd, $J = 5.1, 1.2$ Hz, H-5); δ_C 26.9 (CH), 127.9 (CH), 129.35 (CH); MS (EI) m/z (rel intens) 444 (M^+ , 15), 412 (100), 378 (8), 367 (6), 333 (7). Attempted purification by preparative layer or column chromatography resulted in complete decomposition.

2,3,4,5-Tetrathiophen-2-ylthiophene (21). The crude dithiin **20** (0.030 g, 0.067 mmol) was dissolved in acetic acid (4 mL), and 30% hydrogen peroxide (2 mL) was added. After 12 h the product **21** (21 mg, 75%) was removed by filtration and was found to be identical (mp and 1H NMR) with an authentic sample.⁹

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Supporting Information Available: Experimental details and spectral data for the synthetic intermediates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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