2-(Triphenylphosphonio)-4,5-bis(benzoylthio)-1,3-dithiole Tetrafluoroborate: A Versatile Wittig Reagent for the Synthesis of Unsymmetrical Tetrathiafulvalenes and 1,3-Dithiol-2-ylidene Derivatives

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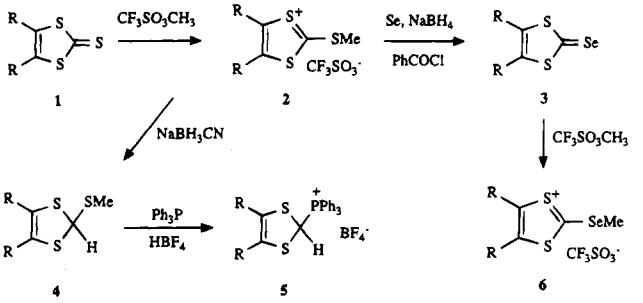
The title Wittig reagent **5** has been prepared in three steps (84% overall yield) from 4,5-bis-(benzoylthio)-1,3-dithiole-2-thione. Reactions of ylide **7**, generated by treatment of **5** with diisopropylethylamine at room temperature, have been exploited in the synthesis of new unsymmetrical tetrathiafulvalenes and 1,3-dithiol-2-ylidene derivatives. Subsequent removal of the benzoyl protecting group with sodium ethoxide liberates the transient TTF–dithiolate or 1,3-dithiole–dithiolate anions which can be alkylated *in situ*. The X-ray crystal structures of compounds **17** and **18** are reported: close nonbonded S···O intramolecular interactions are observed in both structures.

Since the initial reports that tetrathiafulvalene formed stable cation salts possessing unusual electronic properties (e.g., organic metals)[1] compounds containing the 1,3-dithiol-2-ylidene unit have received unabated attention.[2] The important properties of the 1,3-dithiole ring system that render it a particularly attractive building block for new materials are as follows:[2] (i) the ring system can be easily constructed with a range of functional groups (including fused rings) present in the 4,5 positions; (ii) the system is readily oxidized to the stable six π-electron 1,3-dithiolium cation species (cf. the TTF cation radical species responsible for high conductivity); (iii) the presence of sulfur atoms and the planarity of the 1,3-dithiolium cation assists in close intermolecular interactions in the solid state due to $\pi-\pi$ overlap. A combination of these properties has resulted in 1,3-dithiol-2-ylidene units being a key structural feature in many new π-electron donors,[3] conducting polymers,[4] Langmuir–Blodgett film materials,[5] sensors,[6] molecular shuttles,[7] as well as potential nonlinear optical,[8] and ferromagnetic materials.[9]

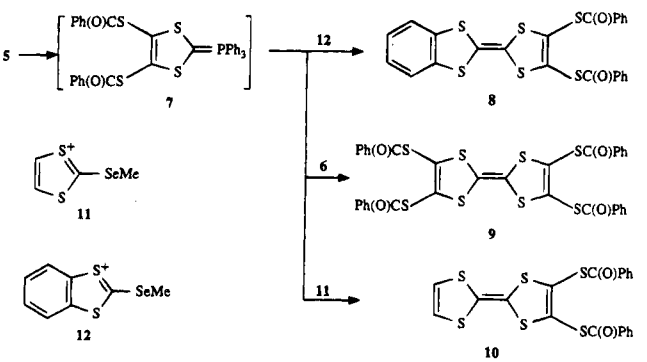
The aim of the present study was to synthesize the title Wittig-reagent **5** (Scheme 1) and to explore the reactivity of ylide **7** (Scheme 2) in the preparation of new tetrathiafulvalenes and 1,3-dithiol-2-ylidene systems. The special feature of reagent **5** is that the benzoyl protecting group can be removed in these products allowing alkylation of the resultant dithiolate anions. Reagent **5** has thus proved to be particularly versatile.

Scheme 1[a]



[a] R = SCOPh.

Scheme 2



The synthesis and reactions of reagent **5** are presented in the schemes. Our starting material was 4,5-bis-(benzoylthio)-1,3-dithiole-2-thione (**1**), which is easily prepared in large batches.[10] *S*-Methylation of **1** using

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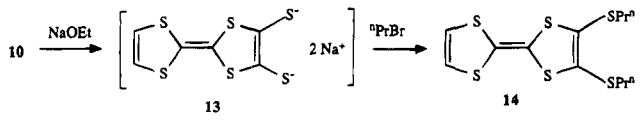
Scheme 3



methyl triflate yielded the dithiolium cation salt **2** (94% yield) which can be stored for a few weeks without decomposition. Attempted reduction of cation **2** with sodium borohydride led to extensive decomposition, whereas sodium cyanoborohydride accomplished the transformation of **2** to **4**. Thioether **4** was isolated as a low melting point solid in quantitative yield and was subsequently treated with triphenylphosphine at 0 °C, followed by addition of tetrafluoroboric acid to afford phosphonium salt **5** in 89% yield. This compound is suitable for further reactions without the need for purification, although recrystallization is profitable for obtaining a more stable, analytically pure sample of **5**, which can be stored at room temperature in the dark for several month without decomposition. The pivotal reaction in our strategy was the generation of ylide **7** from phosphonium salt **5**: this is readily achieved by treatment of the latter compound with diisopropylethylamine or triethylamine in acetonitrile at room temperature. Trapping of the transient ylide **7** by the 2-(methylseleno)-substituted 1,3-dithiolium cation salts **6** (prepared from **2**, via selenone **3**, Scheme 1), **11**, and **12** afforded TTF derivatives **8**–**10**, respectively, in 66–93% yield. This route represents an improvement over the literature synthesis[12] of **9** and provides a clean method of obtaining the new unsymmetrical TTF derivatives **8** and **10**. The reaction of a 1,3-dithiole Wittig (or Wittig–Horner) reagent with a 1,3-dithiolium cation has been used recently on occasion to synthesize unsymmetrical TTF derivatives.[13] This methodology, which can be capricious depending upon the functionality present on the 1,3-dithiole units, has the merit of avoiding the formation of mixtures of self-coupled and cross-coupled products which are notoriously difficult to separate.[14]

We have established that TTF derivative **10** can be cleanly debenzoylated (Scheme 3), thereby serving as a shelf-stable equivalent of the TTF-dithiolate dianion **13**.[15] Treatment of **10** with sodium ethoxide in ethanol at room temperature, followed by addition of *n*-propyl bromide, gave 4,5-bis(propylthio)-TTF (**14**) in 85% yield.

The versatility of ylide **7** as a reactive intermediate in the synthesis of new 1,3-dithiol-2-ylidene derivatives has been demonstrated in the following experiments. Trapping of **7** with the appropriate aldehyde gave compounds

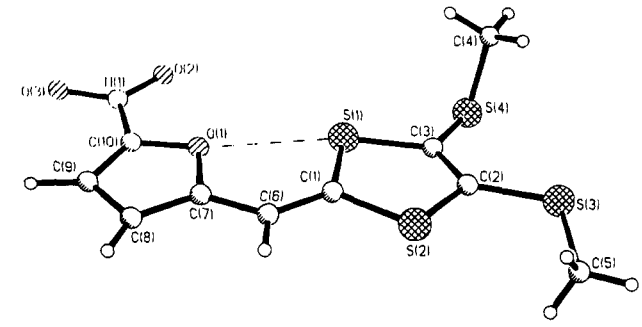
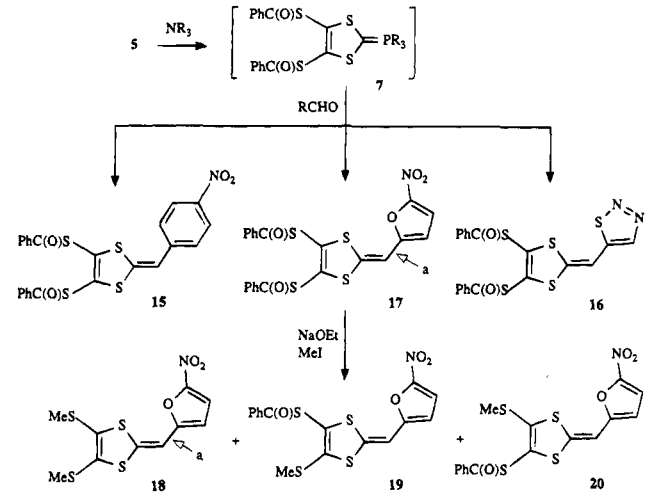


Figure 1. X-ray structure of compound **18**.

Scheme 4



15–**17** (31–75% yield). Deprotection of compound **17** and methylation of the resultant thiolate anion species has been examined. Reaction of **17** with 2 equiv of sodium ethoxide, followed by addition of an excess of methyl iodide, gave bis(methylthio) derivative **18** (93% yield). The same reaction, employing only 1 equiv of ethoxide and an excess of methyl iodide, gave three products which were identified as compound **18** (25% yield) and an unseparable mixture of the two regioisomers **19** and **20** in a 1:1 ratio as judged by ^{1}H-NMR (the combined yield of **19** and **20** is 52%). This experiment was carried out in order to investigate a possible nonbonded intramolecular interaction observed in the solid-state structures of **17** and **18** (discussed below) which could imply restricted rotation about the bonds marked "a" (Scheme 4).

It should be noted that compound **4** could be deprotected in a manner similar to that of **1**. This procedure may be relevant in cases where a desired substituent cannot withstand the methylation step. It can then be introduced at this stage. An example of a procedure for deprotection of **4** and subsequent dialkylation with propyl bromide to afford **21** is given in the Experimental Section.

The molecular structures of compounds **18** and **17**, determined by single X-ray analysis,[16] are shown in Figures 1 and 2, respectively. Compound **18** crystallizes with two independent molecules in the unit cell, arranged in centrosymmetric dimers. Analysis of the bond lengths provides no evidence for any significant degree of in-

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(16) Further data (including packing diagrams) on the X-ray structures of **17** and **18** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

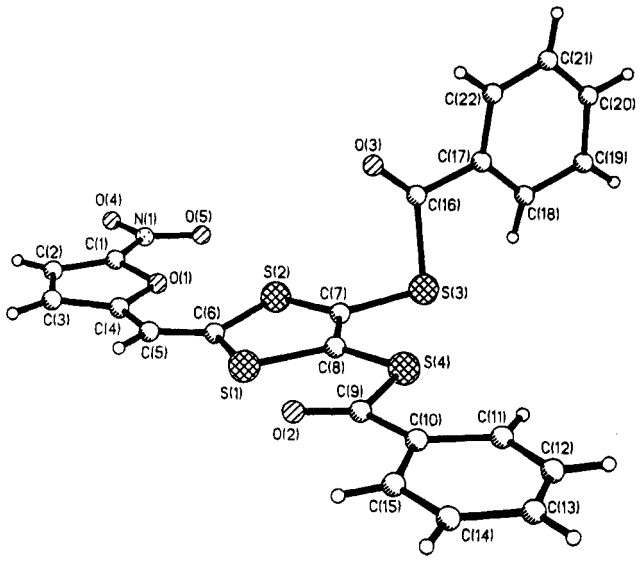

Figure 2. X-ray structure of compound **17**.

tramolecular charge transfer which could arise from the 1,3-dithiol-2-ylidene unit to the nitrofuran (acceptor) unit. The dithiole and furan rings are almost coplanar with a close intramolecular nonbonded contact between O(1)···S-(1) of 2.86 Å (cf. the van der Waals radii of oxygen and sulfur which are 1.40 and 1.80 Å, respectively). The bond lengths and angles within the nitrofuran and dithiol-2-ylidene portions of compounds **17** are very similar to those of compounds **18**. The nonbonded contact O(1)···S-(2) for compound **17** is 2.82 Å. An additional interesting feature of the structure of **17** is that one of the benzoylthio substituents is coplanar with the dithiole ring to which it is attached, and a close nonbonded contact, O(2)···S(1) 2.56 Å, is observed.

Experimental Section

General. Solvents and reagents were standard reagent grade and used as received unless otherwise stated. Dry solvents were obtained by standard techniques.

Preparation of 2. To a slurry of 6.5 g (16.0 mmol) of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione in 60 mL of CH_2Cl_2 was added 2.9 g (17.7 nmole) of methyl triflate. After 1–2 h of stirring the solution became homogeneous, but stirring was continued for a further 3–4 h. The solvent was partially removed under vacuum until precipitation started, and then a layer of dry diethyl ether (100 mL) was placed on top of the CH_2Cl_2 layer. The two layers mixed overnight and completed precipitation. A pale yellow solid was filtered off and dried. Yield: 8.6 g (94%). The compound was best used within a few weeks. Recrystallization from acetonitrile/ether gave an analytically pure product. Mp: 185–86 °C. ^{1}H-NMR (CD_3CN; 250 MHz) δ: 8.07 (4H, d, J = 9 Hz); 7.82 (2H, t, J = 9 Hz); 7.64 (4H, t, J = 9 Hz); 3.21 (3H, s). Anal. Calcd for $C_{19}H_{13}O_5S_6F_3$: C, 40.14; H, 2.28. Found: C, 40.44; H, 2.13. IR (KBr) (cm^{-1}): 1689, 1259, 1208, 1030.

Preparation of 3. A mixture of finely powdered elemental selenium (1.8 g; 23 mmol) and powdered sodium borohydride (1.0 g; 27 mmol) was stirred as a slurry in dry 2-propanol (30 mL) under nitrogen. After 90 min the mixture was homogeneous and colorless. THen 3.0 g of freshly prepared **2** was added and the reddish mixture was stirred for 20 min whereupon benzoyl chloride (4 mL) was added and the mixture was left with stirring for a further 1 h. Water (50 mL) was added to the mixture which subsequently was extracted with three portions of CH_2Cl_2. After the organic phase was dried with $MgSO_4$ the solvent was partly removed under vacuum until precipitation started. Addition of methanol completed precipitation of a red solid. Yield: 1.8 g (76%). Mp: 165–7 °C (lit.[17] mp 139–42 °C). ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 8.02 (2H, d, J = 8 Hz); 7.96 (2H, d, J = 8 Hz); 7.68 (2H, t, J = 8 Hz); 7.52 (4H, t, J = 8 Hz). MS (EI) m/z (rel int): 454 (M^+, 22 (based on ^{80}Se, the ion cluster shows the expected isotopic pattern for an ion with one selenium atom)) 330 (4); 301 (10); 288 (9); 160 (6); 105 (100); 77 (36).

Preparation of 4. A fresh sample of **2** (2.85 g; 5 mmol) was added portionwise to an ice-cooled solution of sodium cyanoborohydride (0.40 g; 6.5 mmol) in absolute ethanol (50 mL) under nitrogen. The solution quickly became homogeneous. After the mixture was stirred for 30 min the solvent was removed on a rotary evaporator (avoiding excess heating) and the remaining oily substance was filtered through a short silica gel column using CH_2Cl_2 as eluent. After evaporation of the solvent in vacuo a pale yellow oil remained. Yield: 2.1 g (100%). This product, which was pure by TLC and ^{1}H-NMR, could be crystallized at low temperature in ether but melted at rt. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 7.95–7.91 (4H, m), 7.63–7.57 (2H, m); 7.49–7.43 (4H, m); 6.22 (1H, s); 2.64 (3H, s). Anal. Calcd for $C_{18}H_{14}O_2S_5$: C, 51.18; H, 3.32. Found: C, 51.01; H, 3.54. IR (KBr) (cm^{-1}): 1691, 1680, 1675, 1448, 1207, 1176. MS (CI/NH_3) m/z (rel int): 423 ($M + H)^+$, 1); 421 (5); 378 (5); 375 (100, $-CH_3S$); 317 (5); 105 (14). (EI): 375 (5); 105 (100).

Preparation of 5. To an ice-cooled solution of **4** (4.2 g, 10 mmol) in dry ether (60 mL) was added triphenylphosphine (3.0 g), and after the phosphine was dissolved completely, HBF_4 (5 mL of a 54% solution in diethyl ether) was added dropwise with stirring. After the mixture was stirred for 20 min the precipitated off-white solid was filtered under suction and dried in a stream of nitrogen. Yield: 6.43 g (89%). The product was suitable for further reactions, but a more stable, analytically pure, product was obtained by additional recrystallization from acetonitrile/ether. Mp: 175–76 °C. ^{1}H-NMR (CD_3CN; 250 MHz) δ: 8.03–7.54 (25H, m); 7.27 (1H, d, J_{HP} = 3 Hz). Anal. Calcd for $C_{35}H_{26}O_2S_4PBF_4$: C, 58.09; H, 3.60. Found: C, 58.15; H, 3.56. IR (KBr) (cm^{-1}): 1685 (s), 1439, 1207, 1110 (s), 1084 (s).

Preparation of 6. Compound **3** (1.0 g; 2.2 mmol) and methyl triflate (0.4 g; 2.4 mmol) were dissolved in dry CH_2Cl_2 (30 mL) and stirred for 3 h. Precipitation was completed by addition of 75 mL of dry ether to afford 0.88 g (65%) of **6** as an off-white solid. Mp: 131–133 °C. ^{1}H-NMR (CD_3CN; 250 MHz) δ: 8.05 (4H, t, J = 7 Hz); 7.77 (2H, pentet, J = 7 Hz); 7.62 (4H, q, J = 7 Hz); 3.15 (3H, s). Anal. Calcd for $C_{19}H_{13}O_5S_5SeF_3$: C, 37.01; H, 2.11. Found: C, 37.02; H, 2.16. IR (KBr) (cm^{-1}): 1687, 1446, 1198, 1174.

Preparation of 8. Compound **5** (250 mg; 0.35 mmol) and **12** (135 mg; 0.35 mmol) were dissolved in 10 mL of dry acetonitrile, and triethylamine (4 mL of a 0.1 M solution in acetonitrile) was added. A dark red solid precipitated rapidly and was filtered off after 15 min and washed with a few drops of methanol. The solid (120 mg 66%) was pure by NMR. An analytical sample was prepared by recrystallization from toluene. Mp: 187 °C. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 8.01 (d, 2H); 7.8–7.1 (m, 12 H). Anal. Calcd for $C_{24}H_{14}O_2S_6$: C, 54.75; H, 2.66. Found: C, 54.55; H, 2.64. IR (KBr) (cm^{-1}): 1687, 1447, 1206, 1177, 889. MS (EI) m/z (rel int): 526 (M^+; 3); 476 (4); 380 (4); 301 (5); 105 (100) ($-$PhCO).

Preparation of 9. Compounds **5** (300 mg; 0.41 mmol) and **6** (260 mg; 0.41 mmol) were mixed in acetonitrile (10 mL). Diisopropylethylamine (0.5 mL) was added to the mixture, whereupon a red solid precipitated and was filtered off after 15 min. This solid was identical by TLC and mixed melting point to an authentic sample of **9**. Yield: 250 mg (82%). Mp: 195–7 °C (lit.[12] mp 195 °C).

Preparation of 10. To a mixture of **3** (0.25 g, 0.73 mmol) and **5** (0.53 g; 0.73 mmol) dissolved in acetonitrile (20 mL) was added diisopropylethylamine (1 mL), producing an almost immediate red coloration. After 15 min the reaction mixture was diluted with CH_2Cl_2 (50 mL) and then washed with water

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(3 × 25 mL), dried with $MgSO_4$, and evaporated under vacuum. The residue was chromatographed on a silica gel column using a CH_2Cl_2/hexane (1:3) mixture as eluent. The red iodine-active fraction was evaporated to afford a dark red solid, which afforded red crystals from hot dichlorobenzene. Yield: 120 mg (35%). Mp: 180 °C. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 7.95–7.26 (10H, m); 6.3 (2H, s). Anal. Calcd for $C_{20}H_{12}O_2S_6$: C, 50.41; H, 2.52. Found: C, 50.09; H, 2.49. IR (KBr) (cm^{-1}): 1688, 1636, 1207, 1178. MS (CI/NH_3): 477 ($(M + H)^+$, 11); 337 (11); 267 (6); 243 (22); 237 (14); 122 (30); 105 (100).

Preparation of 11. Four hundred mg (1.9 mmol) of 1,3-dithiole-2-selenone[17a,18] was dissolved in 10 mL of CH_2Cl_2, and 0.33 g (2.0 mmol) of methyl triflate was added. The mixture was stirred overnight, and then 40 mL of dry ether was added to precipitate an off-white crystalline solid which was filtered and dried under nitrogen. Yield: 600 mg (92%). Mp: 154 °C. ^{1}H-NMR (CD_3CN; 250 MHz) δ: 8.77 (2H, s); 3.11 (3H, s). Anal. Calcd for $C_5H_5S_3SeO_3F_3$: C, 17.64; H, 1.45. Found: C, 18.07; H, 1.58. IR (KBr) (cm^{-1}): 1279 (s); 1235 (s); 1032 (s).

Preparation of 12. Benzo[*c*]-1,3-dithiole-2-selenone (2.3 g, 10 mmol) was dissolved in dry CH_2Cl_2 (15 mL), and methyl triflate (2.0 g, 1.2 mmol) was added. After 3 h dry ether (50 mL) was added slowly with stirring to precipitate an orange crystalline solid (3.7 g, 93%). Mp: 167 °C. ^{1}H-NMR (CD_3CN; 250 MHz) δ: 8.46 (dd, 2H, J_a = 8 Hz; J_b = 3 Hz); 7.91 (dd, 2H, J_a = 8 Hz; J_b = 3 Hz); 3.23 (s, 3H). Anal. Calcd for $C_9H_7O_3F_3S_3Se$: C, 27.34; H, 1.77. Found: C, 27.18; H, 1.79.

Preparation of 14. Compound **10** (600 mg; 1.3 mmol) was dissolved in dry THF (25 mL) under nitrogen, and sodium ethoxide (prepared from 75 mg of sodium dissolved in 10 mL of absolute ethanol, 2.5 equiv) was added. After 10 min of stirring *n*-propyl bromide (1 mL) was added to the dark solution which was stirred for a further 1 h. After evaporation of the solvent, the residue was chromatographed on silica gel using CH_2Cl_2/hexane as eluent (1:3). The yellow, iodine-active fraction was an oil (380 mg, 85%) after drying in vacuo. The compound was pure by ^{1}H-NMR. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 6.32 (2H, s), 2.79 (4H, t, J = 7 Hz), 1.67 (4H, m), 1.04 (6H, t, J = 7 Hz). MS (EI) *m/z* (rel int) 352 (100); 309 (27); 276 (44); 267 (40); 244 (10); 179 (19); 146 (93); 102 (32). HRMS: calcd *m/z* 351.95763; found *m/z* 351.95296.

Preparation of 15. Compound **5** (500 mg; 0.69 mmol) and 4-nitrobenzaldehyde (150 mg; 1.0 mmol) was dissolved in acetonitrile (15 mL), and diisopropylethylamine (1 mL) was added. A yellow crystalline solid precipitated, which was dried to afford 150 mg (43%) of **15**. It was possible to recover 20–25% more of **15** from the mother liquor, using chromatography (CH_2Cl_2 as eluent, silica gel as stationary phase). Mp: 172–75 °C. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 8.41–7.31 (14H; m), 6.61 (1H, s). Anal. Calcd for $C_{24}H_{15}O_4NS_4$: C, 56.58; H, 2.95; N, 2.75. Found: C, 56.31; H, 3.26; N, 2.52. IR (KBr) (cm^{-1}): 1685, 1439, 1207, 1110, 1084. MS (CI/NH_3) *m/z* (rel int): 510 ($(M + H)^+$, 5); 374 (51); 344 (10); 243 (24); 240 (7); 150 (6); 122 (31); 105 (100).

Preparation of 16. Compound **5** (200 mg; 0.28 mmol) was dissolved in acetonitrile (5 mL) with 5-formylthiadiazole[19] (50 mg; 0.4 mmol) and triethylamine (0.25 mL). A yellow solid precipitated immediately. Yield: 40 mg (31%). In the solid state the compound is stable, but in basic solution it decomposed in less than 1 h. Mp: 194–95 °C. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 8.11 (1H, s); 7.95 (4H, d, J = 7.9 Hz); 7.63 (2H; t, J = 7.9 Hz); 7.48 (4H, t, J = 7.9 Hz); 6.87 (1H, s). Anal. Calcd for $C_{20}H_{12}S_5O_2N_2$: C, 50.85; H, 2.54; N, 5.93. Found: C, 51.03; H, 2.66; N, 5.76. MS: neither EI nor CI ionization gave an M^+ ion. Both spectra were dominated by *m/z* 105 (loss of PhCO).

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Preparation of 17. Wittig-reagent **5** (1.12 g; 1.5 mmol) and 5-nitrofurfural (0.2 g; 1.5 mmol) were dissolved in dry acetonitrile (10 mL) and treated with diisopropylethylamine (1 mL). A deep-red solid precipitated and was filtered off. Yield: 0.58 g (75%). Mp: 215–6 °C. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 7.93–7.44 (10H, arom mult); 7.38 (1H, d, J = 3.9 Hz); 6.47 (1H, s); 6.27 (1H, d, J = 3.9 Hz). Anal. Calcd for $C_{22}H_{13}NO_5S_4$: C, 52.91; H, 2.61; N, 2.81. Found: C, 53.22; H, 2.69; N, 2.96. IR (KBr) (cm^{-1}): 1692, 1585, 1484, 1449, 1348, 1239, 1206, 1175. MS: no M^+ ion was observed in EI or CI (NH_3) mass spectrometry.

Preparation of 18. Compound **17** (160 mg; 0.32 mmol) was dissolved in dry THF (25 mL) under nitrogen with stirring. A solution of sodium ethoxide in absolute ethanol (8 mL; 0.1 M) was added all at once. The solution turned from dark reddish to very dark blue immediately. After 5 min methyl iodide (0.5 mL) was added, and the solution became deep red after a few minutes. After an additional 15 min of stirring the solvent was removed in vacuo, and the residue was dissolved in the minimum amount of CH_2Cl_2 and chromatographed on a short silica gel column using CH_2Cl_2 as eluent. The strongly colored fraction was collected and afforded a dark green solid **18** (95 mg, 93% yield) which was pure by TLC (the color was red-violet on the TLC plates and in solution). Metallic-green crystals of X-ray quality were grown by cooling a hot solution of **18** in acetonitrile. Mp: 180–81 °C. ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 7.40 (1H, d, J = 4.8 Hz); 6.40 (1H s); 6.25 (1H, d, J = 4.8 Hz); 2.50 (3H, s); 2.47 (3H, s). Anal. Calcd for $C_{10}H_9O_3NS_4$: C, 37.61; H, 2.82; N, 4.39. Found: C, 37.70; H, 2.82; N, 4.28. MS (EI) *m/z* (rel int): 319 (M^+, 100); 288 (40); 274 (5); 245 (2); 242 (2); 94 (3).

Preparation of 19 and 20. The procedure was similar to the one used for **18** starting with **17** (160 mg) but using only 1 equiv of sodium ethoxide. Separation of three colored fractions was achieved using a silica column and toluene as eluent. The first fraction was solid **18** (26 mg; 25%), and the second (a deep red oil) was the desired monoprotected mixture (68 mg, 52%) which consisted as a 1:1 mixture (from NMR) of the two regioisomers **19** and **20**. Although the spots of the mixture were elongated on analytical TLC-plates indicating the presence of two isomers, a preparative scale separation could not be achieved. The third colored fraction (18 mg; 11%) was starting material **17**. ^{1}H-NMR ($CDCl_3$; 500 MHz) δ: 7.98 (4H, dd, J_a = 7.5 Hz; J_b = 4 Hz); 7.66 (2H, t, J = 7.5 Hz); 7.52 (4H, t, J = 7.4 Hz); 7.41 (1H, d, J = 4.0 Hz); 7.39 (1H, d, J = 4.0 Hz); 6.44 (1H, s); 6.42 (1H, s); 6.27 (1H, d, J = 4.0 Hz); 6.25 (1H, d, J = 4.0 Hz); 2.56 (3H, s); 2.49 (3H, s). MS (CI/NH_3) *m/z* (rel int): 410 ($[M + H]^+$, 8); 275 (10); 274 (15); 135 (10); 139 (32); 122 (100); 105 (35); 78 (12).

Preparation of 2-(Methylsulfanyl)-4,5-bis(propylsulfanyl)[1,3]dithiole (21). Compound **4** (850 mg, 2.0 mmol) was dissolved in dry THF (10 mL) and kept under nitrogen. A solution of sodium ethoxide in ethanol (25 mL; 0.1 M) was added. The solution turned dark immediately, and after 5 min *n*-propyl bromide (0.5 mL) was added. Chromatographic workup using a 1:1 mixture of hexane/CH_2Cl_2 as eluent and silica gel as stationary phase afforded **21** as a yellow oil which was pure by NMR. Yield: 400 mg (67%). ^{1}H-NMR ($CDCl_3$; 250 MHz) δ: 5.76 (1H, s); 2.49–2.88 (2H, mult); 2.72–2.61 (2H, mult); 2.25 (3H, s); 1.77–1.60 (4H, mult); 1.01 (6H, t, J = 7.4 Hz). MS (EI) 298 (M^+, 21); 251 (100); 209 (14); 167 (13); 119 (9); 105 (17); 45 (20); 43 (85); calcd 298.00121, found 298.00123.

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