Supporting Information

Abnormally mild synthesis of bis(dithiolo)pyrroles from 2,5-dimethylpyrroles

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Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Specord M-80 instrument in KBr pellets. ¹H NMR were recorded on a Bruker WM 250 spectrometer (250 MHz) and ¹³C NMR spectra were recorded on a Bruker AM 300 (75.5 MHz) in CDCl₃ solution. CH groups were identified by DEPT experiments. J-values are given in Hz. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument using electron impact ionisation. Light petroleum refers to the fraction bp 40-60°C.

General procedure for the preparation of 3 and 6. Disulfur dichloride (12.5 mmol) was added dropwise at –25 to –35 °C to a stirred solution of DABCO (12.5 mmol) in chloroform (40 ml) under argon. The mixture was stirred at r.t. for 1 h. The corresponding substituted 2,5-dimethylpyrrole (5 mmol) in chloroform (10 ml) was added, the mixture was stirred at 0 °C for 48 h under argon, filtered and solvents were evaporated. The residue was separated by column chromatography (Silica gel Merck 60, light petroleum and then light petroleum – CH₂Cl₂ mixtures).

General procedure for the preparation of 4 from 3. Disulfur dichloride (3.6 mmol) was added dropwise at –25 to –35 °C to a stirred solution of DABCO (3.6 mmol) in chloroform (10 ml) under argon. The mixture was stirred at r.t. for 1 h. The corresponding pentathiepin **3** (0.7 mmol) in chloroform (5 ml) was added, the mixture was stirred at r.t. for 1 h and then refluxed for 15 min, filtered and solvents were evaporated. The residue was separated by column chromatography (Silica gel Merck 60, light petroleum and then light petroleum – CH₂Cl₂ mixtures).

7-Benzyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepin[6,7-c]pyrrole 3a. Yield 60 %. Yellow crystals, mp 154-156°C. Found (%): C, 45.24; H, 3.91; N, 4.35. Calc. for C₁₃H₁₃NS₅ (%): C,

45.45; H, 3.81; N, 4.08. Found M^+ , 342.9651; $C_{13}H_{13}NS_5$ requires M , 342.9652. 1H NMR ($CDCl_3$) δ : 2.30 (6H, s, $2CH_3$), 5.02 (2H, s, CH_2), 6.94 (2H, d, $J = 7.2$ Hz), 7.33 (3H, m, ArH). ^{13}C NMR ($CDCl_3$) δ : 11.4 ($2CH_3$), 48.7 (CH_2), 125.8, 127.9, 129.2 (3 C-H), 129.7, 135.4, 136.1 (3 sp^2 tertiary C). IR, (KBr) ν/cm^{-1} : 2952(C-H), 2908(C-H), 2852(C-H), 1520, 1452, 1440, 1400, 1372, 1352, 1304, 1236, 1028, 1004, 956, 904, 828, 800, 736, 700, 652. MS, m/z (%): 343 (M^+ , 3), 279 (25), 91 (100), 64 (50), 39 (18).

6,7,8-Trimethyl-7H-[1,2,3,4,5]pentathiepine[6,7-c]pyrrole 3b. Yield 36 %. Yellow crystals, mp 157-159°C. Found (%): C, 31.75; H, 3.43; N, 5.18. Calc. for $C_7H_9NS_5$ (%): C, 31.47; H, 3.40; N, 5.25. Found M^+ , 266.9331; $C_7H_9NS_5$ requires M , 266.9339. 1H NMR ($CDCl_3$) δ : 2.48 (6H, s, $2CH_3$), 3.40 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$) δ : 11.3 ($2CH_3$), 31.8 (CH_3), 120.5, 135.2 (2 sp^2 tertiary C). IR, (KBr) ν/cm^{-1} : 2928 (C-H), 2856 (C-H), 1520, 1432, 1424, 1396, 1368, 1348, 1032, 996, 808, 780. MS, m/z (%): 267 (M^+ , 25), 203 (100), 170 (60), 64 (26), 56 (64).

7-Ethyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepine[6,7-c]pyrrole 3c. Yield 40 %. Yellow crystals, mp 159-160°C. Found (%): C, 34.35; H, 3.86; N, 5.09 %. Calc. for $C_8H_{11}NS_5$ (%): C, 34.17; H, 3.95; N, 4.98. Found M^+ , 280.9485. $C_8H_{11}NS_5$ requires M , 280.9495. 1H NMR ($CDCl_3$) δ : 1.28 (3H, t, $J = 7.2$ Hz, CH_3), 2.36 (6H, s, $2CH_3$), 3.80 (2H, q, $J = 7.2$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ : 11.0 (CH_3), 15.4 (CH_3), 40.2 (CH_2), 120.8, 134.4 (2 sp^2 tertiary C). IR, (KBr) ν/cm^{-1} : 2976 (C-H), 1520, 1472, 1440, 1404, 1376, 1348, 1080, 1012, 756. MS, m/z (%): 281 (M^+ , 13), 249 (2), 219 (14), 217 (100), 185 (13), 184 (53), 152 (12).

6,8-Dimethyl-7-propyl-7H-[1,2,3,4,5]pentathiepine[6,7-c]pyrrole 3d. Yield 38 %. Yellow crystals, mp 134-135°C. Found M^+ , 294.9653 $C_9H_{13}NS_5$ requires M , 294.9652. Found (%): C, 36.82; H, 4.52; N, 4.68. Calc. for $C_9H_{13}NS_5$ (%) C, 36.61; H, 4.44; N, 4.75. 1H NMR ($CDCl_3$) δ : 0.95 (3H, t, $J = 7.2$ Hz, CH_3), 1.66 (2H, dd, $J = 7.9$ and 7.2 Hz, CH_2), 2.35 (6H, s, $2CH_3$), 3.67 (2H, t, $J = 7.9$ Hz, CH_2). ^{13}C NMR ($CDCl_3$) δ : 9.9 (CH_3), 12.5 ($2CH_3$), 23.5 (CH_2), 47.00 (CH_2), 120.8, 134.7 (2 sp^2 tertiary C). IR, (KBr) ν/cm^{-1} : 2960 (C-H), 2924 (C-H), 2868 (C-H), 1532, 1512, 1464, 1444, 1384, 1400, 1352, 1172, 1036, 1004, 812, 804. MS, m/z (%): 295 (M^+ , 10), 231 (46), 198 (12), 83 (17), 64 (46), 4. (100).

7-Isopropyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepine[6,7-c]pyrrole 3e. Yield 37 %. Yellow crystals, mp 139-140°C. Found (%): C, 36.77; H, 4.64; N, 4.59. Calc. for $C_9H_{13}NS_5$ (%) C, 36.61; H, 4.44; N, 4.75. Found M^+ 294.9650. $C_9H_{13}NS_5$ requires M , 294.9652. 1H NMR ($CDCl_3$) δ : 1.49 (6H, d, $J = 6.8$ Hz, $2CH_3$), 2.43 (6H, s, $2CH_3$), 4.41 (1H, sept, $J = 6.8$ Hz, CH); δ_c ($CDCl_3$) 12.5 ($2CH_3$), 21.7 ($2CH_3$), 49.4 (C-H), 121.4, 134.6 (2 sp^2 tertiary C). IR, (KBr) ν/cm^{-1} : 2996 (C-H), 2972 (C-H), 2852 (C-H), 1532, 1516, 1460, 1436, 1408, 1388, 1360, 1304, 1260, 1156, 1132, 1080, 1010, 800, 724. MS, m/z (%): 295 (M^+ , 30) 231 (100), 189(16), 156(22), 83(15), 64 (18), 43 (27).

4-Benzyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione 4a. Yield 84 %. Red crystals, mp 221-223°C. Lit. data: mp 223-224°C.^[5]

4-Methyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione 4b. Yield 85 %. Red crystals, mp 190-192°C. Found (%): C, 28.70; H, 1.02; N, 4.80. Calc. for C₇H₃NS₆ (%): C, 28.68; H, 1.03; N, 4.78. Found M⁺, 292.8595. C₇H₃NS₆ requires M, 292.8589. ¹H NMR (CDCl₃) δ 4.64 (3H, s, CH₃). ¹³C NMR (CDCl₃) δ 29.5 (CH₃), 136.3 and 143.7 (C=C-CS), 202.6 (C=S), IR, (KBr) ν/cm⁻¹: 2964(C-H), 2856 (C-H), 1496 1428, 1422, 1362, 1270, 1146, 1086, 1034, 1014, 825(C=S), MS, m/z (%): 293 (M⁺, 13), 260 (4), 229 (5), 216 (3), 160 (7), 112 (32), 100 (33), 64 (72), 44 (100).

4-Ethyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione 4c. Yield 80 %. Red crystals, mp 240-242°C. Lit. data: mp 242-243°C.^[5]

4-Propyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione 4d. Yield 74 %. Red crystals, mp 175-177°C. Found C, 33.94; H, 2.33; N, 4.36. Calc. for C₉H₇NS₆ C, 33.66; H, 2.20; N, 4.36. Found 320.8897. Calc. for C₉H₇NS₆ 320.8903. ¹H NMR (CDCl₃) δ: 0.95 (3H, t, *J* = 7.2 Hz, CH₃), 1.88 (2H, dd, *J* = 7.9 and 7.2 Hz, CH₂), 5.27 (2H, t, *J* = 7.9 Hz, CH₂). ¹³C NMR (Py-d₅) δ 10.0 (CH₃), 25.9 and 41.0 (2 CH₂), 135.4 and 149.8 (C=C-CS), 199.7(C=S) IR, (KBr) ν/cm⁻¹: 2964 (C-H), 2920 (C-H), 1648, 1432, 1376, 1332, 1186, 1144, 1088, 1004, 832(C=S); MS, m/z (%): 321 (M⁺, 40), 281(25), 247(23), 221(21), 207(28), 112(36), 100(42), 64(49), 41(100).

4-Isopropyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione 4e. Yield 79 %. Red crystals, mp 172-173°C. Found C, 33.76; H, 2.36; N, 4.58. Calc. for C₉H₇NS₆ C, 33.66; H, 2.20; N, 4.36. Found 320.8902. Calc. for C₉H₇NS₆ M, 320.8903. ¹H NMR (CDCl₃) δ 1.8 (6H, d, *J* = 6.5 Hz, CH₃), 6.98 (1H, sept, *J* = 6.5 Hz, CH). ¹³C NMR (Py-d₅) δ 22.5 (CH₃), 46.4 (CH), 135.5 and 149.9 (C=C-CS), 200.1 (C=S) IR, (KBr) ν/cm⁻¹: 2964(C-H), 2924(C-H), 2856(C-H), 1476 1428, 1412, 1352, 1304, 1260, 1176, 1096, 1044, 1024, 840(C=S), 800(C=S). MS, m/z (%): 321 (M⁺, 100), 305 (10), 288 (40), 245 (16), 224(14), 203(14), 160(16), 126(18), 123 (40), 100(60), 88 (25), 64(60), 41(78).

7-Methyl-6,8-diphenyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole 6. Yield 62 %. Yellow crystals, mp 252-253°C. Found (%): C, 52.35; H, 3.48; N, 3.22. Calc. for C₁₇H₁₃NS₅ (%): C, 52.18; H, 3.35; N, 3.58. Found M⁺, 390.9669. C₁₇H₁₃NS₅ requires M, 390.9651. ¹H NMR (CDCl₃) δ: 3.34 (3H, s, CH₃), 7.46 (10H, m, ArH). ¹³C NMR (CDCl₃) δ: 34.8 (CH₃), 125.7, 128.5, 128.9 (3 C-H), 131.1, 130.3, 139.9 (3 sp² tertiary C). IR, (KBr) ν/cm⁻¹: 3052, 1472, 1440, 1428, 1376, 1076, 1008, 920, 812, 780, 752, 700. MS, m/z (%): 391 (M⁺, 20), 327 (100), 295 (52), 280 (15), 118 (53).

Figure S1. ^1H NMR spectrum of 7-benzyl-6,8-dimethyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3a** (CDCl_3).

Figure S2. ^{13}C NMR spectrum of 7-benzyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepinol[6,7-*c*]pyrrole **3a** (CDCl_3).

Figure S3. Mass-spectrum of 7-benzyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepinol[6,7-c]pyrrole **3a**.

Figure S4. ^1H NMR spectrum of 6,7,8-trimethyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3b** (CDCl_3).

Figure S5. ^{13}C NMR spectrum of 6,7,8-trimethyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3b** (CDCl_3).

Figure S6. Mass-spectrum of 6,7,8-trimethyl-7H-[1,2,3,4,5]pentathiepine[6,7-c]pyrrole **3b**.

Figure S7. ^1H NMR spectrum of 7-ethyl-6,8-dimethyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3c** (CDCl_3).

Figure S8. ^{13}C NMR spectrum of 7-ethyl-6,8-dimethyl-7*H*-[1,2,3,4,5]pentathiepinol[6,7-*c*]pyrrole **3c** (CDCl_3).

Figure S9. Mass-spectrum of 7-ethyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3c**.

Figure S10. ^1H NMR spectrum of 6,8-dimethyl-7-propyl-7H-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3d** (CDCl_3).

Figure S11. ^{13}C NMR spectrum of 6,8-dimethyl-7-propyl-7*H*-[1,2,3,4,5]pentathiepinol[6,7-*c*]pyrrole **3d** (CDCl_3).

Figure S12. Mass-spectrum of 6,8-dimethyl-7-propyl-7H-[1,2,3,4,5]pentathiepine[6,7-c]pyrrole **3d**.

Figure S13. ^1H NMR spectrum of 7-isopropyl-6,8-dimethyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3e** (CDCl_3).

Figure S14. ^{13}C NMR spectrum of 7-isopropyl-6,8-dimethyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **3e** (CDCl_3).

Figure S15. Mass-spectrum of 7-isopropyl-6,8-dimethyl-7H-[1,2,3,4,5]pentathiepinol[6,7-*c*]pyrrole **3e**.

Figure S16. ^1H NMR spectrum of 4-methyl-3*H*-bis[1,2]dithiolol[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4b** (CDCl_3).

Figure S17. ^{13}C NMR spectrum of 4-methyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4b** (CDCl_3).

Figure S18. Mass-spectrum of 4-methyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4b**.

Figure S19. ^1H NMR spectrum of 4-propyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4d** (CDCl_3).

Figure S20. ^{13}C NMR spectrum of 4-propyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5-(4*H*)-dithione **4d** (pyridine- d_5).

Figure S21. Mass-spectrum of 4-propyl-3*H*-bis[1,2]dithiolol[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4d**.

Figure S22. ^1H NMR spectrum of 4-isopropyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4e** (CDCl_3).

Figure S23. ^{13}C NMR spectrum of 4-isopropyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3',4'-*d*]pyrrole-3,5-(4*H*)-dithione **4e** (pyridine- d_5).

Figure S24. Mass-spectrum of 4-isopropyl-3*H*-bis[1,2]dithiolol[4,3-*b*:3',4'-*d*]pyrrole-3,5(4*H*)-dithione **4e**.

Figure S25. ^1H NMR spectrum of 7-methyl-6,8-diphenyl-7*H*-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **6** (CDCl_3).

Figure S26. ^{13}C NMR spectrum of 7-methyl-6,8-diphenyl-7H-[1,2,3,4,5]pentathiepine[6,7-*c*]pyrrole **6** (CDCl_3).

Figure S27. Mass-spectrum of 7-methyl-6,8-diphenyl-7H-[1,2,3,4,5]pentathiepinol[6,7-*c*]pyrrole 6.