Supplementary Material (ESI) for Chemical Communications

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A bromine catalysed dimerisation of α,α'-dihalomonopyrrolo-TTF

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ELECTRONIC SUPPLEMENTARY INFORMATION

(7 Pages)

CONTENT

Experimental Details

CH_2Cl_2 was distilled before use and THF was distilled from Na/Ph_2CO before use. Compound 1 was synthesized according to the literature procedure.[1] Other chemicals and solvents were used as received. Column chromatography was performed with silica gel 230-400 mesh from Merck. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Gemini 300 MHz at room temperature. Undeuterated solvent residues were used as internal standard. FT-MALDI-MS and HiRes-FT-MALDI-MS spectra were recorded on Ionspec 4.7 Tesla ultima Fourier Transform mass spectrometer using 2,5-dihydroxybenzoicacid (DHB) as matrix, while MALDI-TOF-MS spectre were recorded on a Kratos Kompact MALDI–TOF instrument using a DHB matrix. Cyclic voltammetry and differential pulse voltammetry were carried out in a 1:1 mixture of THF and MeCN using an ECO chemie PGSTAT10 potentionstat with a Pt working electrode, a Pt counter electrode, a Ag/$AgNO_3$ reference electrode, and Bu_4NPF_6 (0.1 M) as the supporting electrolyte. Elemental analyses were performed by Atlantic Microlab, Inc., Georgia.

5-Tosyl-4,6-dibromo-2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (2a)

Compound **1** (1.00 g, 1.66 mmol) was dissolved in anhydrous THF (50 mL) and stirred in an atmosphere of argon. The mixture was cooled to –78 ºC and LDA (3.0 mL of a 1.66 M solution, 5.0 mmol) was added, whereupon the reaction mixture was stirred at –78 ºC for 30 min. CNBr (0.71 g, 6.65 mmol) was added in one portion resulting in a colour change from yellow to orange. Stirring was continued for 2.5 h at –78 ºC. The reaction mixture was allowed to warm to room temperature and stirred for a further 20 min, before H_2O (100 mL) was added. The resulting mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined extracts were dried ($MgSO_4$). The solvent was removed and the crude product purified by column chromatography (500 mL SiO_2, Ø = 6 cm, eluent: CH_2Cl_2–petroleum ether, 3:7) to give the title compound **2a** (0.88 g, 70%) as a yellow solid. Mp. 92.2–92.8 ºC. Anal. Found: C, 39.81; H, 4.00; N, 1.93; S, 29.29. Calc. for $C_{25}H_{29}Br_2NO_2S_7$: C, 39.52; H, 3.85; N, 1.84; S, 29.54. ^{1}H NMR (300 MHz/$CDCl_3$/TMS) δ 0.89 (t, 6H, J = 7.1 Hz, CH_2CH_3), 1.25–1.43 (m, 8H, $CH_2CH_2CH_3$), 1.59 (quintet, 4H, J = 7.2 Hz, SCH_2CH_2), 2.44 (s, 3H, Ts-CH_3), 2.79 (t, 4H, J = 7.2 Hz, SCH_2), 7.33 (d, 2H, J = 8.2 Hz, Ts-*H*), 7.84 (d, 2H, J = 8.2 Hz, Ts-*H*). MS (FT-MALDI) *m/z* 679 ([M + H – Br]$^+$), 603 ([M + H – Ts]$^+$).

5-Tosyl-4,6-diiodo-2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (2b)

Compound **1** (1.00 g, 1.66 mmol) was dissolved in anhydrous THF (50 mL) in an atmosphere of nitrogen. The mixture was cooled to –78 °C and LDA (3.37 mL of a 1.48 M solution, 5.00 mmol) was added, whereupon the mixture was stirred at –78 °C for 30 min. Iodine (2.53 g, 9.98 mmol) was added in one portion. Stirring was continued for a further 2 h at –78 °C and then at room temperature for 1 h. H_2O (100 mL) was added followed by addition of an aqueous solution of Na_2SO_3 (50 mL, 20%) and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried ($MgSO_4$) and the solvent removed. The crude product was purified by column chromatography (500 mL SiO_2, Ø = 6 cm, eluent: CH_2Cl_2–petroleum ether 1:1) to give **2b** (1.21 g, 85%) as an orange solid. Mp. 107.4–107.5 ºC. Anal. Found: C, 35.47; H, 3.32; N, 1.73; S, 26.41. Calc. for $C_{25}H_{29}I_2NO_2S_7$: C, 35.17; H, 3.42; N, 1.64; S, 26.29. ^{1}H NMR (300 MHz/$CDCl_3$/TMS) δ 0.89 (t, 6H, J = 7.2 Hz, CH_2CH_3), 1.25-1.43(m, 8H $CH_2CH_2CH_3$), 1.61 (quintet, 4H, J = 7.3 Hz, SCH_2CH_2), 2.43 (s, 3H, Ts-CH_3), 2.79 (t, 4H, J = 7.3 Hz, SCH_2), 7.32 (d, 2H J = 8.6 Hz, Ts-H), 7.85 (d, 2H, J = 8.6 Hz, Ts-H). ^{13}C NMR (75 MHz/$CDCl_3$/TMS) δ 14.1, 22.3, 29.5, 30.8, 36.5, 55.4, 108.2, 117.6, 127.7, 128.0, 130.2, 134.7, 139.4, 146.1 (one line is missing/overlapping). MS (HiRes-FT-MALDI) *m/z* 852.8368 ($M^{\bullet+}$). Calc. for $C_{25}H_{29}I_2NO_2S_7^{\bullet+}$ 852.8327.

5-Methyl-4,6-dibromo-2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (3a)

Compound **2a** (1.50 g, 1.97 mmol) and MeI (2.80 g, 19 mmol) were dissolved in anhydrous THF (50 mL) under an atmosphere of nitrogen and stirred at room temperature. NaOMe (7.0 mL of a 25% solution in MeOH, 21 mmol) was added in one portion and the reaction mixture was stirred for 30 min. H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (500 mL SiO_2, Ø = 6 cm, eluent: CH_2Cl_2–petroleum ether, 3:7) to give **3a** (0.81 g, 67%) as an unstable orange powder. ^{1}H NMR (300 MHz/$CDCl_3$/TMS) δ 0.90 (t, 6H, J = 7.0 Hz, CH_2CH_3), 1.20–1.43 (m, 8H, $CH_2CH_2CH_3$), 1.63 (quintet, 4H, J = 7.3 Hz, SCH_2CH_2), 2.81 (t, 4H, J = 7.3 Hz, SCH_2), 3.53 (s, 3H, NCH_3). ^{13}C NMR (75 MHz/$CDCl_3$/TMS) δ 14.1, 22.3, 29.6, 30.8, 35.2, 36.4, 93.6, 114.4, 115.0, 120.3, 127.7. MS (HiRes-FT-MALDI) *m/z*

616.8716 ($M^{\bullet+}$). Calc. for $C_{19}H_{25}Br_2NS_6^{\bullet+}$ 616.8673. Crystals suitable for X-ray crystallography were prepared as described in the experimental procedure for compound **4a**.

5-Methyl-4,6-diiodo-2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (3b)

Compound **2b** (0.80 g, 0.94 mmol) and MeI (2.66 g, 18.80 mmol) were dissolved in anhydrous THF (30 mL) under an atmosphere of nitrogen and stirred at room temperature. NaOMe (3.0 mL of a 25% solution in MeOH, 9.38 mmol) was added in one portion and the reaction mixture was stirred for 30 min. H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried ($MgSO_4$) and the concentrated. The crude product was purified by column chromatography (500 mL SiO_2, Ø = 6 cm, eluent: CH_2Cl_2–petroleum ether, 3:7) to give **3b** (0.58 g, 87%) as a yellow solid. Mp. 107.8–108.4 ºC. Anal. Found: C, 32.32; H, 3.52; N, 1.89; S, 27.07. Calc. for $C_{19}H_{25}I_2NS_6$: C, 31.98; H, 3.53; N, 1.96; S, 26.96. ^{1}H NMR ($CDCl_3$/300 MHz/TMS): δ = 0.91 (t, 6H, J = 7.0 Hz, CH_2CH_3), 1.30–1.44 (m, 8H, $CH_2CH_2CH_3$), 1.64 (quintet, 4H, J = 7.3 Hz, SCH_2CH_2), 2.82 (t, 4H, J = 7.3 Hz, SCH_2), 3.58 (s, 3H, NCH_3). MS (HiRes-FT-MALDI) *m/z* 712.8422 ($M^{\bullet+}$). Calc for $C_{19}H_{25}I_2NS_6^{\bullet+}$ 712.8395. Crystals suitable for X-ray crystallography were grown by slow diffusion of MeOH into a solution of **3b** in CH_2Cl_2.

1,3,8,10-Tetrabromo-5,6-dihydro-2,9-dimethyl-5,6-bis(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-pyrrolo[3',4'-8,9]-1,2,5,8-tetrathiacino[3,4-*c*]pyrrole (4a)

Method A. Compound **3a** (0.50 g, 0.81 mmol) was dissolved in CH_2Cl_2 (1 mL) followed by the addition of MeOH (4 mL) such that compound **3a** started to precipitate. The solution was heated to redissolve the precipitate. The mixture was kept at a temperature of 4 ºC for 5 days, whereupon the mixture was filtered affording a small amount of **3a** as yellow crystals suitable for X-ray crystallography. The filtrate (obtained as a dark solution) was concentrated and the resulting residue was purified by column chromatography (300 mL SiO_2, Ø = 45 mm, eluent: 1:4 CH_2Cl_2/petroleum ether) to give **4a** (0.25 g, 50%) as an orange-yellow solid.

Method B. Compound **3a** (0.50 g, 0.81 mmol) was dissolved in CH_2Cl_2 (10 mL) followed by addition of a solution of Br_2 in CH_2Cl_2 (1 drop, from a solution made by adding 1 drop of Br_2 in 5 mL of CH_2Cl_2). The reaction mixture was kept under N_2 at 4 ºC for 24 h leaving a dark solution which subsequently was concentrated. The resulting residue was purified by column

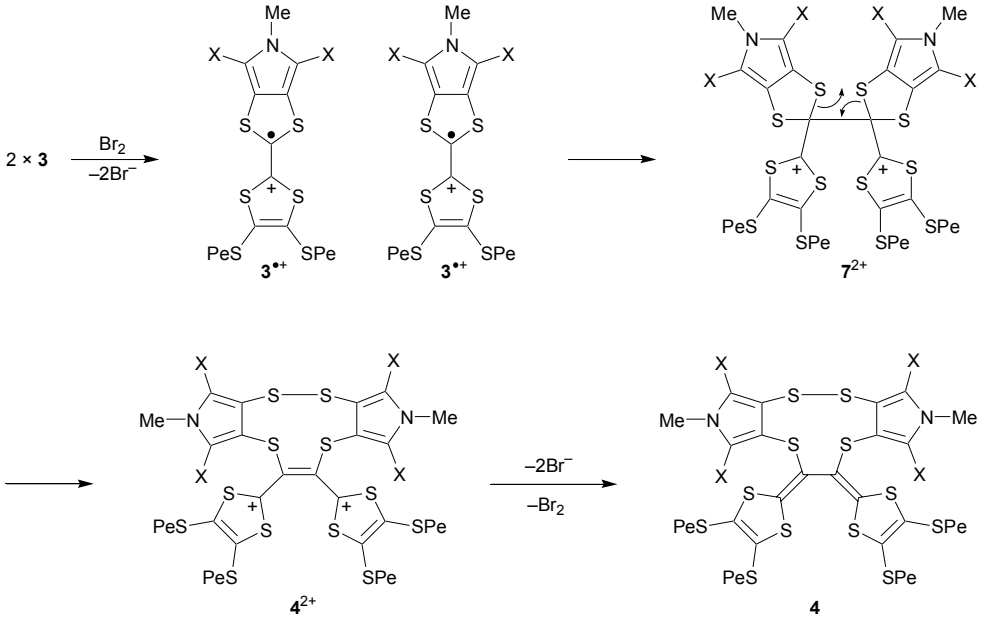
chromatography (300 mL SiO_2, Ø = 45 mm, eluent: 1:4 CH_2Cl_2/petroleum ether) to give **4a** (0.34 g, 68%) as an orange-yellow solid. Mp. 104.7–105.8 ºC (dec). ^{1}H NMR ($CDCl_3$/300 MHz/TMS) δ0.92 (t, 6H J = 7.4 Hz, CH_2CH_3), 0.94 (t, 6H, J = 7.4 Hz, CH_2CH_3), 1.30–1.46 (m, 16H, $CH_2CH_2CH_3$), 1.66 (quintet, 8H, J = 7.3 Hz, SCH_2CH_2), 2.80–2.94 (m, 8H, SCH_2), 3.67 (s, 6H, NCH_3). MS (HiRes-FT-MALDI) *m/z* 1233.7320 ($M^{\bullet+}$). Calc. for $C_{38}H_{50}Br_4N_2S_{12}^{\bullet+}$ 1233.7350.
Crystals suitable for X-ray crystallography were grown by slow diffusion of MeOH into a solution of **4a** in CH_2Cl_2.

1,3,8,10-Tetraiodo-5,6-dihydro-2,9-dimethyl-5,6-bis(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-pyrrolo[3',4'-8,9]-1,2,5,8-tetrathiacino[3,4-*c*]pyrrole (4b)

Compound **3b** (0.15 g, 0.21 mmol) was dissolved in CH_2Cl_2 (1 mL) followed by addition of a solution of Br_2 in CH_2Cl_2 (1 mL of a 2.03 mM solution of Br_2 in CH_2Cl_2, 0.0020 mmol). The reaction mixture was stirred under N_2 for 4.5 h, before an aqueous solution of Na_2SO_3•$7H_2O$ (1.5 g in 3 mL H_2O) was added. The mixture was poured into CH_2Cl_2 (50 mL) and separated. The organic phase was dried ($MgSO_4$). Evaporation of the solvent gave an oil, which was purified by column chromatography (300 mL SiO_2, Ø = 45 mm, eluent: 1:4 CH_2Cl_2/cyclohexane) to give the title compound **4b** (0.089 g, 59%) as a yellow solid. Mp. 119.9–121.5 ºC (dec). ^{1}H NMR ($CDCl_3$/300 MHz/TMS) δ 0.91 (t, 6H, J = 7.0 Hz, CH_2CH_3), 0.92 (t, 6H, J = 7.1 Hz, CH_2CH_3) 1.28–1.46 (m, 16 H, $CH_2CH_2CH_3$), 1.55–1.76 (m, 8H, SCH_2CH_2), 2.72–2.86 (m, 8H, SCH_2), 3.76 (s, 6H, NCH_3). (MALDI–TOF) *m/z* (%) 1427 (M^+, 100), 1301 ($[M + H - I]^+$, 20), 1173 ($[M + H - 2 \times I]^+$, 33). (HiRes-FT-MALDI) *m/z* 1171.9562 ($[M - 2 \times I]^+$). Calc. for $C_{38}H_{50}I_2N_2S_{12}^{\bullet+}$ 1171.8690. Crystals suitable for X-ray crystallography were grown by slow diffusion of MeOH into a solution of **4b** in CH_2Cl_2.

Alternative Mechanism for Dimer Formation

An alternative mechanism for the dimer formation is depicted in Scheme S1. In the first step, the monomer **3** is oxidised by bromine to generate the radical cation $\mathbf{3}^{\bullet+}$. Dimerisation of two equivalents of $\mathbf{3}^{\bullet+}$ form the intermediate $\mathbf{7}^{2+}$, which subsequently rearrange to produce $\mathbf{4}^{2+}$. Finally, $\mathbf{4}^{2+}$ is reduced by bromide affording the neutral dimer **4** and bromine.



Scheme S1. Alternative mechanism for formation of the dimers **4**.

Reference

J. O. Jeppesen, K. Takimiya, F. Jensen, T. Brimert, K. Nielsen, N. Thorup and J. Becher, *J. Org. Chem.*, 2000, **65**, 5794.