Dimerization of Monobenzoylated Monopyrrolotetrathiafulvalene

Kent A. Nielsen,* Andrew D. Bond, Karina R. Larsen

Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark Fax +45 66158780; E-mail: kan@ifk.sdu.dk

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Abstract: Introduction of one benzoyl functional group into the 4position of monopyrrolotetrathiafulvalene (MPTTF) affords MPTTF derivatives incorporating one hydrogen-bonding donor and one acceptor. This results in dimerization of the MPTTF derivatives in solution and in the solid state.

Key words: tetrathiafulvalene, functionalization, benzoylation, dimerization, pyrroles

Tetrathiafulvalenes¹ (TTFs) have attracted significant attention for many years due to the discovery of TTF containing organic metals,² and superconducting³ salts, and for their use in molecular systems such as chemical sensors,⁴ switches,⁵ and electronic devices.⁶ In continuation of our work on the development of useful monopyrrolotetrathiafulvalene⁷ (MPTTF) building blocks, we report that introduction of one benzoyl group in the 4-position of the MPTTF unit **1** (Scheme 1) results in novel MPTTF derivatives **4a** and **4b** carrying one hydrogen-bonding donor (pyrrole NH proton) and one hydrogen-bonding acceptor (carbonyl oxygen). The MPTTF units **4a** and **4b** self-assemble in solution and in the solid state to form the dimeric structures **4a·4a** and **4b·4b**.

Monobenzovlation of MPTTF $\mathbf{1}^7$ in its 4-position was carried out according to a modified literature⁸ procedure (Scheme 1). Addition of 5.0 equivalents of ethylmagnesium bromide to an anhydrous THF solution of MPTTF 1, followed by the addition of either 7.5 equivalents of benzovl chloride (2) or 6.0 equivalents of 4-cyanobenzovl chloride (3), gave after fifteen minutes or five hours, respectively, one major spot on thin-layer chromatography. purifications chromatographic gave Column the monobenzoylated MPTTF units 4a and 4b (Scheme 1) as orange and red solids in 86 and 60% yield, respectively. Recrystallization was carried out by diffusion of a MeOH solvent layer into a CH₂Cl₂ solution: 4a was isolated as fine orange plates and 4b as fine dark red plates. We have also prepared N-alkylated derivatives, for which dimerization should not be expected on account of removal of the NH donor. The N-alkylations (Scheme 1) were carried out by deprotonation of 4a using excess sodium hydride followed by the addition of either iodomethane or 1-iodopropane, resulting in the isolation of 5a and 5b in 85 and 77% yield, respectively.

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Scheme 1 Synthesis of monobenzoylated MPTTF derivatives 4a, and 4b, and the N-alkylated derivatives 5a, and 5b starting from the MPTTF unit 1

For the analytically pure products 4a, 4b, 5a, and 5b, high-resolution matrix-assisted laser desorption/ionization mass spectrometry HRMS (MALDI-FT) showed exact masses m/z 551.0597, 576.0549, 565.0765, and 593.0971, respectively, corresponding to M*+ (calcd mass *m*/*z* M^{•+} 551.0573, 576.0526, 565.0726, and 593.1043). The UV-Vis spectra of 1, 4a, 4b, 5a, and 5b (Figure 1) showed strong absorbance in the region between 200 and 400 nm. In the region between 400 and 600 nm (insert in Figure 1) higher absorbance was observed for 4a, 4b, 5a, and **5b** than for the parent MPTTF unit **1**. This change in absorbance is attributed to electron delocalization from the electron-rich MPTTF unit to the electron-withdrawing benzoyl substituent. Solution oxidation potentials (Table 1) obtained from cyclic voltammograms revealed two pairs of reversible redox waves for all compounds (Figure 2a), corresponding to oxidation to the radical cation (MPTTF⁺⁺) and then to the dication (MPTTF²⁺). From differential pulse measurements (Figure 2b) it can be seen that each oxidation corresponds to an equal number of electrons. Table 1 summarizes the oxidation potentials

obtained. In all cases, higher oxidation potentials are observed for the MPTTF derivatives than for the parent MPTTF unit **1**. For **4a**, changes in the first and second oxidation potential of $\Delta E^1 = 80$ mV and $\Delta E^2 = 80$ mV were observed, whereas for **4b** slightly larger changes of $\Delta E^1 = 100$ and $\Delta E^2 = 90$ mV were observed. This difference is attributed to the electron-withdrawing nature of the CN group of the 4-cyanobenzoyl substituent. Cyclic voltammetry of the N-alkylated products **5a** and **5b** resulted in a smaller change for the second oxidation potential ($\Delta E^2 = 60$ mV) compared to **4a** ($\Delta E^2 = 80$ mV).



Figure 1 UV-Vis absorption spectra of 1, 4a, 4b, 5a, and 5b (2.0×10^{-5} M) recorded in MeCN at 298 K

Table 1 Oxidation Potentials $E_{1/2}^{1}$ and $E_{1/2}^{2}$ of the MPTTF Derivatives **1**, **4a**, **4b**, **5a**, and **5b** Determined by Cyclic Voltammetry^a

Compound	$E_{1/2}^{1}(V)$	$E_{1/2}^{2}(V)$	$\Delta E^{1}(\mathbf{V}) 1$	$\Delta E^{2}\left(\mathbf{V}\right)1$
1	0.12	0.44	-	-
4 a	0.20	0.52	0.08	0.08
4b	0.22	0.53	0.10	0.09
5a	0.20	0.50	0.08	0.06
5b	0.20	0.50	0.08	0.06

^a Cyclic voltammetry conditions: Ag/AgNO₃ electrode, Pt electrode, 20 °C, Bu_4NPF_6 (0.1 M in MeCN), scan rate 0.1 V s⁻¹. Concentration of compound: 10^{-3} M.

Single crystals of **4b** and **5a** suitable for X-ray diffraction analysis were obtained by diffusion of a MeOH solvent layer into a CH_2Cl_2 solution containing the compound. The structure analysis of **4b** (Figure 3) contains intermolecular hydrogen bonds that produce a centrosymmetric **4b**·**4b** dimer structure in the solid state. The two hydrogen bonds in the dimer are formed between the NH proton from one molecule of **4b** to the carbonyl oxygen of the second molecule of **4b**. For the MPTTF unit **5a** (Figure 4), elimination of the NH proton means that dimer formation is not observed. For both structures, the carbonyl group and the benzene ring are twisted out of the plane of the



Figure 2 (a) Cyclic voltammetry and (b) differential pulse spectra of 1, 4a, 4b, 5a, and 5b recorded in MeCN at 298 K

MPTTF unit, by approximately 8 and 42°, respectively, in **4b**, and by approximately 15 and 72°, respectively, in **5a**.

Results from the X-ray crystal structure analysis encouraged us to investigate the dimerization of **4a** and **4b** in solution. Upon dilution of a concentrated solution of **4b** (156–2.0 mM, see Figure S25 in the Supporting Information), a significant upfield peak shift $\Delta \delta = 0.76$ ppm for the NH proton was observed. This indicates that the MPTTF unit forms intermolecular aggregates in solution. By fitting the data (for **4a**, see Figures S23 and S24 in the



Figure 3 X-ray crystal structure of **4b** showing the dimer formation **4b 4b**; H atoms are omitted except for the NH protons



Figure 4 X-ray crystal structures of 4b and 5a; H atoms are omitted except for the NH protons

Supporting Information), assuming a monomer to dimer equilibrium, dimerization constants $K_D = 1.0$ and 2.0 M⁻¹ were obtained for **4a** and **4b**, respectively.

In conclusion, we have developed a synthetic method that allows the parent MPTTF unit **1** to be monobenzoylated in the 4-position, and demonstrated that the resulting MPTTF unit **4a** can be N-alkylated in good yields. Further, it was shown that the MPTTF units **4a** and **4b** form dimers in solution and this was also established for **4b** in the solid state, utilizing hydrogen bonding between the pyrrole NH proton and the carbonyl oxygen, and thereby demonstrating control of the intermolecular arrangement between MPTTF units.

All reactions were carried out under a dry N2 atmosphere unless otherwise stated. Benzoyl chloride was distilled under reduced pressure prior to use. All other chemicals were purchased from commercial sources and were used as received. Solvents were dried according to literature procedures.9 TLC was carried out using aluminum sheets pre-coated with silica gel 60 F₂₅₄ (Merck 5554). The plates were inspected under UV light (254 nm) and, if required, developed in I₂ vapor. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040-0.063 mm). Melting points were determined on a Büchi melting point apparatus and are uncorrected. $^{1}\mathrm{H}\,\mathrm{NMR}\,(300\,\mathrm{MHz})$ and $^{13}\mathrm{C}\,\mathrm{NMR}\,(75\,\mathrm{MHz})$ spectra were recorded on a Gemini-300BB instrument, using TMS or the residual solvent as the internal standard, which were assigned on the basis of Nudelman.10 Fourier transform matrix-assisted laser-desorption/ionization mass spectrometry (FT-MALDI-MS) was performed on an IonSpec 4.7 Tesla Ultima Fourier Transform mass spectrometer, utilizing a 2,5-dihydroxybenzoic acid (DHP) matrix. Electrochemical experiments were carried out at r.t. in N2-purged MeCN solution with an Autolab/PGSTAT 10 instrument interfaced to a personal computer, using cyclic voltammetry (CV) technique. Working and counter electrodes were made of Pt, and the reference electrode was Ag/AgNO₃. The concentration of the examined compounds was 10⁻³ M and 0.10 M *n*-Bu₄NPF₆ was added as supporting electrolyte. Cyclic voltammograms were obtained with a sweep rate of 100 mV s⁻¹. The half-wave potentials $E_{1/2}$ reported were obtained from an average of the cathodic and anodic cyclic voltammetric peaks. Ultraviolet-visible (UV-Vis) measurements were performed on a Shimadzu UV-1601PC instrument at 298 K. Microanalyses were performed by the Atlantic Microlab, Inc., Atlanta, Georgia, USA. X-ray diffraction data were collected using a Bruker Nonius X8-APEXII instrument with MoKα radiation.

2-[4,5-Bis(pentylthio)-1,3-dithiol-2-ylidene]-4-benzoyl-1,3dithiolo[4,5-c]pyrrole (4a)

MPTTF (1; 0.22 g, 0.50 mmol) was dissolved in anhyd THF (5 mL) in an atmosphere of argon. EtMgBr (0.83 mL of a 3.0 M solution in Et₂O, 2.5 mmol) was slowly added over a period of 5 min at r.t., causing an exothermic reaction with evolution of gas and a color change from yellow to orange. The reaction mixture was stirred at r.t. for 30 min, whereafter benzoyl chloride (2; 0.53 g, 0.44 mL, 3.75 mmol) was added over a period of 5 min, causing a color change from orange to dark red. The mixture was stirred for 15 min at r.t. before sat. aq NH₄Cl (5 mL) was carefully added. The resulting suspension was extracted with CH₂Cl₂ (50 mL), then the organic phase was washed with $H_2O(3 \times 20 \text{ mL})$ and dried (MgSO₄). Evaporation of the solvent gave a dark red oil, which was purified by column chromatography (200 mL SiO₂, $\emptyset = 4$ cm; CH₂Cl₂) to give 4a as an analytically pure orange solid; yield: 0.24 g (86%). Recrystallization from CH₂Cl₂-MeOH gave 4a as fine orange plates; mp 105-107 °C.

IR (KBr): 1605 cm⁻¹.

¹H NMR (CDCl₃/TMS): $\delta = 0.89$ (t, J = 6.8 Hz, 3 H), 0.89 (t, J = 6.8 Hz, 3 H), 1.23–1.42 (m, 8 H), 1.54–1.68 (m, 4 H), 2.78 (t, J = 7.6 Hz, 2 H), 2.80 (t, J = 7.6 Hz, 2 H), 6.89 (s, 1 H), 7.47–7.56 (m, 2 H), 7.58–7.65 (m, 1 H), 7.73–7.78 (m, 2 H), 9.76 (br s, 1 H).

¹³C NMR (CDCl₃/TMS): δ = 13.9 (2 overlapping peaks), 22.2, 22.2, 29.3, 29.4, 30.6, 30.6, 36.2, 36.2, 112.4, 116.5, 117.9, 122.4, 124.0, 127.4, 127.6, 128.0, 128.9, 130.2, 132.4, 137.2, 183.8.

HRMS (MALDI-FT): m/z calcd for $C_{25}H_{29}NOS_6^{++}$: 551.0573; found: 551.0597.

CV (MeCN, vs. Ag/AgNO₃): $E_{1/2}^2 = 0.20$ V, $E_{1/2}^2 = 0.52$ V.

UV-Vis (MeCN, 298 K): λ_{max} = 430 nm, ϵ = 4645 L mol cm⁻¹.

Anal. Calcd for $C_{25}H_{29}NOS_6$ (551.9): C, 54.41; H, 5.30; N, 2.54; S, 34.86. Found: C, 54.53; H, 5.29; N, 2.61; S, 34.96.

2-[4,5-Bis(pentylthio)-1,3-dithiol-2-ylidene]-4-(4-cyanobenzoyl)-1,3-dithiolo[4,5-*c*]pyrrole (4b)

MPTTF (1; 0.30 g, 0.67 mmol) was dissolved in anhyd THF (3 mL) in an atmosphere of argon. EtMgBr (1.12 mL of a 3.0 M solution in Et₂O, 3.35 mmol) was slowly added over a period of 5 min at r.t., causing an exothermic reaction with evolution of gas and a color change from yellow to orange. The reaction mixture was stirred at r.t. for 30 min, whereafter 4-cyanobenzoyl chloride (3; 0.68 g, 4.0 mmol) was added in one portion, causing a gas evolution and a color change from orange to dark red. The mixture was stirred for 5 h at r.t. before a solution of sat. aq NH₄Cl (5 mL) was added carefully. The suspension was extracted with CH₂Cl₂ (100 mL), the organic phase washed with H_2O (3 × 50 mL), and dried (MgSO₄). Evaporation of the solvent gave a dark red oil, which was purified by column chromatography (300 mL SiO₂, $\emptyset = 4.5$ cm; CH₂Cl₂-MeOH, 19:1) to give 4b as an analytically pure dark red solid; yield: 0.23 mg (60%). Recrystallization from CH₂Cl₂-MeOH gave 4b as fine dark red plates suitable for X-ray crystal structure analysis; mp 168-169 °C.

IR (KBr): 2231, 1601 cm⁻¹.

¹H NMR (CDCl₃/TMS): δ = 0.90 (t, *J* = 7.1 Hz, 6 H), 1.22–1.42 (m, 8 H), 1.55–1.68 (m, 4 H), 2.80 (t, *J* = 7.2 Hz, 2 H), 2.80 (t, *J* = 7.3 Hz, 2 H), 6.95 (d, *J* = 3.1 Hz, 1 H), 7.79–7.85 (m, 4 H), 9.51 (br s, 1 H).

¹³C NMR (CDCl₃/TMS): δ = 13.9 (2 overlapping peaks), 22.2 (2 overlapping peaks), 29.3, 29.4, 30.6, 30.6, 36.2, 36.3, 113.9, 115.8, 116.3, 117.4, 118.0, 123.2, 123.4, 127.6, 127.6, 128.5, 130.8, 132.7, 140.9, 181.7.

HRMS (MALDI-FT): m/z calcd for $C_{26}H_{28}N_2OS_6^{*+}$: 576.0526; found: 576.0549.

CV (MeCN, vs. Ag/AgNO₃): $E_{1/2}^{1} = 0.22$ V, $E_{1/2}^{2} = 0.53$ V.

UV-Vis (MeCN, 298 K): $\lambda_{max} = 430 \text{ nm}, \epsilon = 4510 \text{ L mol cm}^{-1}$.

Anal. Calcd for $C_{26}H_{28}N_2OS_6$ (576.9): C, 54.13; H, 4.89; N, 4.86; S, 33.35. Found: C, 54.07; H, 4.82; N, 4.98; S, 33.61.

2-[4,5-Bis(pentylthio)-1,3-dithiol-2-ylidene]-4-benzoyl-5-methyl-1,3-dithiolo[4,5-*c*]pyrrole (5a)

MPTTF (**4a**; 22.1 mg, 0.040 mmol) was dissolved in anhyd DMF (2 mL) and the solution was degassed with N₂ for 15 min before NaH (0.016 g of a 60% suspension in mineral oil, 0.40 mmol) was added in one portion. The reaction mixture was stirred for 30 min at r.t., causing the initially yellow solution to become orange. MeI (0.04 mL, 85.2 mg, 0.6 mmol) was added in one portion, causing a new color change from orange to yellow. The reaction mixture was stirred for 1 h and then purged with N₂, followed by the addition of brine (10 mL). The yellow precipitate was filtered, then washed with H₂O (2 × 10 mL) and MeOH (10 mL). After drying in vacuo, the yellow solid was purified by column chromatography (50 mL SiO₂, \emptyset = 2.5 cm; CH₂Cl₂) to give **5a** as an analytically pure orange solid; yield: 19.2 mg (85%); mp 81–82 °C.

IR (KBr): 1629 cm⁻¹.

¹H NMR (CDCl₃/TMS): δ = 0.89 (t, J = 6.9 Hz, 6 H), 1.24–1.41 (m, 8 H), 1.60 (sext, J = 7.3 Hz, 4 H), 2.75 (t, J = 7.3 Hz, 2 H), 2.79 (t, J = 7.3 Hz, 2 H), 3.95 (br s, 3 H), 6.69 (s, 1 H), 7.46–7.54 (m, 2 H), 7.57–7.64 (m, 1 H), 7.67–7.73 (m, 2 H).

HRMS (MALDI-FT): m/z calcd for $C_{26}H_{31}NOS_{6}^{*+}$: 565.0724; found: 565.0765.

CV (MeCN, vs. Ag/AgNO₃): $E_{1/2}^{1} = 0.20 \text{ V}, E_{1/2}^{2} = 0.50 \text{ V}.$

UV-Vis (MeCN, 298 K): $\lambda_{max} = 430 \text{ nm}, \epsilon = 4980 \text{ L mol cm}^{-1}$.

Anal. Calcd for $\rm C_{26}H_{31}NOS_6$ (565.9): C, 55.18; H, 5.52; N, 2.48; S, 34.00. Found: C, 55.14; H, 5.41; N, 2.41; S, 34.26.

2-[4,5-Bis(pentylthio)-1,3-dithiol-2-ylidene]-4-benzoyl-5-propyl-1,3-dithiolo[4,5-c]pyrrole (5b)

MPTTF (**4a**; 22.1 mg, 0.040 mmol) was dissolved in anhyd DMF (2 mL) and the solution was degassed with N₂ for 15 min before NaH (0.016 g of a 60% suspension in mineral oil, 0.40 mmol) was added in one portion. The reaction mixture was stirred for 30 min at r.t., causing the initially yellow solution to become orange. 1-Io-dopropane (5.9 μ L, 10.2 mg, 0.06 mmol) was added in one portion. The reaction mixture was stirred for 24 h and then purged with N₂, followed by the addition of brine (10 mL). The yellow precipitate was filtered, then washed with H₂O (2 × 10 mL) and MeOH (10 mL). After drying in vacuo, the yellow solid was purified by column chromatography (50 mL SiO₂, $\emptyset = 2.5$ cm; CH₂Cl₂) to give the title compound **5b** as an analytically pure orange solid; yield: 18.3 mg (77%); mp 64–65 °C.

IR (KBr): 1631 cm⁻¹.

¹H NMR (CDCl₃/TMS): $\delta = 0.89$ (t, J = 7.0 Hz, 6 H), 0.93 (t, J = 7.4 Hz, 3 H), 1.23–1.42 (m, 8 H), 1.60 (sext, J = 7.4 Hz, 4 H), 1.79 (sext, J = 7.2 Hz, 2 H), 2.75 (m, J = 7.4 Hz, 4 H), 4.28 (br s, 2 H), 6.75 (s, 1 H), 7.46–7.53 (m, 2 H), 7.57–7.64 (m, 1 H), 7.66–7.72 (m, 2 H).

HRMS (MALDI-FT): m/z calcd for $C_{28}H_{35}NOS_6^{++}$: 593.1043; found: 593.0971.

CV (MeCN, vs. Ag/AgNO₃): $E_{1/2}^{1} = 0.20$ V, $E_{1/2}^{2} = 0.50$ V.

UV-Vis (MeCN, 298 K): $\lambda_{max} = 430$ nm, $\epsilon = 4250$ L mol cm⁻¹.

Anal. Calcd for $C_{28}H_{35}NOS_6$ (593.98): C, 56.62; H, 5.94; S, 32.39. Found: C, 56.86; H, 5.95; S, 32.47.

X-ray Crystal Data¹¹

Crystal data for **4b**: empirical formula $C_{26}H_{28}N_2OS_6$; formula weight 576.86; triclinic; space group PI; a = 8.7845(15) Å, b = 9.4268(16) Å, c = 17.316(3) Å, $a = 99.188(4)^\circ$, $\beta = 93.327(3)^\circ$, $\gamma = 108.269(3)^\circ$; V = 1335.2(4) Å³; Z = 2; $D_{calcd} = 1.435$ Mg m⁻³; $\lambda = 0.7107$ Å; absorption coefficient = 0.536 mm⁻¹; F(000) = 604; T = 120(2) K; crystal size = $0.55 \times 0.13 \times 0.02$ mm.

Crystal data for **5a**: empirical formula $C_{26}H_{31}NOS_6$; formula weight 565.88; monoclinic; space group $P2_1/c$; a = 16.124(2) Å, b = 5.3533(5) Å, c = 32.152(4) Å, $a = 90^\circ$, $\beta = 99.778(4)^\circ$, $\gamma = 90^\circ$; V = 2734.9(5) Å³; Z = 4; $D_{calcd} = 1.374$ Mg m⁻³; $\lambda = 0.7107$ Å; absorption coefficient = 0.521 mm⁻¹; F(000) = 1192; T = 180(2) K; crystal size = $0.25 \times 0.03 \times 0.01$ mm.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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- (11) CCDC 861255 (4b) and CCDC 861256 (5a) contain the supplementary crystallographic data for compounds described in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033, E-mail: deposit@ccdc.cam.ac.uk].