Unexpected Side Chain Oxidation in a Swivel Cruciform Oligothiophene

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1. General methods

Unless otherwise indicated, all starting materials were purchased from commercial sources (Aldrich, Acros, ABCR) and used without further purification. All solvents were applied in commercial p.a. quality and dried/distilled prior to use. All reactions were carried out under argon atmosphere by use of Schlenk techniques. The microwave assisted oligomer syntheses used a CEM Discover microwave synthesizer utilizing sealed 10 mL reaction vials. $^1$H-, $^{13}$C- and $^{13}$C($^1$H)-NMR spectra were recorded on a Bruker ARX 400 spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) using residual solvent protons as internal standards. The coupling constants are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet) and m (multiplet). The FD-Mass-spectra were measured with a Fisons Instruments Sectorfield Mass Spectrometer ZAB 2-SE-FPD.

2. Experimental Section

2,2´,5,5´-tetrabromo-3,3´-bithiophene$^{[1,2]}$, 5-tri-n-butylstannyl-5´-hexyl-2,2´-bithiophene$^{[3]}$ and 2,5-bis(5´-hexyl-2,2´-bithien-5-yl)benzene (DHTPTT)$^{[4]}$ were synthesized according to literature procedures.

2.1. Synthesis of the two swivel-cruciform oligomers DHPT-SC and DHBPT-SC

2.1.1. 2,2´,5,5´-Tetrakis(5´-hexyl-2,2´-bithien-5-yl)-3,3´-bithiophene (DHPT-SC)

0.320 g (0.66 mmol) of 2,2´,5,5´-tetrabromo-3,3´-bithiophene, 1.79 g (3.32 mmol) of 5-tri-n-butylstannyl-5´-hexyl-2,2´-bithiophene and 0.12 g (0.10 mmol) of Pd(PPh)$_3$ were dissolved in
50 mL of dry toluene under argon atmosphere. After degassing/ refilling the flask with argon for several times, the resulting mixture was stirred under reflux overnight. The reaction mixture was cooled down to room temperature, treated with 5 mL of 4N HCl in dioxane and diluted with chloroform. The organic phase was successively washed twice with 20 mL of aqueous 2N HCl, twice with 20 mL of saturated, aqueous EDTA-solution and twice with 20 mL of saturated, aqueous NaHCO$_3$ solution. The organic phase was then dried over MgSO$_4$ and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (eluent: hexane/toluene = 9:1) and the product re-crystallized from heptane. The product was obtained as a dark yellow powder (yield: 0.36 g; 47 %).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$, ppm): δ 0.87 (t; 6H; $^3$J = 6.74 Hz), 0.89 (t; 6H; $^3$J = 7.03 Hz), 1.33 (m; 24H; 18, 19, 20, 34, 35, 36, 55, 56, 57, 71, 72, 73), 1.66 (m; 8H; 17, 33, 54, 70), 2.73 (t; 4H; $^3$J = 7.53 Hz), 2.79 (t; 4H; $^3$J = 7.55 Hz), 6.60 (d; 2H; 13; 51; $^3$J = 3.41 Hz), 6.68 (d; 2H; 30, 67; $^3$J = 3.38 Hz), 6.84 (d; 2H; 12, 52; $^3$J = 3.51 Hz), 6.86 (d; 2H; 8, 46; $^3$J = 3.91 Hz), 6.92 (d; 2H; 7, 47; $^3$J = 3.75 Hz), 6.98 (d; 2H; 31, 68; $^3$J = 3.48 Hz), 7.01 (d; 2H; 25, 62; $^3$J = 3.77 Hz), 7.02 (s; 2H; 4, 42), 7.09 (d; 2H; 26, 63; $^3$J = 3.70 Hz)

$^{13}$C NMR (100 MHz, C$_2$D$_2$Cl$_4$, ppm): δ 14.49, 14.51, 22.90, 22.91, 29.05, 29.08, 30.45, 30.50, 31.79, 31.81, 31.83, 31.86, 123.54, 123.99, 124.01, 124.90, 125.16, 125.29, 126.24, 126.70, 132.19, 133.82, 134.19, 134.40, 135.00, 135.19, 137.53, 138.47, 146.19, 146.35

FD-MS, m/z: 1160.3 ([M]$^+$), 580.5 ([M]$^{2+}$)

2.1.2. 2,5-Bis(5'-hexyl-2,2'-bithien-5-yl)-1-chlorobenzene (Cl-DHTPTT)

0.60 g (2.22 mmol) of 1,4-dibromo-2-chlorobenzene, 2.50 g (4.63 mmol) of 5-tri-n-butylstannyl-5'-hexyl-2,2'-bithiophene and 0.10 g (0.09 mmol) of Pd(PPh$_3$)$_4$ were dissolved in 150 mL of dry toluene under argon atmosphere. After degassing/ refilling the flask with argon for several times, the resulting mixture was stirred under reflux overnight. The reaction mixture was cooled down to room temperature, treated with 5 mL of 4N HCl in dioxane and diluted with chloroform. The organic phase was successively washed twice with 20 mL of 2N
aqueous HCl, once with 20 mL of saturated, aqueous EDTA-solution and once with 20 mL of saturated, aqueous NaHCO₃ solution. The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (eluent: hexane/toluene = 9:1) and the product re-crystallized from ethanol. The resulting product forms yellow crystals (yield: 0.51 g; 38%).

\[ ^1H NMR (400 MHz, C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}, ppm): \delta 0.82 (t; 6H; 23, 39; \(^3J = 6.76\) Hz), 1.15-1.35 (m; 14H; 20, 21, 22, 36, 37, 38), 1.60 (m; 4H; 19, 35), 2.73 (t; 4H; 18, 34; \(^3J = 7.58\) Hz), 6.64 (d; 2H; 16, 32; \(^3J = 3.33\) Hz), 6.97 (Ψt; 2H; 17, 33), 7.02 (d; 1H; 28; \(^3J = 3.80\) Hz), 7.04 (d; 1H; 11; \(^3J = 3.86\) Hz), 7.19 (d; 1H; 27; \(^3J = 3.73\) Hz), 7.28 (d; 1H; 12; \(^3J = 3.77\) Hz), 7.41 (dd; 1H; 4; \(^3J = 8.20\) Hz, \(^4J = 1.77\) Hz), 7.49 (d; 1H; 3; \(^3J = 8.19\) Hz), 7.61 (d; 1H; 6; \(^3J = 1.79\) Hz)

\[ ^13C NMR (100 MHz, C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}, ppm): \delta 14.49, 22.89, 29.05, 30.48, 31.81, 31.84, 123.40, 124.04, 124.11, 124.22, 124.30, 125.11, 125.28, 125.31, 127.42, 128.76, 131.36, 131.53, 132.46, 134.47, 134.48, 134.65, 138.01, 138.62, 139.10, 140.02, 146.34, 146.46 \]

FD-MS, \[ m/z: 609.1 ([M]^+) \]

2.1.3. 2,2',5,5'-Tetrakis(5'-hexyl-2,2'-bithien-5-yl)-1,1'-biphenyl (DHBPT-SC)

0.10 g (0.16 mmol) 2,5-bis(5'-hexyl-2,2'-bithien-5-yl)-1-chlorobenzene, 0.06 g (0.22 mmol) Ni(COD)\textsubscript{2}, 0.04 g (0.26 mmol) 2,2'-bipyridine and 0.1 mL (0.09 g, 0.82 mmol) of 1,5-cyclooctadiene were dissolved in 5 mL of dry, degassed THF in a 10 mL microwave vial. The resulting reaction mixture was irradiated for 15 min in the CEM microwave synthesizer (300 W, 120°C). The solution was cooled down to room temperature and diluted with chloroform. The solution was successively washed with 20 mL of 2N aqueous HCl, 20 mL of saturated, aqueous NaHCO₃ solution, 20 mL of saturated, aqueous EDTA-solution and 20 mL of brine. The organic phase was then dried over MgSO₄ and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (eluent: hexane/toluene =
4:1), suspended in ethanol while heating and filtered. The product was recrystallized from \( \text{CH}_2\text{Cl}_2/ \text{ethanol} \) and obtained as yellow, crystalline material (0.05 g; 54 %).

\[
{^1}\text{H NMR} \ (400 \text{ MHz, C}_2\text{D}_2\text{Cl}_4, \text{ppm}): \ \delta \ 0.81 \ (t; 6\text{H}; {^3}J = 6.60 \text{ Hz}), 0.82 \ (t; 6\text{H}; {^3}J = 6.64 \text{ Hz}), 1.18-1.35 \ (m; 24\text{H}; 19, 20, 21, 35, 36, 37, 58, 59, 73, 74, 75), 1.58 \ (m; 8\text{H}; 18, 34, 56, 72), 2.67 \ (t; 4\text{H}; 33, 55; {^3}J = 7.64 \text{ Hz}), 2.72 \ (t; 4\text{H}; 17, 71; {^3}J = 7.58 \text{ Hz}), 6.36 \ (d; 2\text{H}; 27, 49; {^3}J = 3.79 \text{ Hz}), 6.54 \ (d; 2\text{H}; 31, 53; {^3}J = 3.49 \text{ Hz}), 6.63 \ (d; 2\text{H}; 15, 69; {^3}J = 3.51 \text{ Hz}), 6.71 \ (d; 2\text{H}; 26, 48; {^3}J = 3.78 \text{ Hz}), 6.73 \ (d; 2\text{H}; 32, 54; {^3}J = 3.48 \text{ Hz}), 6.95 \ (d; 2\text{H}; 16, 70; {^3}J = 3.50 \text{ Hz}), 7.02 \ (d; 2\text{H}; 10, 64; {^3}J = 3.76 \text{ Hz}), 7.22 \ (d; 2\text{H}; 11, 65; {^3}J = 3.77 \text{ Hz}), 7.43 \ (d; 2\text{H}; 3, 41; {^3}J = 7.98 \text{ Hz}), 7.55 \ (m; 4\text{H}; 4, 6, 42, 44) 
\]

\[
{^{13}}\text{C NMR} \ (100 \text{ MHz, C}_2\text{D}_2\text{Cl}_4, \text{ppm}): \ \delta \ 14.50, 22.91, 29.08, 29.10, 30.45, 30.50, 31.81, 31.83, 31.86, 123.52, 123.62, 123.90, 124.31, 124.56, 125.02, 125.26, 125.41, 127.37, 128.33, 130.17, 133.02, 133.50, 134.74, 134.86, 137.97, 138.53, 139.59, 140.52, 141.58, 145.70, 146.18 
\]

FD-MS, \( m/z \): 1146.9 ([M]+), 573.3 ([M]+)

### 2.2. Chemical oxidation of DHBPT-SC

To a solution of 0.10 g (0.09 mmol) DHBPT-SC in 150 mL of dry dichloromethane a solution of 0.11 g (0.70 mmol) anhydrous FeCl₃ in 2 mL of dry nitromethane was added at 0 °C under argon atmosphere. After 30 min, the reaction was quenched by adding 50 mL of dry methanol. The quenched mixture was stirred for additional 1 h, successively washed twice with 30 mL of brine and 30 mL of saturated, aqueous NH₄Cl solution. After drying the organic phase over MgSO₄ the solvents were removed under reduced pressure. Two different yellow colored oxidation products (P1 and P2) were isolated by column chromatography on silica gel (eluent: hexane/toluene = 1:1). The mixture contains ca. 0.08 g (80 %) starting material (DHBPT-SC).
P1: 0.008 g (0.007 mmol; 8 %)

$^1$H NMR (400 MHz, CD$_2$Cl$_4$, ppm): δ 0.81 (m; 12H; 22, 38, 60, 76), 1.25-1.35 (m; 24H; 29, 20, 21, 35, 36, 37, 57, 58, 59, 73, 74, 75), 1.52-1.70 (m; 8H; 18, 34, 56, 72), 2.67 (t; 4H; 33, 55; $^3$J = 7.60 Hz), 2.72 (t; 2H; 71; $^3$J = 7.62 Hz), 3.21 (s; 3H; 78), 4.22 (t; 1H; 17; $^3$J = 7.63 Hz), 6.37 (d; 2H; 31, 53; $^3$J = 3.50 Hz), 6.71 (d; 2H; 26, 48; $^3$J = 3.76 Hz), 6.73 (d; 2H; 32, 54; $^3$J = 3.46 Hz), 6.79 (d; 1H; 15; $^3$J = 3.61 Hz), 6.95 (d; 1H; 70; $^3$J = 3.49 Hz), 6.99 (d; 1H; 16; $^3$J = 3.55 Hz), 7.02 (d; 1H; 64; $^3$J = 3.76 Hz), 7.08 (d; 1H; 10; $^3$J = 3.74 Hz), 7.23 (d; 1H; 65; $^3$J = 3.87 Hz), 7.24 (d; 1H; 11; $^3$J = 3.83 Hz), 7.43 (d; 1H; $^3$J = 8.36 Hz), 7.44 (d; 1H; $^3$J = 7.75 Hz), 7.56 (m; 4H; 4, 6, 42, 44)

$^{13}$C NMR (100 MHz, CD$_2$Cl$_4$, ppm): δ 14.46, 14.50, 16.63, 22.89, 22.91, 25.72, 29.08, 29.10, 30.03, 30.45, 30.49, 31.83, 31.85, 31.92, 56.84, 79.85, 120.62, 123.36, 123.52, 123.62, 123.91, 124.34, 124.56, 124.62, 125.03, 125.26, 125.47, 126.43, 127.37, 127.41, 128.33, 128.41, 130.19, 132.39, 133.17, 133.51, 134.73, 134.85, 136.69, 137.62, 138.54, 139.58, 139.61, 140.47, 140.51, 141.58, 142.80, 145.72, 146.19, 146.26

FD-MS, m/z: 1177.3 ([M$^+$]), 1145.5 ([M-CH$_3$O$^+$]), 572.6 ([M$^{2+}$])

P2: 0.010 g (0.008 mmol; 9 %)

$^1$H-NMR (400 MHz, CD$_2$Cl$_4$, ppm): δ 0.81 (m; 12H; 22, 38, 60, 76), 1.15-1.40 (m; 24H; 19, 20, 21, 35, 36, 37, 57, 58, 59, 73, 74, 75), 2.67 (t; 4H; 33, 55; $^3$J = 7.59 Hz), 3.21 (s; 6H; 78, 80), 4.23 (t; 2H; 17, 71; $^3$J = 6.74 Hz), 6.38 (d; 2H; 27, 49; $^3$J = 3.79 Hz), 6.54 (d; 2H; 31, 53; $^3$J = 3.50 Hz), 6.72 (d; 2H; 26, 48; $^3$J = 3.78 Hz), 6.74 (d; 2H; 32, 54; $^3$J = 3.50 Hz), 6.79 (d; 2H; 15, 69; $^3$J = 3.62 Hz), 6.99 (d; 2H; 16, 70; $^3$J = 3.55 Hz), 7.08 (d; 2H; 10, 64; $^3$J = 3.75 Hz), 7.24 (d; 2H; 11, 65; $^3$J = 3.78 Hz), 7.44 (d; 2H; 3, 41; $^3$J = 8.37 Hz), 7.57 (m; 4H; 4, 6, 42, 44)
$^{13}$C NMR (100 MHz, C$_2$D$_2$Cl$_4$, ppm): $\delta$ 14.34, 14.37, 22.80, 25.64, 29.02, 30.40, 31.73, 31.78, 31.87, 38.18, 56.76, 79.85, 123.36, 123.49, 123.62, 124.58, 124.78, 124.97, 125.47, 126.23, 127.37, 128.49, 130.18, 133.21, 133.44, 134.87, 136.69, 137.68, 138.62, 139.63, 140.53, 142.23, 145.70, 146.34
FD-MS, $m/z$: 1207.5 ([M]$^+$), 1175.4 ([M-CH$_3$O]$^+$), 1143.3 ([M-2 CH$_3$O]$^+$), 603.7 ([M]$^{2+}$)

3. References

Figure 1: $^1$H NMR spectrum of 2,2',5,5'-tetrakis(5'-hexyl-2,2'-bithien-5-yl)-3,3'-bithiophene (DHPT-SC)
Figure 2: $^{13}$C NMR spectrum of 2,2',5,5'-tetakis(5'-hexyl-2,2'-bithien-5-yl)-3,3'-bithiophene (DHPT-SC)
Figure 3: $^1$H NMR spectrum of 2,2',5,5'-tetrakis(5'-hexyl-2,2'-bithien-5-yl)-1,1'-biphenyl (DHBPT-SC).
Figure 4: $^{13}$C NMR spectrum of 2,2',5,5'-tetrakis(5'-hexyl-2,2'-bithien-5-yl)-1,1'-biphenyl (DHBPT-SC)
Figure 5: $^1$H NMR spectrum of P1 obtained by chemical oxidation of DHBPT-SC.
Figure 6: $^{13}$C NMR spectrum of P1 obtained by chemical oxidation of DHBPT-SC
Figure 7: $^1H-^1H$-short range-COSY-NMR spectrum of P1 obtained by chemical oxidation of DHBPT-SC
Figure 8: $^1H-^1H$-long range-COSY-NMR spectrum of P1 obtained by chemical oxidation of DHBPT-SC
Figure 9: $^1$H NMR spectrum of P$^2$ obtained by chemical oxidation of DHBPT-SC.
Figure 10: $^{13}$C NMR spectrum of P2 obtained by chemical oxidation of DHBPT-SC
Figure 11: $^1H^1H$ short range-COSY-NMR spectrum of P2 obtained by chemical oxidation of DHBPT-SC
Figure 12: $^1\text{H}^1\text{H}$-long range-COSY-NMR spectrum of P2 obtained by chemical oxidation of DHBPT-SC