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Unexpected Side Chain Oxidation in a Swivel Cruciform Oligothiophene

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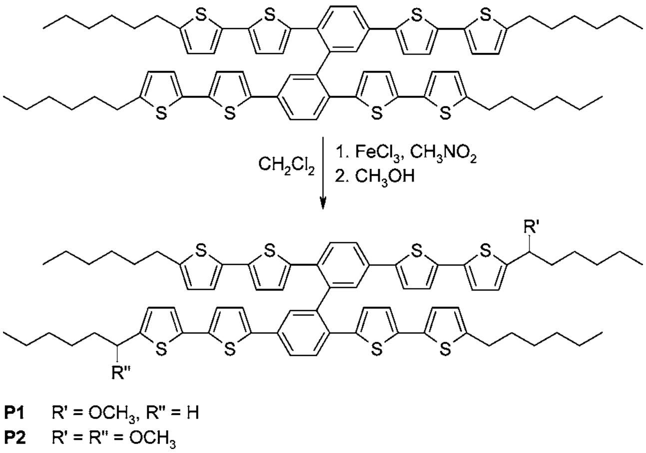
ABSTRACT



Two swivel cruciform oligothiophenes are investigated for the occurrence of oxidative ring closure reactions. Surprisingly, instead of intramolecular cyclizations, a regioselective side chain oxidation of two of the four α-methylene groups next to the terminal thiophene rings is detected for one of the oligomers. Such side chain oxidations may be one unintended degradation pathway in oligothiophene-based organic semiconductors used as the active layer of organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), and organic solar cells (OSCs).

Conjugated swivel cruciform oligomers with oligothiophene building blocks are a new class of soluble, semiconducting oligomers showing high potential for an application in organic field effect transistors (OFET). Typical for these compounds is their 3-dimensional cruciform structure as a result of the covalent link between two linear oligomer segments. They show an increased solubility in organic solvents as compared to the corresponding linear oligothiophenes due to the rotational freedom around the central single-bond.[1] In OFET experiments, the swivel cruciform oligothiophenes showed a rather high charge carrier mobility of up to 0.012 cm^2/Vs and a high current on/off ratio of $>10^5$ of solution-processed devices.[2,3] Two examples of such swivel cruciform oligothiophenes—2,2′,5,5′-tetrakis(5‴-hexyl-2″,2‴-bithien-5″-yl)-3,3′-bithienyl (DHPT-SC) and

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(1) Bilge, A.; Zen, A.; Forster, M.; Li, H.; Galbrecht, F.; Nehls, B. S.; Farrell, T.; Neher, D.; Scherf, U. *J. Mater. Chem.* **2006**, *16*, 3177–3182.
(2) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrell, T. *J. Am. Chem. Soc.* **2006**, *128*, 3914–3915.
(3) Zen, A.; Pingel, P.; Neher, D.; Scherf, U. *Phys. Status Solidi A* **2008**, *205*, 440–448.

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2,2′,5,5′-tetrakis(5‴-hexyl-2″,2‴-bithien-5″-yl)-1,1′-biphenyl (DHBPT-SC)—are shown in Figure 1.

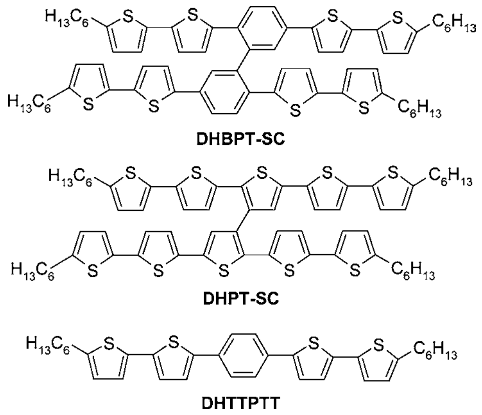
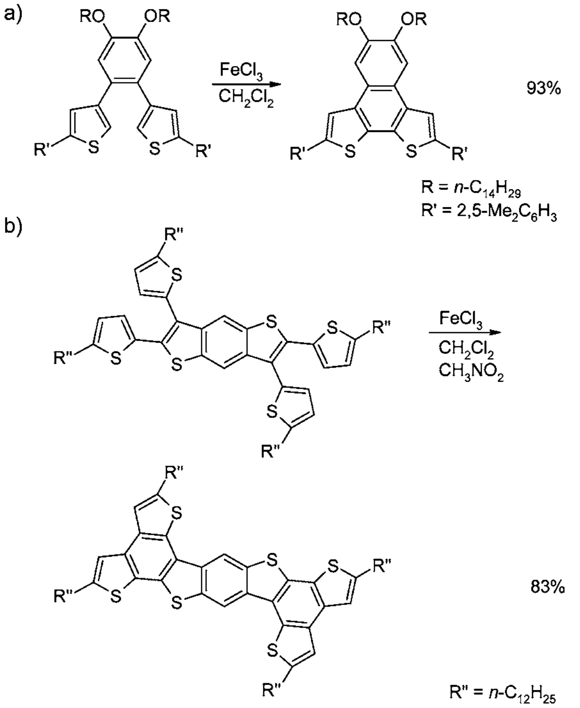


Figure 1. Chemical structures of the investigated swivel-cruciform oligothiophenes DHBPT-SC and DHPT-SC and the linear oligomer DHTTPTT.

For future OFET applications, high charge carrier mobilities of the active layers are mandatory. The charge carrier mobility strongly depends on the orientation of the molecules in the film and the amount of interactions between their π-systems. One principle for increasing the π-interaction is the planarisation of the molecules, as realized and proven in highly condensed aromatic hydrocarbons like pentacene or hexabenzocoronene.[4−6] But the often observed low solubility of such highly crystalline substances complicates the processing of these substances.[7,8]

One concept for the synthesis of highly condensed, aromatic systems is the oxidative cyclization of suitable oligoarylene precursors. For this purpose, different chemical and photochemical methods with a variety of oxidizing agents have been developed. Such reactions have been successfully applied in ring closure reactions of oligoarylenes containing thienyl-units.[9−14] $FeCl_3$ was established as one of the most powerful oxidizing agents for this kind of reactions. Hereby, Swager et al. investigated the intramolecular cyclization of several bisthienylbenzene derivates showing a quasi-reversible oxidation wave in their cyclic voltammograms. The resulting condensed napthodithiophene systems could be obtained with a yield of up to 93% by using $FeCl_3$ in CH_2Cl_2/CH_3NO_2 as oxidizing agent (Scheme 1).[13] Cao et al. described the cyclization of a tetrathienyldithienobenzene oligomer. They also used $FeCl_3$ in CH_2Cl_2/CH_3NO_2 as the oxidizing agent and achieved the corresponding doubly condensed arylene system with a yield of 83% (Scheme 1).[14] Roncali et al. have reported photochemical cyclizations of 2-(thien-3-yl)-3-(thien-2-yl)thiophenes to benzo[1,2-b:3,4-b′:5,6-b″]trithiophenes with I_2/O_2 as the oxidizing agent.[12]

Scheme 1. Oxidative Cyclization using $FeCl_3$ as Oxidizing Agent after (a) Swager et al[13] and (b) Cao et al.[14]



On the basis of these observations, we also expected the occurrence of such oxidative ring-closing reactions in our swivel-cruciform oligothiophenes under formation of higher condensed aromatic systems. Therefore, the electrochemical oxidation of the two oligothiophenes DHPT-SC and DPBPT-SC was first investigated by cyclic voltammetry CV (solvent: CH_2Cl_2, electrolyte: n-Bu_4NPF_6, Ar-atmosphere, electrode: Pt, Fc/Fc^+ as internal standard, scan rate: 0.1 V/s; see Figure 2).[15] In the cyclic voltammogram of DHPT-SC two oxidation peaks ($E_1 = 0.415$V; $E_2 = 0.650$V, referenced vs Fc/Fc^+) and the corresponding reduction peaks of oxidized intermediates ($E_3 = 0.555$V; $E_4 = 0.335$V) are detectable thus demonstrating a (quasi) reversible oxidation of the swivel cruciform molecules under formation of fairly stable oxidation products.[2]

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(4) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747.
(5) Kastler, M.; Pisula, W.; Wasserfallen, D.; Pakula, T.; Müllen, K. *J. Am. Chem. Soc.* **2005**, *127*, 4286–4296.
(6) Kikuzawa, Y.; Mori, T.; Takeuchi, H. *Org. Lett.* **2007**, *9*, 4817–4820.
(7) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5026–5048.
(8) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem.* **2008**, *120*, 4138–4167.
(9) Cho, D. M.; Parkin, S. R.; Watson, M. D. *Org. Lett.* **2005**, *7*, 1067–1068.
(10) Brooks, P.; Donati, D.; Pelter, A.; Poticelli, F. *Synthesis* **1999**, *8*, 1303–1305.
(11) Perrine, D. M.; Kagan, J.; Huang, D.-B.; Zeng, K.; Teo, B.-K. *J. Org. Chem.* **1987**, *52*, 2213–2216.
(12) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 273–276.
(13) Tovar, J. D.; Rose, A.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 7762–7769.
(14) Zhou, Y.; Liu, W.-J.; Ma, Y.; Wang, H.; Qi, L.; Cao, Y.; Wang, J.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 12386–12387.
(15) Bilge, A. PhD thesis, BU Wuppertal, **2006**.

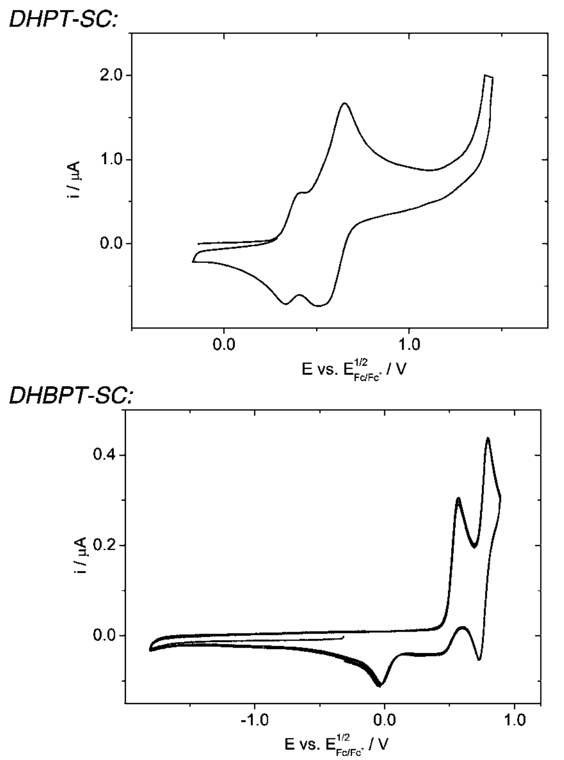

Figure 2. Cyclic voltamogramms of DHPT-SC and DHBTP-SC Conditions: solvent: CH_2Cl_2; electrolyte: n-Bu_4NPF_6; Ar-atmosphere, Pt electrode (Pt-wire in a sealed glass tube; Fc/Fc^+ as internal standard; scan rate: 0.1 V/s).

Compared to the oxidative behavior of DHPT-SC, DHBPT-SC exhibits a different characteristic in our CV measurements (Figure 1). In its cyclic voltammogram also two oxidation peaks (E_1 = 0.570V; E_2 = 0.795V) are detectable, but only one rereduction peak (E_3 = 0.725V) corresponding to the second oxidation step is observed. Instead of the second rereduction peak a new reduction wave shifted to a lower potential of $E_4 = -0.06$V is observed. This reduction peak is assigned to the reduction of an intermediate that is formed in an irreversible chemical reaction. A possible oxidative chemical reaction that may occur in DHBPT-SC could be the proposed intramolecular cyclization to a higher condensed aromatic system. However, the absence of the corresponding reoxidation peak in the following oxidation scans is a first indication that an instable product is formed in the reduction at lower potential.

To clarify the occurring processes, we started a series of chemical oxidation experiments. The two swivel cruciform starting materials have been synthesized in an improved synthetic scheme by modification of the initially applied procedure.[16] For this, we have reacted 5-tri-n-butylstannyl-5′-hexyl-2,2′-bithiophene[17] in a Stille-type aryl-aryl coupling with 2,2′,5,5′-tetrabromo-3,3′-bithiophene toward DHPT-SC or 1,4-dibromo-2-chlorobenzene to obtain 2,5-bis(5′-hexyl-2,2′-bithien-5-yl)-1-chlorobenzene Cl-DHTTPTT. This linear intermediate was finally transformed into the second swivel cruciform DHBPT-SC in a Yamamoto-type aryl-aryl coupling (see Supporting Information).

In the following oxidation experiments we applied well-established oxidation (cyclization) procedures as described in the literature for related aromatic precursors ($FeCl_3$ in CH_3NO_2/CH_2Cl_2; $Cu(OTf)_2/AlCl_3$ in CS_2; UV-light with I_2 or O_2 as oxidizing agent) followed by an analysis of the products formed in course of the reaction.

Only using $FeCl_3$ in CH_3NO_2/CH_2Cl_2 as oxidizing agent and after quenching the reaction mixture with methanol we could isolate two oxidation products of DHBPT-SC (P1: yield ca. 8% and P2: yield ca. 9%, Figure 3) in addition to the main fraction of recovered, unreacted starting material (ca. 80%): One of them shows lower symmetry (P1), the other higher symmetry ^{1}H and ^{13}C NMR-spectrum (P2). A constant number of aromatic hydrogens in all ^{1}H NMR-spectra indicates the absence of cyclization events. In the ^{1}H NMR spectra of the two oxidation products P1 and P2 especially the hydrogen signals of the terminal thienyls are shifted to lower field (see Supporting Information).

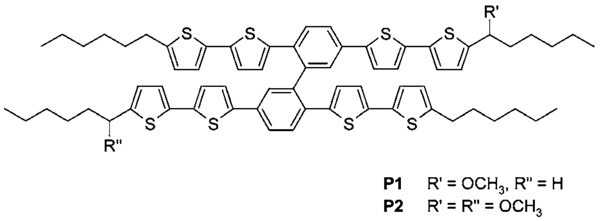

Figure 3. Structures of the two observed oxidation products P1 and P2 of DHBPT-SC.

For the two oxidation products P1 and P2, we observed an increased molar mass with Δm of 31.0 (P1) and 61.2 units (P2). On the basis of the ^{1}H, ^{13}C NMR, and the FD-mass spectra, it was possible to fully assign the chemical structure of the two products P1 and P2 which are formed in a side chain oxidation of one or two aliphatic α-methylene groups of the hexyl substituents (Figure 3).

For the formation of the products P1 and P2 we are proposing the mechanism displayed in Scheme 2.

After oxidation of DHBPT-SC to a radical monocation, this intermediate undergoes a deprotonation to a “benzylic” radical, which is subsequently oxidized to the corresponding “benzylic” cation. The deprotonation of the radical cation takes place preferentially at the α-methylenes of the hexyl substituents since the resulting benzylic radical is mesomerically stabilized. Quenching of the reaction mixture by adding methanol results in a methoxy addition at the cation under formation of the $-OCH_3$ substituents. The oxidation

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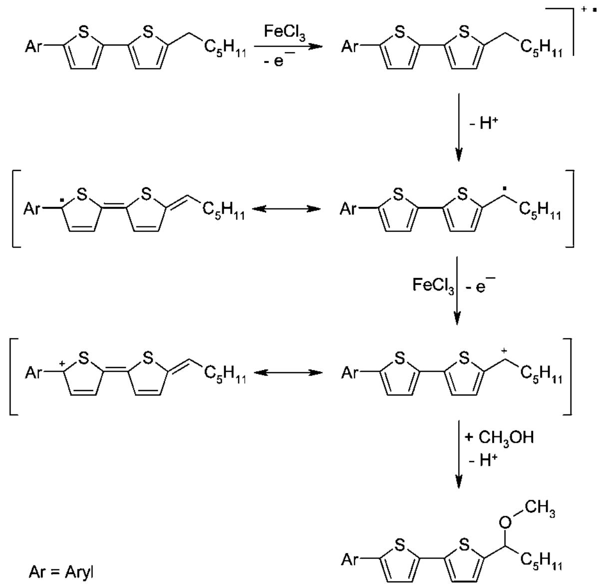
(16) Zen, A.; Pingel, P.; Jaiser, F.; Neher, D.; Grenzer, J.; Zhuang, W.; Rabe, J. P.; Bilge, A.; Galbrecht, F.; Nehls, B. S.; Farrell, T.; Scherf, U.; Abellon, R. D.; Grozema, F. C.; Siebbeles, L. D. A. *Chem. Mater.* **2007**, *19*, 1267–1276.

(17) Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Botta, C. *Tetrahedron* **2002**, *58*, 2245–2251.

Scheme 2. Proposed Mechanism for the Formation of the Two Oxidation Products P1 and P2



of two methylene groups in the second oxidation product should be a stepwise process.

Due to the strong selective oxidation of just two of the four methylene groups, we expect a strict thermodynamically controlled deprotonation of the radical cations. One should notice that DHBPT-SC contains two pairs of chemically nonequivalent methylene groups. In all experiments, we observed the regioselective oxidation of only one sort of them.

Also the cruciform pentathiophene dimer DHPT-SC was reacted with $FeCl_3$ under similar conditions. In contrast to DHBPT-SC, we did not find any indications for side chain oxidations and could only recover unreacted starting material. Also 2,5-bis(5′-hexyl-2,2′-bithien-5-yl)benzene DHTTPTT (for the chemical structure see Figure 1), synthesized according to the literature,[18] as linear, “monomeric” counterpart to the swivel cruciform dimer DHBPT-SC was stable under the oxidative reaction conditions ($FeCl_3$ in CH_3NO_2/CH_2Cl_2).

The different reactivities of the two dimers DHPT-SC and DHBPT-SC toward oxidation with $FeCl_3$ in CH_2Cl_2/CH_3NO_2 may be related to different energetic positions of the HOMO/LUMO energy levels of the corresponding radical cations which are formed in the first oxidation (electron transfer) step. Only the lower HOMO energy level of the wider HOMO/LUMO energy gap (band gap) oligomer DHBPT-SC may allow a deprotonation at the α-methylenes of the alkyl side chains thus leading to the observed side chain oxidation. However, the absence of any side chain oxidation in the linear, “monomeric” oligomer DHTTPTT is somewhat striking. One possible explanation for the increased oxidative stability of the linear oligomer could be a more planar conformation of DHTTPTT and the corresponding radical cation as related to the missing *ortho*-substituents at the central phenylene moiety. The planarized structure should lead to an energetic stabilization of the corresponding radical cation and subsequently to a distinctly decreased deprotonation tendency at the side chain methylenes.

To summarize, the swivel cruciform dimer DHBPT-SC undergoes an unexpected side chain oxidation of two α-methylenes of the four hexyl side chains. Intramolecular cyclizations could not be observed for both swivel cruciforms most probably due to steric constraints that do not allow a close proximity of the corresponding carbon centers. These findings may be of considerable importance as possible degradation channels of alkylated oligo- or polythiophene based organic semiconductors in OFETs, OLEDs, and OSCs upon charging.

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Supporting Information Available: Representative synthetic procedures and characterization data for DHPT-SC, DHBPT-SC, and the corresponding oxidation products. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Tian, H.; Wang, J.; Shi, J.; Yan, D.; Wang, L.; Geng, Y.; Wang, F. *J. Mater. Chem.* **2005**, *15*, 3026–3033.