APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 859–863
Published online 20 May 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.917

Synthesis and X-ray single-crystal structure study of 5,5′-bis(silyl)-functionalized 3,3′-dibromo-2,2′-dithiophenes

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Received 18 February 2005; Revised 24 February 2005; Accepted 25 February 2005

A high-yield synthesis toward 5,5′-bis(silyl)-functionalized 3,3′-dibromo-2,2′-dithiophenes with very efficient work-up procedure is presented. The molecular structures of two silyl functionalized dibromo-dithiophenes in the solid state have been determined to investigate the structural influences of different functional groups on the degree of π-conjugation within the dithiophene moieties, as well as their packing properties. The planar alignment of the *tert*-butyldimethylsilyl-functionalized dibromo-dithiophene shows a significantly higher degree of conjugation of the π-system with a more favorable molecular packing than the skewed arrangement of the triisopropylsilyl-substituted species. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: oligothiophenes; electronic materials; synthesis; X-ray structure

INTRODUCTION

Thiophene-based materials play an important role in the field of molecular electronics owing to their extraordinary electronic properties. Oligomeric and polymeric systems, in particular, are successfully established in a broad variety of applications, such as organic light-emitting diodes or organic field-effect transistors.[1] A very important feature for the performance of such materials is the degree of π-conjugation, which has an intrinsic impact on their electronic properties. The same is true for the molecular packing, which is essential for the conduction properties of the materials with respect to organic transistor applications.[2] Since the band gap of optoelectronic materials depends strongly on the degree of π-conjugation (with planar systems showing a much more favorable band gap than distorted systems) we had an interest in how the substitution pattern of silyl functionalities would affect this issue in dibromo-dithiophenes and to what extent the π-conjugation would be disturbed by a distortion of the thiophene unit alignment. In the context of our work on phosphorus–thiophene hybrid materials for molecular electronics, we rely on the title compounds as starting materials for the synthesis of dithieno[3,2-*b*:2′,3′-*d*]phospholes (**1**).[3,4] It should be mentioned that 3,3′-dibromo-5,5′-bis(trimethylsilyl)-2,2′-dithiophene (see Scheme 1, SiR_3 = $SiMe_3$), which is comparable to the compounds presented, has been described by Ohshita *et al*.[5] before; however, the yield of the product obtained is reduced due to an extensive work up.

In this contribution we now report on the efficient, high-yield synthesis of the two new, silyl-functionalized dibromo-dithiophenes **3** and **4**, as well as on the crystal structure determinations of 3,3′-dibromo-5,5′-bis(triisopropylsilyl)-2,2′-dithiophene (**4**) and 3,3′-dibromo-5,5′-bis(*tert*-butyl-dimethylsilyl)-2,2′-dithiophene (**5**).

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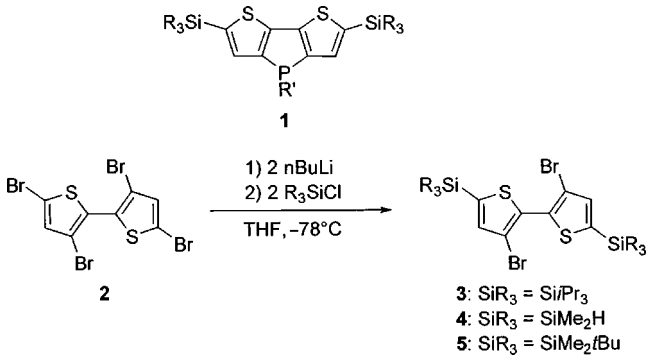
Contract/grant sponsor: Fonds der Chemischen Industrie.
Contract/grant sponsor: BMBF.
Contract/grant sponsor: Professor Dr J. Okuda.

EXPERIMENTAL

Synthesis of the materials

Reactions were carried out in dry glassware and under an inert atmosphere of purified argon using Schlenk techniques. Solvents were dried over appropriate drying agents and then distilled. *n*-BuLi (2.5 M in hexane), Me_2SiHCl and i-Pr_3SiCl were used as received from Acros. 3,3′,5,5′-Tetrabromo-2,2′-bithiophene (**2**) was prepared by literature methods.[6]

The title compounds were prepared according to the reported procedure in the case of **5**[3,4] or as follows. To



Scheme 1.

a solution of 3,3′,5,5′-tetrabromo-2,2′-bithiophene (3.62 g, 7.5 mmol) in tetrahydrofuran (THF; 40 ml) *n*-BuLi (6 ml, 15 mmol) was added dropwise at −78 °C. The solution was stirred for 15 min and the corresponding chlorosilane (Me_2HSiCl: 2 ml, 18 mmol; i-Pr_3SiCl: 3.8 ml, 18 mmol) was added dropwise to the reaction mixture at that temperature. The reaction mixture was allowed to warm slowly to room temperature and the solvent was subsequently removed under vacuum. The residue was taken up in pentane (ca 60 ml) and filtered over neutral alumina. Evaporation of the solvent under vacuum provided the product **3** (R = i-Pr_3Si (TIPS)) as beige crystals (4.35 g, 91% yield) and **4** as a bright yellow oil (R = Me_2SiH: 3.11 g, 94% yield).

3. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.13$ (s, 2H, Ar-H), 4.52 (sept., ^3J(H,H) = 7.4 Hz, 6H, CH), 1.09 (d, ^3J(H,H) = 7.4 Hz, 36H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.2, 136.7, 133.9, 112.3, 18.4, 13.5. MS (EI, 70 eV), m/z (relative intensity): 636 (100) [M^+], 593 (80) [M^+ − i-Pr], 550 (30) [M^+ − 2i-Pr].

4. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.18$ (s, 2H, Ar-H), 4.52 (sept., ^3J(H,H) = 3.8 Hz, 2H, SiH), 0.39 (d, ^3J(H,H) = 3.8 Hz, 12H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 139.0$, 137.9, 134.2, 113.0, −3.4. MS (70 eV): m/z (relative intensity): 440 (100) [M^+], 382 (25) [M^+ − $SiMe_2H$], 280 (60) [M^+ − 2Br], 59 (30) [$SiMe_2H^+$].

Suitable single crystals for X-ray structure studies of **3** and **5** were obtained from concentrated pentane solutions at room temperature.

Analyses

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer. Chemical shifts were referenced to external tetramethylsilane (^{13}C, ^{1}H). Electron ionization (70 eV) mass spectra were run on a Finnigan 8230 spectrometer. Diffraction data were collected on a Bruker SMART D8 goniometer with APEX CCD detector. The structures were solved by direct methods (SHELXTL) and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding model.

RESULTS AND DISCUSSION

All compounds are accessible by reaction of 3,3′,5,5′-tetrabromodithiophene with two equivalents of *n*-BuLi in THF at −78 °C followed by the addition of the respective silyl chloride. Complete removal of the solvent and subsequent addition of pentane allowed for an efficient separation of the products from the LiCl via filtration and afforded compounds **3**–**5** in very good to almost quantitative yields. The TIPS- (**3**) and *tert*-BuMe_2Si-functionalized (TBDMS, **5**) dithiophenes were obtained as beige solids, whereas the $SiMe_2H$-functionalized compound **4** was isolated as a yellow oil. The ^{1}H and ^{13}C NMR data for the new compounds **3** and **4** only show one set of signals for each species, indicating that free rotation of the thiophene subunits around their connecting bond is possible in solution.

In order to investigate whether the different silyl substituents had an influence on the degree of π-conjugation of the dithiophene moieties in the solid state, compounds **3** and **5** were subjected to X-ray single-crystal structure determinations. To the best of our knowledge, no example of a dithiophene bearing bromo as well as silyl substituents has been described by means of X-ray crystallography, although corresponding dithiophenes with bromo[7] *or* silyl[8] substitutents have been characterized by this method.

Crystal structure determinations

The TIPS-substituted compound **3** crystallizes in space group $P\bar{1}$ (Table 1) and the molecular structure is shown in Fig. 1. The two thiophene subunits show a gauche conformation with a torsion angle of about 72° between them, compared with the 68° observed for 3,3′-dibromodithiophene reported by Antolini *et al.*[7] The distortion of the π-conjugation is evident in the very long C(4)–C(5) bond of 1.463(2) Å bridging the two thiophene subunits and the significantly distinct single and double bonds of the thiophenes (see Table 2). However, an extension of the π-conjugation throughout the silicon centers in **3** can be anticipated in the slightly elongated C(1)–Si(1) and C(8)–Si(2) bonds of 1.888(2) Å and 1.885(2) Å respectively and the relatively long C(1)–C(2) and C(7)–C(8) bonds of 1.374(2) Å and 1.378(2) Å respectively. These observations support the presence of electron acceptor centers, such as silyl functionalities, being beneficial for the optimization of the band gap of the materials. The crystal packing of **3** (Fig. 2) shows noticeable π-stacking interactions and can be analyzed in terms of a two-layer structure governed by intermolecular Br–Br contacts amounting to approximately 3.85 Å. Two Br–Br contacts to an adjacent dithiophene molecule of the second layer are observed with each molecule, resulting in the formation of a 12-membered ring consisting of eight carbon atoms and four bromine atoms (Fig. 3).

The TBDMS-functionalized compound **5**, on the other hand, shows a planar orientation of the two thiophene subunits in the solid state with a transoid anti-arrangement

Table 1. Crystal data and structure refinement for **3** and **5**

	3	**5**
Empirical formula	$C_{26}H_{44}Br_2S_2Si_2$	$C_{20}H_{32}Br_2S_2Si_2$
Formula weight	636.73	552.58
Temperature (K)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions	$a = 8.244(2)$ Å, $\alpha = 85.90(3)°$	$a = 7.5754(13)$ Å, $\alpha = 90°$
	$b = 11.740(2)$ Å, $\beta = 79.08(3)°$	$b = 11.3005(19)$ Å, $\beta = 95.267(3)°$
	$c = 16.902(3)$ Å, $\gamma = 74.31(3)°$	$c = 14.737(3)$ Å, $\gamma = 90°$
Volume (Å^3)	1546.1(5)	1256.3(4)
Density (calc.) (Mg m^{-3})	1.368	1.461
Z	2	2
Absorption coefficient (mm^{-1})	2.847	3.492
$F(000)$	660	564
Crystal size (mm^3)	0.70 × 0.40 × 0.20	0.57 × 0.46 × 0.31
θ range for data collection (°)	1.23 to 28.08	2.27 to 28.35
Index ranges	$-10 \le h \le 10, -15 \le k \le 15, -22 \le l \le 22$	$-10 \le h \le 10, -15 \le k \le 15, -19 \le l \le 19$
Reflections collected	20 929	16 843
Independent reflections	7467 ($R_{int} = 0.0236$)	3120 ($R_{int} = 0.1017$)
Completeness to θ	28.08°, 99.4%	28.35°, 99.9%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.5998 and 0.2405	0.3368 and 0.1975
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7467/0/289	3120/0/118
Goodness-of-fit on F^2	1.056	1.075
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0255$, $wR_2 = 0.0641$	$R_1 = 0.0303$, $wR_2 = 0.0829$
R indices (all data)	$R_1 = 0.0309$, $wR_2 = 0.0662$	$R_1 = 0.0325$, $wR_2 = 0.0838$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.810 and −0.380	2.025 and −0.585
CCDC deposition no.	264 079	264 078

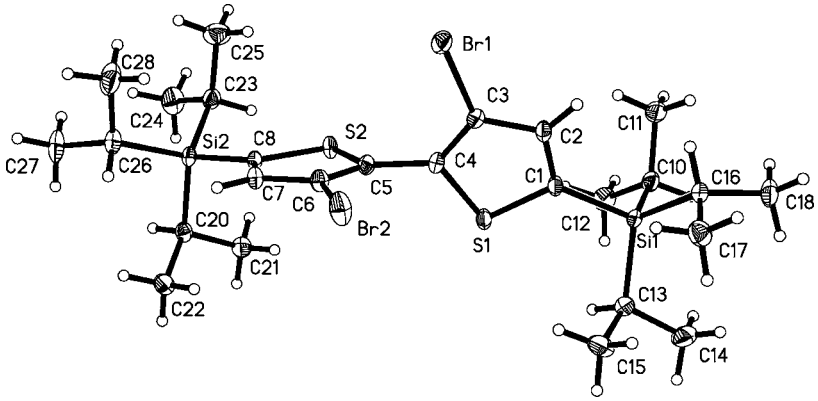


Figure 1. Molecular structure of **3** in the solid state at the 50% probability level.

due to the position of the center of the molecule about an inversion center of the unit cell (Fig. 2). The structure much resembles that of 5,5′-bis(trimethylsilyl)-2,2′-dithiophene; this is surprising, since in **3** and in 3,3′-dibromo-2,2′dithiophene[7] the presence of the bromo-substituents seems to induce gauche conformations in the solid state. However, the planar structure of **5** leads to a noticeable increase of the degree of conjugation of the π-system, resulting

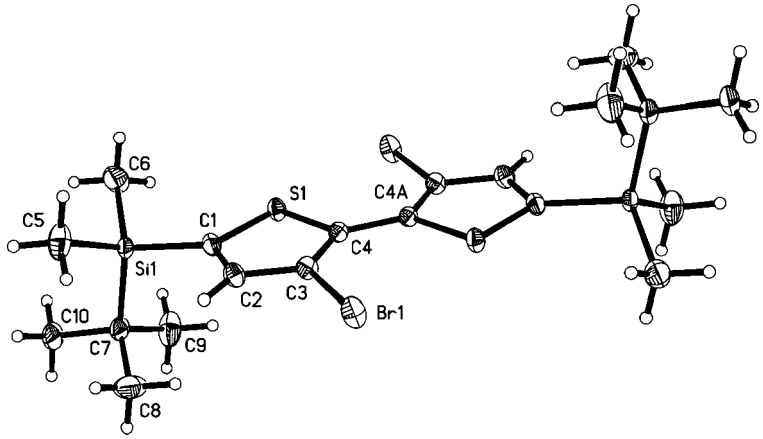


Figure 2. Molecular structure of **5** in the solid state at the 50% probability level. Symmetry transformations to generate equivalent atoms: $2-x$, $2-y$, $-z$.

Table 2. Selected bond lengths (Å) for **3** and **5**

	3	5
Br1–C3	1.8876 (16)	1.886 (2)
Br2–C6	1.8862 (16)	
S1–C1	1.7318 (16)	1.722 (2)
S1–C4	1.7328 (16)	1.742 (2)
Si1–C1	1.8881 (16)	1.887 (2)
Si2–C8	1.8848 (17)	
C1–C2	1.374 (2)	1.373 (3)
C3–C2	1.419 (2)	1.419 (3)
C3–C4	1.368 (2)	1.394 (3)
C5–C4/C4–C4A	1.463 (2)	1.449 (4)

in a shortened C(4)–C(4A) bond of 1.449(4) Å bridging the two thiophene subunits, and a significantly longer adjacent double bond C(3)–C(4) of 1.394(3) Å. Again, the extension of the π-conjugated system throughout the silicon centers is apparent in the elongated C(1)–Si(1) bond of 1.887(2) Å, which is comparable to that observed for **3**. The other bond lengths (see Table 2) are similar to compound **3** and the related dithiophenes.[7,8] The packing diagram of **5** (Fig. 3) shows the dominating effect of the *tert*-butyl groups of the silyl substituents building up layers in an undulating herringbone-type structure, which is also observed for a variety of optoelectronic materials.[1,2]

In conclusion, the molecular structure of **5** in the solid state indicates the beneficial influences of a planar arrangement of the dithiophene moiety on the degree of π-conjugation leading, as well as to a favorable molecular packing. With respect to potential applications in molecular electronics, it seems desirable, therefore, to utilize the steric and electronic features of appropriate functional groups (e.g. silyl, as shown here) to accommodate certain materials requirements.

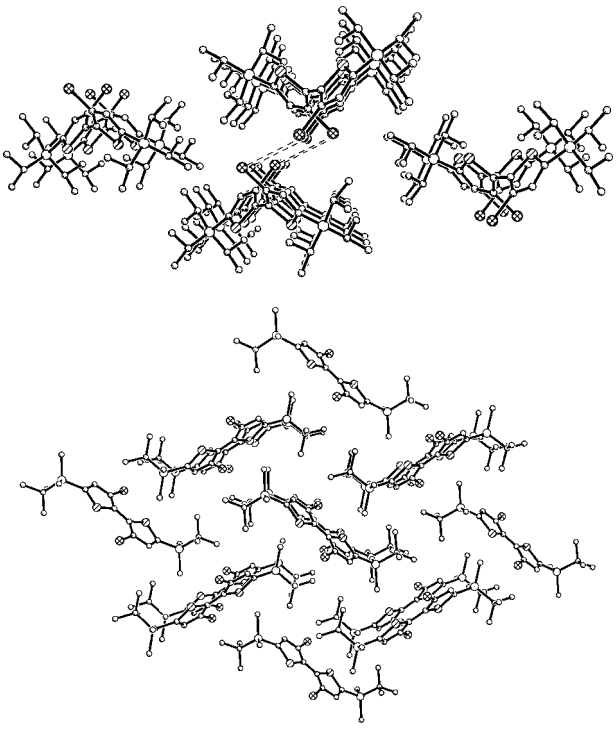


Figure 3. Packing diagrams for **3** (top) and **5** (bottom). Hydrogen atoms are omitted for clarity.

Acknowledgements

Financial support from the Fonds der Chemischen Industrie, the BMBF and from Professor Dr J. Okuda is gratefully acknowledged. The author would further like to thank Professor Dr U. Englert for the X-ray data collection and helpful discussions.

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