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Bithienylsilanes: unexpected structure and reactivity

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Abstract

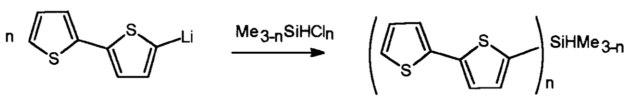
5-(2,2′-Bithienyl)hydrosilanes were prepared by reaction of bithienyl lithium with chlorodimethylsilane, dichloromethylsilane and trichlorosilane. It was shown that 5-(2,2′-bithienyl)dimethylsilane possesses higher reactivity in the hydrosilylation reaction of monosubstituted acetylene derivatives compared with (2-thienyl)dimethylsilane. The elongation of the π-conjugated chain leads to increasing selectivity of the hydrosilylation reaction. An unusual structure for bis[5-(2,2′-bithienyl)]methylsilane has been established by X-ray analysis.

Keywords: Bithiophene; Silane; Hydrosilylation; Coupling; X-ray determination

1. Introduction

During the last decade the number of π-conjugated oligomers and polymers investigated as advanced materials for electronic and optical applications has increased rapidly. Thiophene-based oligomers belong to one of the most carefully studied types of materials and have received a great deal of attention for both fundamental and practical reasons. In view of their interesting electrochemical, electronic and optical abilities [1] these compounds are studied for non-linear optical properties, electrical semiconducting properties in the doped state, neutral electronic properties in thin film applications such as active layers in field-effect transistors and in electroluminescent devices [2]. Recent synthesis of linear silyl-containing thiophene-based materials possessing a regular alternating arrangement of silanylenes and π-electron heterocyclic moieties represents an area of current active interest [3]. The unusual electrical and optical properties are generally attributed to the delocalization of electrons through silylene moieties. The introduction of the reactive functional groups to the silicon atom gave possibilities for simple and easy construction of hyperbranched polysilylthiophenes [4].

In the present report we describe the synthesis of bithienylhydrosilanes, which according to X-ray crystallographic study have unprecedented molecular structure. By virtue of the reactive Si–H bond present in these compounds, various bithiophenes and thus oligothiophene derivatives can be prepared.



n =1 (**1**), 2 (**2**) and 3 (**3**)

Scheme 1.

2. Results and discussion

In previous investigations, we found that thienylhydrosilanes are more active [5] in the hydrosilylation of allylamines, allylsilanes, vinylsilanes and different acetylene derivatives than the corresponding phenylhydrosilanes. To study the influence of the π-conjugated chain elongation on reactivity of hydrosilanes we synthesized bithienylhydrosilanes (**1**–**3**) bearing one, two or three bithienyl groups at the silicon atom. These compounds were prepared by coupling of bithienyl lithium with chlorodimethylsilane, dichloromethylsilane and tri-

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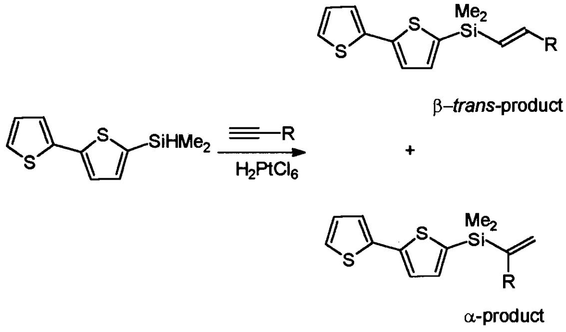


R=Me₃C, Me₃Si, Et₂NCH₂, COOMe, Ph

Scheme 2.

chlorosilane, respectively (Scheme 1). To prevent the substitution of the Si–H bond by bithienyl group the reaction was carried out at −78°C. In such conditions the yields of compounds **1**–**3** achieved 71–80%.

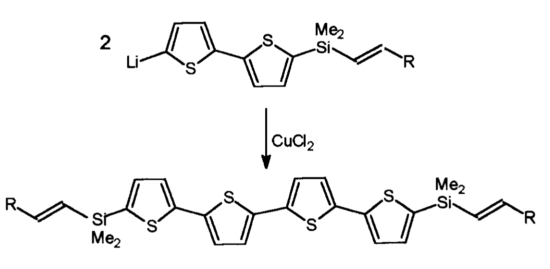
It has been shown that in the presence of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) 5-(2,2′-bithienyl)dimethylsilane (**1**) reacts exothermally with 3,3-dimethyl-1-butyne, trimethylsilylacetylene, 3-diethylaminoprop-1-yne, phenylacetylene and methyl propiolate. In the case of 3,3-dimethylbut-1-yne and 3-diethylamino-1-propyne the hydrosilylation proceeds regioselectively and stereospecifically to give solely β-*trans*-products **4** (R = *t*-Bu) or **6** (R = Et_2NCH_2), respectively. The replacement of the *tert*-butyl group by trimethylsilyl in the acetylene derivative leads to an insignificant decrease in regioselectivity and formation of the β-*trans*- and α isomers, the β-*trans*-product **5** (R = Me_3Si) being predominant (96:4). The ratio of the β-*trans*-/α products formed in the reaction of phenylacetylene with hydrosilane **1** is 72:28 (Scheme 2). The hydrosilylation of methyl propiolate by silane **1** gives almost the same isomer mixture (73:27) (Table 1). Comparing (2-thienyl)dimethylsilane and 5-(2,2′-bithienyl)dimethylsilane (**1**) in hydrosilylation reactions it may be concluded that elongation of the π-conjugated chain results in a considerable increase in reactivity. For example, the hydrosilylation of *N*-propargylamines with (2-thienyl)dimethylsilane carried out at 20°C for 180 days or at 50°C for 6 h yields traces of products. Only by raising the temperature to 200°C were higher yields (50–80%) achieved. Contrarily, the addition of 5-(2,2′-bithienyl)dimethylsilane (**1**) to the triple C≡C bond of acetylene derivatives in the presence of Speier's catalyst occurs easily at room temperature and proceeds exothermally. As a rule the hydrosilylation was completed during 0.5 h to give the hydrosilylation products with almost quantitative yields. It should be noted that the regioselectivity of the reaction rises with the elongation of the π-conjugated chain. The single exception is the reaction of phenylacetylene hydrosilylation. Both in the case of (2-thienyl)dimethylsilane and 5-(2,2′-bithienyl)dimethylsilane (**1**) the isomeric ratio of products remains the same.

These compounds can be successfully used for synthesis of oligothiophene derivatives. For example, β-(*E*)-[5-(2,2′-bithienyl)dimethylsilyl]-*R*-ethylenes **4** and **5** were lithiated by BuLi into the 5′-position of the bithiophene heterocycle. Subsequent oxidative coupling of the lithium derivatives [6] by the action of anhydrous $CuCl_2$ yields quaterthiophenes **7** (R = *t*-Bu) and **8** (R = Me_3Si), containing silylvinyl terminal groups (Scheme 3).

The unusually high activity of 5-(2,2′-bithienyl)dimethylsilane (**1**) induced us to study physicochemical

Table 1
Hydrosilylation of acetylenes RC≡CH with 5-(2,2′-bithienyl)dimethylsilane (**1**) (20°C, 1 h, catalyst $H_2PtCl_6{\cdot}6H_2O$) and ^1H-NMR data for the mixture of isomers

Compound (R)	Yield (%)	β-(*E*)-/α isomer ratio (GC and ^1H-NMR data)	δ (^1H)-NMR (ppm)				
			R	SiMe	HC=CH	=CH_2	Bithiophene ring protons
Me_3C (**4**)	80	100/0	1.12	0.48	5.68 (J = 20.46 Hz) 6.25 (J = 20.46 Hz)		7.1–7.28
Me_3Si (**5**)	92	96/4	0.09 0.16	0.4 0.41	7.08 (J = 21.8 Hz) 7.20 (J = 21.8 Hz)	6.73 (J = 5.6 Hz)	7.0–7.25
Et_2NCH_2 (**6**)	85	100/0	0.62 (t, J = 7.8 Hz) 2.04 (q, J = 7.8 Hz) 2.80 (d, J = 5.2 Hz)	0.3	5.73 (J = 18.1 Hz) 5.93 (J = 18.1 Hz)		6.88–7.16
COOMe	88	73/27	3.76 3.78	0.48 0.54	6.27 (J = 20.4 Hz) 7.02 (J = 20.4 Hz)	6.12 (J = 2.1 Hz) 6.78 (J = 2.1 Hz)	6.95–7.26
Ph	81	72/28	7.19–7.25	0.41 0.49	6.58 (J = 18.8 Hz) 7.08 (J = 18.8 Hz)	5.56 (J = 2.8 Hz) 6.01 (J = 2.8 Hz)	6.97–7.30



R=Me$_3$C (**7**), Me$_3$Si (**8**)

Scheme 3.

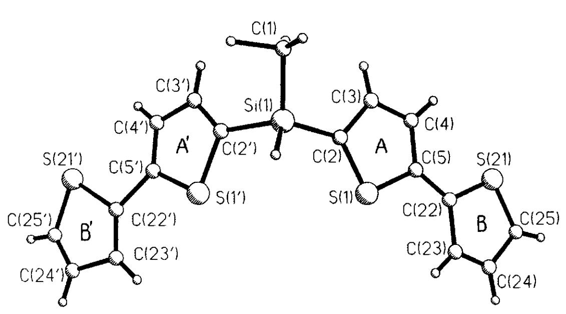


Fig. 1. Molecular structure of hydrosilane **2**.

and structural features of bithienylhydrosilanes. As is clear from Table 2, the increase in the number of heterocyclic substituents at the silicon atom is accompanied by a bathochromic shift in UV–vis spectra from 311 nm for hydrosilane **1** to 325 nm for hydrosilane **3** and an increase of the ν_{Si-H} bond frequency in IR spectra. The low field shift of the Si–H protons from 4.56 to 5.80 ppm and the shielding effect of the silicon atom were detected in ^{1}H and ^{29}Si-NMR spectra. The same tendencies were observed in spectra of 2-thienylhydrosilanes. The similarity of physicochemical properties and considerable difference of reactivity were a reason to study the molecular structure of bithienylhydrosilanes. Crystals of hydrosilane **2** suitable for X-ray analysis were obtained by crystallization from hexane.

*2.1. Molecular structure of bis[5-(2,2′-bithienyl)]methylsilane (**2**)*

The molecular structure of hydrosilane **2** is shown in Fig. 1. Table 3 gives the values of bond lengths and angles in molecule **2**. Comparison of the structural data available for unsubstituted [7], 5-monosubstituted [8], series of 5,5′- [9], 3,3′- [10], 4,4′- [11], 3,4′-disubstituted [12] and more substituted [13] 2,2′-bithiophenes with the results obtained for bithienylhydrosilane **2** clearly indicates an unprecedented type of conjugation in the last compound. Four thiophene heterocycles A, B, A′ and B′ are planar within error limits. The rings A and B are coplanar; cycles A′ and B′ are slightly twisted (3.2(4)°), both bithienyl fragments adopt transoid orientation. According to ^{1}H and ^{13}C-NMR data for hydrosilane (**2**) in CDCl$_3$ two bithienyl substituents of this compound are quite identical, however, in the solid state these two groups are different (Scheme 4). One bithienyl group (cycles A′ and B′) has the usual structure which was found in most of the studied bithiophenes. Simultaneously the second bithienyl fragment (cycles A and B) represents a stable mesomeric form of semiquinoid type characterized by a true double C=C bond C(5)–C(22) between two heterocycles (1.387 Å) and C(23)–C(24) (1.254 Å) in the terminal thiophene

Table 2
Spectroscopic characterization of 2-thienyl-[5e] and 5-(2,2′-bithienyl)hydrosilanes **1**–**3**

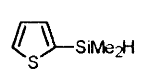
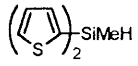
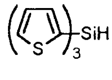
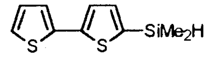
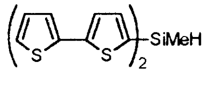
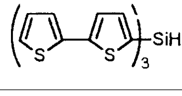
Silane	UV (nm)	ν Si-H (cm^{-1})	δ ^{1}H Si-H (ppm)	J_{Si-H} (Hz)	δ ^{29}Si (ppm)
		2132	4,59	194.3	-23.19
		2150	5.20	203.1	-31.29
		2160	5.78		-40.7
	311	2110	4.56	194.4	-23.3
	318	2115	5.18	207.5	-32.0
	325	2125	5.80	220.1	-41.6

Table 3
Bond lengths (Å) and angles (°) for molecule **2**

	Crystal state	Calculated value
S(1)–C(2)	1.672(14)	1.713
S(1′)–C(2′)	1.779(15)	
S(1)–C(5)	1.786(14)	1.738
S(1′)–C(5′)	1.668(15)	
S(21)–C(22)	1.657(14)	1.744
S(21′)–C(22′)	1.801(15)	
S(21)–C(25)	1.682(15)	1.719
S(21′)–C(25′)	1.697(16)	
Si(1)–C(2)	1.845(13)	1.842
Si(1)–C(2′)	1.898(14)	
Si(1)–C(1)	1.846(10)	1.892
C(2)–C(3)	1.437(21)	1.370
C(2′)–C(3′)	1.301(22)	
C(3)–C(4)	1.370(21)	1.433
C(3′)–C(4′)	1.413(22)	
C(4)–C(5)	1.363(22)	1.375
C(4′)–C(5′)	1.352(25)	
C(5)–C(22)	1.387(23)	1.444
C(5′)–C(22′)	1.604(24)	
C(22)–C(23)	1.436(22)	1.381
C(22′)–C(23′)	1.323(23)	
C(23)–C(24)	1.254(22)	1.435
C(23′)–C(24′)	1.563(23)	
C(24)–C(25)	1.435(24)	1.374
C(24′)–C(25′)	1.210(25)	
C(2)–S(1)–C(5)	95.7(8)	92.3
C(5′)–S(1′)–C(2′)	90.7(8)	
C(22)–S(21)–C(25)	97.0(8)	91.6
C(25′)–S(21′)–C(22′)	82.5(10)	
C(2)–Si(1)–C(1)	110.2(9)	109.5
C(1)–Si(1)–C(2′)	104.7(9)	
C(2)–Si(1)–C(2′)	114.8(4)	114.5
C(3′)–C(2′)–S(1′)	107.9(11)	111.7
C(3)–C(2)–Si(1)	109.0(12)	
C(3′)–C(2′)–Si(1)	123.3(11)	126.5
C(3)–C(2)–Si(1)	132.0(12)	
S(1)–C(2)–Si(1)	128.5(9)	121.7
S(1′)–C(2′)–Si(1)	118.7(9)	
C(4)–C(3)–C(2)	113.7(12)	112.8
C(2′)–C(3′)–C(4′)	115.9(15)	
C(5)–C(4)–C(3)	116.8(13)	112.8
C(5′)–C(4′)–C(3′)	110.2(16)	
C(4)–C(5)–C(22)	131.5(14)	125.5
C(4′)–C(5′)–C(22′)	129.3(15)	
C(4)–C(5)–S(1)	105.7(15)	110.3
C(4′)–C(5′)–S(1′)	113.6(11)	
C(22)–C(5)–S(1)	122.7(12)	124.2
C(22′)–C(5′)–S(1′)	116.9(9)	
C(5)–C(22)–C(23)	129.3(13)	126.1
C(23′)–C(22′)–C(5′)	129.2(13)	
C(5)–C(22)–S(21)	123.7(10)	123.3
C(5′)–C(22′)–S(21′)	110.3(12)	
C(23′)–C(22′)–S(21′)	120.5(12)	110.6
C(23)–C(22)–S(21)	107.0(11)	
C(24)–C(23)–C(22)	113.9(15)	112.9
C(22′)–C(23′)–C(24′)	101.8(13)	
C(23)–C(24)–C(25)	117.5(17)	112.5
C(25′)–C(24′)–C(23′)	112.8(18)	
C(24)–C(25)–S(21)	104.5(13)	112.3
C(24′)–C(25′)–S(21′)	122.4(17)	

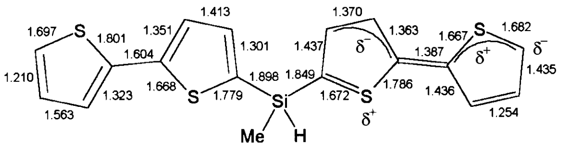
ring B, contrary to C(5′)–C(22′) of 1.604 Å and C(23′)–C(24′) of 1.563 Å in the A′B′ bithienyl substituent.

The stereoscopic view of the molecular arrangement in the crystal of hydrosilane **2** is shown in Fig. 2. The crystal structure is characterized by the herringbone molecular packing motif typical for planar bithiophenes. The shortest intermolecular contacts are 3.668 Å (C···C) and 3.813 Å (C···S). The polar axis of symmetry along the *z* direction occurs in the structure, therefore according to [14] the crystal symmetry of hydrosilane **2** may promote pyroelectric and piezoelectric effects. However, the semiconductor properties complicate the investigations of these effects.

2.2. Theoretical calculations

To compare the structure of isolated hydrosilane molecule **2** with results obtained by X-ray diffraction in the solid state, molecular orbital (MO) calculations of the electronic structure in the ground state have been carried out. The computations were fulfilled in MNDO PM3 approximation [15] of the self-consistent field theory. The calculated bond lengths and angles obtained by full optimization of geometrical parameters are also given in Table 3. Isolated molecule **2** is characterized by C_s symmetry, therefore the symmetrically equivalent geometrical parameters are not shown in Table 3. As follows from Table 3 the geometry of the isolated molecule is near to standard; the strongly planar five-membered cycles A and B are mutually coplanar.

For interpretation of the calculations the electronic structures of thiophene (T) and 2,2′-bithiophene (TT) molecules were also calculated. Fig. 3 shows the scheme of HOMO and LUMO level displacement for T, TT and hydrosilane **2**. It should be noted that in the series of T, TT and **2** the HOMO and LUMO energies are converged as in the case of unsaturated hydrocarbons. Thus, the calculations show the possibility of semiconductor properties for compound **2**. Fig. 3 also illustrates the orbital structure of HOMO and LUMO for molecule **2**. It can be noticed that HOMO increases the orders of C(2)–C(3), C(4)–C(5), C(22)–C(23), C(24)–C(25) bonds and, consequently, shortens these bonds. At the same time, HOMO decreases the orders of C(3)–C(4), C(5)–C(22), C(23)–C(24) bonds and promotes their lengthening. On the contrary, LUMO increases the orders of the latter bonds and decreases the orders of the former. For molecule **2** in crystal form the calculated highest occupied MO can be approximately written as $c(\varphi_{\mathrm{HOMO}}+\varphi_{\mathrm{LUMO}})$, where φ_{HOMO} and φ_{LUMO} are HOMO and LUMO of molecule TT and c is a normalizing coefficient, and moreover, φ_{HOMO} is localized on A′, B′ cycles, whilst φ_{LUMO} is on A and B cycles.



Scheme 4.

The calculated heat of formation for isolated molecule **2** is 4.66 eV (107.4 kcal mol^{-1}). Since the molecular geometry in crystal **2** differs from optimal, the energy of the molecule increases and the calculated heat of formation in the solid state is 12.76 eV (294.1 kcal mol^{-1}). According to the calculation, the dipole moment value for isolated molecule **2** is 0.63 D. However, the value (1.70 D) and direction of the dipole moment for the molecule of hydrosilane **2** in crystal form differ from those found for the isolated state. The increase in the dipole moment stabilizes the crystal structure by means of electrostatic interactions. If the multipole contributions are neglected, the electrostatic term of crystal lattice energy is proportional to $K\mu^2$, where μ is the dipole moment and the coefficient K depends on lattice type. The space group for crystals **2** is $Pna2_1$; for this lattice type the value K is maximal and equal to 2.57. Thus, it may be expected that the increase in molecular energy in crystals of hydrosilane **2** will be compensated for a gain of lattice energy.

3. Experimental

The quantum chemical calculations of electronic structure for the studied systems were performed by the SCF method of MO theory using the PM3 approximation [15] for valence electrons. The geometrical parameters were optimized. Equilibrium geometries on potential surfaces are located by the Davidson–Fletcher–Powell algorithm [16]. The initial geometrical parameters for the calculations were taken from X-ray structure analysis data.

For X-ray crystal structure analysis a four-circle single-crystal Sintex P2$_1$ diffractometer with graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71069$ Å) radiation was used for intensity data collection. Reflection intensities were collected at room temperature using the $\theta/2\theta$ scan

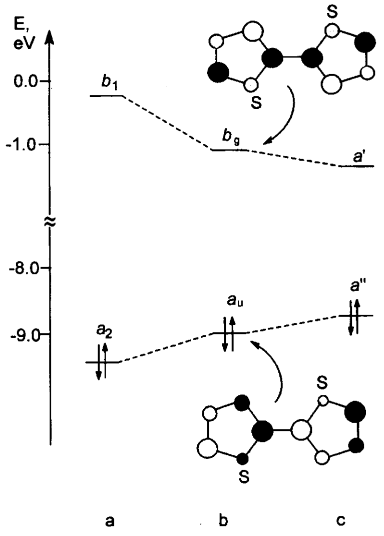


Fig. 3. The HOMO and LUMO levels for thiophene **2** (a), bithiophene (b) and bithienylsilane (c).

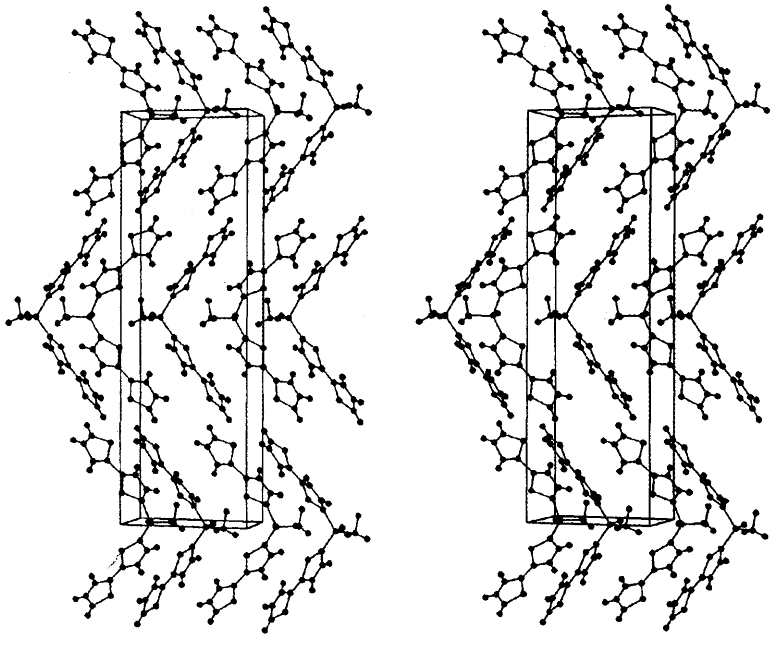


Fig. 2. Stereoview of packing of hydrosilane **2**.

technique. Multisolution direct method package SHELX-86 [17] was used for solution of the structure. SHELXL-93 programs [18] were used for the refinement calculations. Other crystallographic, measurement and refinement data for hydrosilane **2** are listed in Table 4.

3.1. General considerations and materials

All reactions were performed under an atmosphere of dry argon, all solvents used in reactions were dried by standard procedures. The following reagents were obtained from commercial sources and used without further purification: 2-bromothiophene, *n*-BuLi (hexane solution, 2.5 M), chlorodimethylsilane, dichloromethylsilane, trichlorosilane, trimethylsilylacetylene, 3,3-dimethylbut-1-yne, phenylacetylene, methyl propiolate, 3-diethylaminoprop-1-yne. 2,2′-Bithiophene was prepared by catalytic coupling of 2-thienylmagnesium bromide with 2-bromothiophene. Column chromatography was carried out using 60-200 mesh silica gel from Acros.

The ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on a Varian Mercury 200 spectrometer at 200.06, 50.31 and 39.74 MHz correspondingly at 303 K. The chemical shifts are given relative to TMS from solvent ($CDCl_3$) signal ($\delta_H = 7.25$). Mass spectra were recorded on a Hewlett Packard apparatus (70 eV). UV–vis spectra were obtained on a Hitachi UV spectrometer U 3200. IR-spectra were recorded with a Perkin–Elmer 580B spectrometer. GC analysis was performed on a Varian 3700 instrument equipped with flame-ionizing detector using a capillary column 5 m × 0.53 mm, df = 2.65 μ, HP-1. The carrier gas was nitrogen. The melting points were determined on a digital melting point analyser (Fisher), the results are given without correction.

Table 4
Crystal data, measurement conditions and refinement results for compound **2**

Molecular weight Mr	374.61
Crystal size (mm^3)	0.20 × 0.20 × 0.25
Crystal system	Orthorhombic
Space group	$Pna2_1$
Cell parameters:	
a (Å)	9.848(2)
b (Å)	5.759(1)
c (Å)	31.017(5)
Unit cell volume V (Å^3)	1759.3(6)
Molecular multiplicity Z	4
F(000)	776
Absorption coefficient μ (mm^{-1})	0.601
Data collection	
$2\theta_{\max}$ (°)	50
H	0–11
K	0–6
L	0–36
Number of measured independent reflections	1587
Number of observed reflections ($I > 2\sigma(I)$)	896
Refinement data	
R factor	0.0554
Goodness of fit	0.952
(Δ/σ)max	0.083
Number of parameters	214
Flack's x parameter	0.0(3)

*3.2. Synthesis of bithienylsilanes (**1–3**)*

A solution of 2.5 M *n*-BuLi in hexane (4 ml) was added dropwise to a solution of 2,2′-bithiophene (1.66 g, 0.01 mol) dissolved in 40 ml of dry ether at −40°C. After 1 h corresponding chlorosilane was quickly added at −78°C and the mixture was stirred for 2 h at room temperature. Then the reaction mixture was hydrolyzed and extracted with CH_2Cl_2, the organic layer dried over $MgSO_4$ and evaporated. In the case of dimethyl[5-(2,2′-bithienyl)]silane (**1**) the residue was distilled. Hydrosilanes **2** and **3** were chromatographed on silica gel using petroleum ether as eluent.

*3.2.1. 5-(2,2′-Bithienyl)dimethylsilane (**1**)*

B.p. 110°C, 2 mmHg. Yield 80%. MS: *m*/*e* 224 ($M^{\bullet +}$). ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 0.65 (6H, s), 4.88–4.95 (1H, m), 7.42–7.58 (5H, m, arom). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): −1.87, 124.9, 125.3, 125.5, 126.1, 128.8, 136.9, 138.2, 144.1. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): −23.3. Anal. Calc. for $C_{10}H_{12}SiS_2$: C, 53.52; H, 10.07; S, 28.58. Found: C, 53.50; H, 10.12; S, 28.91%.

*3.2.2. Bis[5-(2,2′-bithienyl)]methylsilane (**2**)*

M.p. 93°C. Yield 75%. MS: *m*/*e* 374 ($M^{\bullet +}$). ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 0.73 (3H, s), 5.15–5.24 (1H, m), 6.97–7.31 (10H, m, arom). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): −2.0, 125.2, 125.5, 125.7, 126.2, 128.8, 137.9, 138.4, 145.2. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): −32.0. Anal. Calc. for $C_{17}H_{14}SiS_4$: C, 54.50; H, 3.77; S, 34.23. Found: C, 54.50; H, 3.72; S, 34.71%.

*3.2.3. Tris[5-(2,2′-bithienyl)]silane (**3**)*

M.p. 104°C. Yield 71%. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 5.80 (1H, s, $J_{Si-H} = 220.1$ Hz), 7.00 (1H, dd, $J = 0.2$ Hz, $J = 0.8$ Hz), 7.2–7.24 (2H, m), 7.28 (1H, d, $J = 3.6$ Hz), 7.39 (1H, d, $J = 3.6$ Hz). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): 125.5, 126.0, 126.2, 128.9, 130.9, 137.7, 139.9, 146.3. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): −41.6 Hz. Anal. Calc. for $C_{24}H_{16}SiS_6$: C, 54.92; H, 3.07; S, 36.66. Found: C, 54.87; H, 3.15; S, 36.42%.

3.3. Hydrosilylation of acetylene derivatives

A mixture of hydrosilane (0.01 mol), alkyne (0.01 mol) and 10^{-4} M% of Speier's catalyst was stirred for

0.5–1 h in a Wheaton vial at room temperature. Processes were controlled by GC. Products were purified using column chromatography.

3.3.1. *β-(E)-[5-(2,2′-bithienyl)dimethylsilyl]-tert-butylethylene (**4**)*

MS: *m*/*e* 306 ($M^{\bullet+}$). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): − 0.4, 29.9, 36.6, 118.7, 125.0, 125.6, 126.0, 128.8, 136.7, 137.8, 138.2, 144.7, 163.6. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): − 23.2. Anal. Calc. for $C_{16}H_{22}S_2Si$: C, 62.69; H, 7.23; S, 20.92. Found: C, 62.72; H, 7.34; S, 21.07%.

3.3.2. *β-(E)-[5-(2,2′-bithienyl)dimethylsilyl]-trimethylsilylethylene (**5**)*

MS: *m*/*e* 322 ($M^{\bullet+}$). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): − 0.9, − 0.7, 124.7, 125.3, 126.0, 128.7, 136.4, 138.4, 143.3, 148.0, 150.8, 152.3, 154.7. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): − 4.3, − 15.4. Anal. Calc. for $C_{15}H_{22}S_2Si_2$: C, 55.78; H, 6.86; S, 19.86. Found: C, 55.72; H, 6.84; S, 19.02%.

3.3.3. *β-(E)-[5-(2,2′-bithienyl)dimethylsilyl]-diethylaminomethylethylene (**6**)*

MS: *m*/*e* 335 ($M^{\bullet+}$). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): − 0.3, 26.4, 31.4, 36.5, 117.5, 124.6, 125.2, 126.1, 128.8, 136.4, 137.5, 137.9, 145.6, 163.4. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): − 22.5. Anal. Calc. for $C_{17}H_{25}NS_2Si$: N, 4.17; C, 60.84; H, 7.51; S, 19.11. Found: N, 4.15; C, 60.95; H, 7.43; S, 19.18%.

3.3.4. *Isomeric mixture of β-trans and α-products (R = COOMe)*

MS: *m*/*e* 308 ($M^{\bullet+}$). Anal. Calc. for $C_{14}H_{16}O_2S_2Si$: C, 54.51; H, 5.23; S, 20.79. Found: C, 54.55; H, 5.27; S, 19.87%.

3.3.5. *Isomeric mixture of β-trans and α-products (R = Ph)*

MS: *m*/*e* 326 ($M^{\bullet+}$). Anal. Calc. for $C_{18}H_{18}S_2Si$: C, 66.21; H, 5.56; S, 19.64. Found: C, 66.26; H, 5.61; S, 19.55%.

3.4. *Synthesis of quaterthiophenes **7** and **8***

To a solution of 0.02 mol of 5-substituted 2,2′-bithiophene (**4** or **5**) in 30 ml of dry ether, 0.02 mol of *n*-BuLi in hexane were added dropwise. After 1 h, the reaction mixture was cooled to − 30°C and $CuCl_2$ (0.02 mol) was added by portions. Then the solution was allowed to warm to room temperature, and treated with 40 ml of 3M HCl. The mixture was extracted with CH_2Cl_2, the organic layer washed with brine, dried over $MgSO_4$ and evaporated. After evaporation the residue was washed with ether recrystallized from ethanol to give coresponding quaterthiophenes as bright yellow solids.

3.4.1. *5,5‴′-bis[(E)-tert-Butylethenyldimethylsilyl]-2,2′:5′,2″:5″,2‴-quaterthiophene (**7**)*

M.p. 142–143°C (from EtOH). Yield 70%. MS: *m*/*e* 611 ($M^{\bullet+}$). ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 0.38 (12H, s), 1.03 (18H, s), 5.62 (2H, d, *J* = 18 Hz), 6.18 (2H, d, *J* = 18 Hz), 7.05–7.25 (8H, m, arom). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): − 1.2, 29.0, 35.3, 119.8, 124.2, 124.9, 135.3, 135.9, 136.4, 139.4, 142.3, 160.2. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): − 14.2. Anal. Calc. for $C_{32}H_{42}S_4Si_2$: C, 62.89; H, 6.93; S, 20.99. Found: C, 62.79; H, 6.98; S, 21.10%.

3.4.2. *5,5‴-bis[(β-(E)-Trimethylsilylethenyl)-dimethylsilyl]2,2′:5′,2″:5″,2‴-quaterthiophene (**8**)*

M.p. 163–165°C (from EtOH). Yield 79%. ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 0.08 (18H, s), 0.39 (12H, s), 6.71 (4H, d, *J* = 22 Hz), 6.99–7.13 (4H, m, arom), 7.21–7.25 (4H, m, arom). ^{13}C-NMR (50.31 MHz, $CDCl_3$, ppm): − 0.9, − 0.7, 98.1, 124.7, 125.2, 125.4, 125.5, 126.0, 128.9, 136.9, 137.3, 139.3, 143.4, 147.4, 147.9, 154.8. ^{29}Si-NMR (39.74 MHz, $CDCl_3$, ppm): − 7.0 (Me_3Si), − 15.4 (Me_2Si). Anal. Calc. for $C_{30}H_{42}S_4Si_4$: C, 56.02; H, 6.58; S, 19.94. Found: C, 56.14; H, 6.68; S, 20.03%.

4. Supplementary material

Atomic coordinates and components of temperature factor tensors have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136564. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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