Studies of Silylfurans, Furylsilanes, and Silylthiophenes: Structure of 2,5-Disilylthiophene[†]

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2-Silyl- and 2,5-disilylfuran (2-$H_3SiC_4H_3O$, 2,5-$(H_3Si)_2C_4H_2O$) have been obtained from furan by lithiation with ^tBuLi, followed by treatment with H_3SiBr at very low temperatures (−196 to −80 °C) in diethyl ether, as distillable liquids (bp 72 and 108 °C, respectively). Di-2-furyl- and tri-2-furylsilane ($(2\text{-}C_4H_3O)_nSiH_{4-n}$, $n = 2, 3$) are the products of the reaction of 2-furyllithium with $Si(OMe)_4$, followed by reduction using $LiAlH_4$ in diethyl ether/tetrahydrofuran. The methoxysilane precursors $(2\text{-}C_4H_3O)_nSi(OMe)_{4-n}$ ($n = 2, 3$) have also been isolated. The analogous reactions of $(MeO)_4Si$ with equivalent quantities of (a) lithiated thiophenes and (b) $LiAlH_4$ gave 2-silyl- and 2,5-disilylthiophene. Comprehensive NMR data have been compiled for all compounds, and the composition was confirmed by mass spectrometry. The crystal and molecular structure of 2,5-disilylthiophene has been determined by low-temperature "in situ" single-crystal X-ray diffraction, and ab initio calculations (MP2/6-31G*) have been carried out for this compound and the corresponding disilylfuran. The experimental and theoretical results are in excellent agreement and show that there are no silicon-induced irregularities as compared to methylated furans or thiophenes. Minor conformational differences can be ascribed to packing forces in the crystal. Low-temperature solution NMR experiments have shown that there is no aggregation via *inter*molecular donor−acceptor interactions in these systems.

Introduction

Silylated polythiophenes are currently of considerable interest owing to their intrinsic photophysical and photochemical properties.[1−3] Hybrid polymers based on alternating poly(hetero)arene and polysilanyl domains are particularly promising as auxiliaries for the production of electronic devices.[4−7]

Simple monomers which could serve as precursors or components of such materials have been studied in several laboratories in the past, but these investigations were mainly oriented either at the biological activity of this family of compounds[8] or at certain physical and spectroscopic properties, including their NMR,[9] mass,[10] and photoelectron spectra[11] and their polarizability (Kerr constants).[12]

In some of the earlier studies, silylthiophenes and -furans were considered as model systems for delineating substituent effects of silicon and the heavier group 14 elements, mainly in connection with the formerly popular $d_\pi p_\pi$ bonding concept.[9−12] There has also been a debate about the significance of intra- and intermolecular dative bonding involving pentacoordinate silicon (Ge, Sn, ...) atoms, but the results were not really conclusive.[13]

Heterocycles such as pyridine, thiophene, and furan with *hydrido*silyl substituents are important systems for several obvious reasons: (1) the simplicity of their molecular structure makes them amenable to detailed experimental and theoretical studies, (2) their Si−H groups offer extra functionalities which are reactive under mild conditions, and (3) there are convenient direct routes from silane (Si−H) to disilanediyl (−Si−Si−) functions (stoichiometric or catalytic dehydrogenative coupling), which are relevant to the generation of polymers with the desired photophysical properties.

In this context we have recently investigated the preparation, properties, and molecular structure of

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[†] Dedicated to Professor J. P. Fackler, Jr., on the occasion of his 65th birthday.

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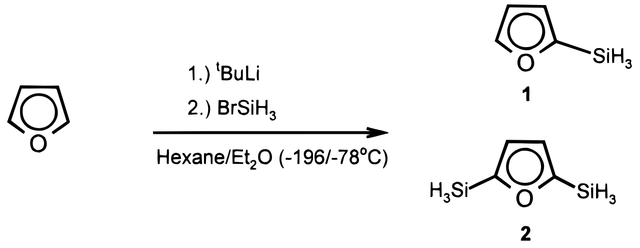
several silylpyridines,[14] and this work has now been extended to silylfurans and -thiophenes.

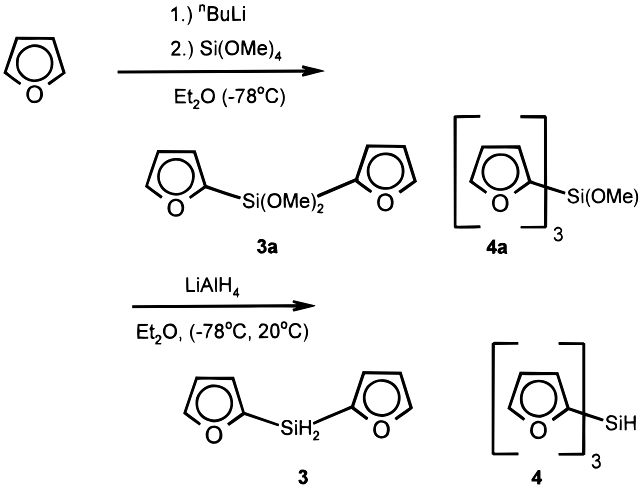
Preparations

For some of the following preparations there is precedent in the literature, as indicated in each individual case. However, only very few of the compounds have been presented with satisfactory sets of data,[17] while others have only been introduced as entries in larger tables without any details being given of their preparations and with very limited analytical and spectroscopic data.[10,11,16]

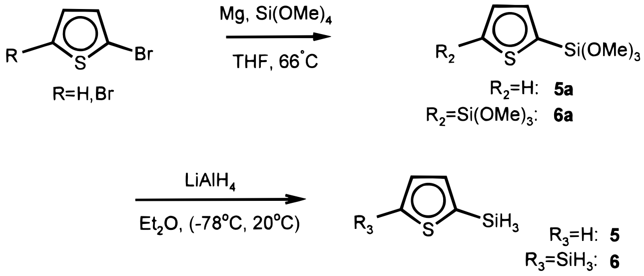
For the synthesis of 2-silyl- (**1**) and 2,5-disilylfuran (**2**), anhydrous furan was first treated with 1 or 2 equiv of *tert*-butyllithium in hexane/diethyl ether at −78 °C. The reaction mixtures were subsequently warmed to room temperature and then cooled again to −196 °C in order to connect the vessel to a vacuum line and condense in equivalent quantities of bromosilane H_3SiBr. Careful workup and fractional distillation gave the products in 31 and 15% yields, respectively, as colorless liquids. The symmetrical species **2** is a new compound, but compound **1** was previously made via the $(EtO)_4Si$ or Cl_3SiH routes (below).[10b] The properties given for the literature products are in agreement with our own results.



Di- (**3**) and trifurylsilane (**4**) were prepared via the established alkoxysilane route. This involves furylation of $(RO)_4Si$ with furyllithium, followed by reduction of the alkoxyfurylsilanes with $LiAlH_4$. In the present work tetramethoxysilane was used and the intermediates difuryldimethoxysilane (**3a**) and trifurylmethoxysilane (**4a**) were isolated. **3** and **4** are distillable liquids, the physical constants of which have been reported.[10b] Their spectroscopic data have now been compiled and used in comparative discussions.



Following a similar procedure, 2-silylthiophene (**5**) has now been prepared via the in situ Grignard method of Shea et al.,[15] using 2-bromothiophene and $(MeO)_4Si$ to give 2-thienyltrimethoxysilane (**5a**), which was reduced with $LiAlH_4$ to give acceptable yields (45%) of a readily distillable, colorless liquid (bp 112 °C).[12] Starting from 2,5-dibromothiophene, 2,5-disilylthiophene (**6**) was obtained via 2,5-bis(trimethoxysilyl)thiophene (**6a**). Product **6** was identified using literature data,[16,17] complemented by additional measurements.



Compounds **1**−**6** are all liquids with very low melting points. They are very sensitive to air and moisture and must be handled under an inert atmosphere. However, none of the samples was found to be spontaneously inflammable. Only compound **6** could be obtained as single crystals under very carefully controlled conditions (see below).[18]

Spectroscopy

The compounds have been identified by elemental analysis (**1, 6**) and/or by their mass spectra (CI). The solution NMR spectra are also fully consistent with the proposed structures. The resonances of the silicon nuclei for the furan and thiophene compounds appear in very narrow ranges around δ −70.3 (**5**, **6**) and −76.3 ppm (**1**, **2**) with coupling constants $^1J_{SiH} = 209-211$ Hz (for all four compounds) (Table 1). These results indicate a standard bonding situation for (hetero)aryl-bound H_3Si groups with tetracoordinate silicon atoms. The proton resonances $\delta(H_3Si)$ also show no anomalies (Table 1), and both the ^1H and ^{29}Si NMR spectra of compounds **1** and **2** are independent of temperature. The quartet ^{29}Si signal of the monosilylated furan **1**, for example, does not undergo a significant shift upon cooling from +20 to −80 °C in d_8-toluene, and the coupling constant $^1J_{SiH}$ is virtually constant over this range of temperature, suggesting that there is no significant donor/acceptor association equilibrium in solution. Any change in the coordination number of silicon from 4 to 5 is expected to be reflected by the δ and J parameters of this nucleus, and thus any aggregation associated with a gain in free energy $-\Delta G$ of

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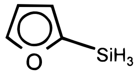
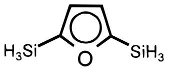
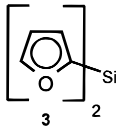
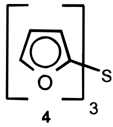
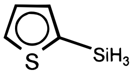
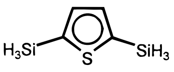
Table 1. $^{29}Si/^{1}H$ NMR Data (ppm) of 2-Silylthiophenes and -furans

Compound	$\delta(^{29}Si)$ ($^{1}J_{SiH}$)	$\delta(^{1}H)$ for SiH-functions
 **1**	-76.0 (209 Hz)	4.11
 **2**	-76.3 (211 Hz)	4.08
 **3**	-63.9 (215 Hz)	4.95
 **4**	-58.0 (216 Hz)	5.69
 **5**	**-69.7(207 Hz)**	4.35
 **6**	-70.3 (209 Hz)	4.21

only a few kilocalories per mole should be obvious at the low-temperature limit of the experiment.

Structural Studies

The silylfurans and -thiophenes are colorless liquids with very low melting points or melting ranges in the cases when glassy solids are generated upon cooling. Compound **6** (mp −57 °C) could be obtained as single crystals by in situ crystal growth between 215 and 133 K on the diffractometer. The crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ molecules in the unit cell. The individual molecules have no crystallographically imposed symmetry, but the disposition of the atoms follows quite closely the requirements of point group C_2 symmetry with the 2-fold axis passing through the sulfur atom (parts a and b of Figure 1).

As becomes obvious from a projection parallel to the planar heteroarene ring (Figure 1a), the two silicon atoms are coplanar with the heterocycle. The silicon-bound hydrogen atoms are twisted out of this plane by a conrotatory movement of the two $-SiH_3$ groups. This conformation avoids eclipsed arrangements of hydrogen atoms in the molecular plane. The configuration at the silicon atoms is almost ideally tetrahedral and shows no significant distortion.

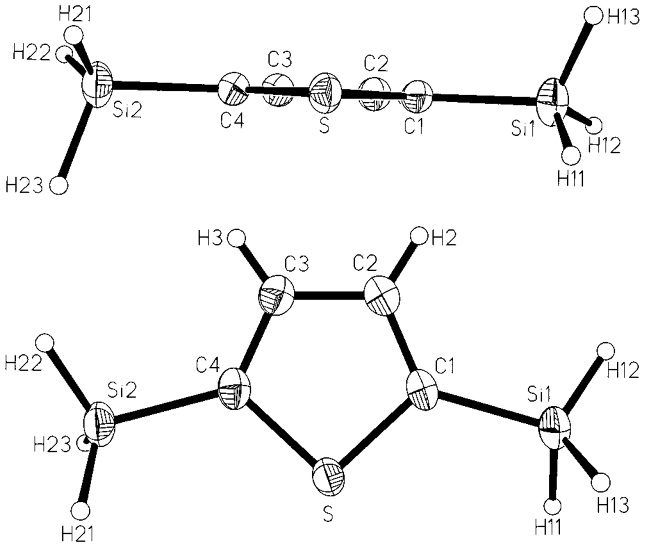


Figure 1. (a, top) Molecular structure of 2,5-disilylthiophene (**6**) in the crystal with atomic numbering (ORTEP, 50% probability ellipsoids for heavy atoms, arbitrary radii for the hydrogen atoms). The projection is parallel to the molecular plane. (b, bottom) The projection is perpendicular to the molecular plane. For selected interatomic distances and angles see Table 3.

Table 2. Crystal Data and Data Collection and Structure Refinement Details for Disilylthiophene (6)

Crystal Data	
empirical formula	$C_4H_8SSi_2$
fw	144.34
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	9.126(2)
b, Å	9.889(1)
c, Å	9.073(2)
β, deg	103.56(1)
V, Å^3	796.0(3)
D_{calcd}, g cm^{-3}	1.204
Z	4
$F(000)$	304
μ(Mo Kα), cm^{-1}	6.05
cryst dimens, mm	0.4 × 0.4 × 0.5
Data Collection	
temp, K	133
scan mode	ω
hkl range	−11 to +4; −12 to 0; −11 to +11
((sin θ)/λ)$_{max}$, Å^{-1}	0.64
no. of measd rflns	2610
no. of unique rflns	1728 ($R_{int} = 0.1197$)
no. of rflns used for refinement	1725
Refinement	
least-squares params	96
final R values ($I > 2\sigma(I)$)	
R1^a	0.0354
wR2^b	0.0728
goodness-of-fit on F^2	1.092
ρ_{fin}(max/min), e Å^{-3}	+0.505/−0.262

[a] $R1 = \Sigma(||F_o|| - ||F_c||)/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0341$; $b = 0.1017$.

The projection on to the molecular plane (Figure 1b) reveals a structure very similar to that of 2,5-di*methyl*thiophene. The C−S−C angles are 94.27(7) and 93.38(5)° for R = SiH_3 and CH_3, respectively. This is also true for the $(H_3)Si-C-S$ and $(H_3)C-C-S$ angles, which are 121.36(8) and 121.24(6)°. This result shows that there is no "silicon effect" in compound **6**, which would draw the silicon and sulfur atoms closer together (owing to *intra*molecular donor/acceptor interactions to give pentacoordinate silicon) than the methyl carbon and sulfur

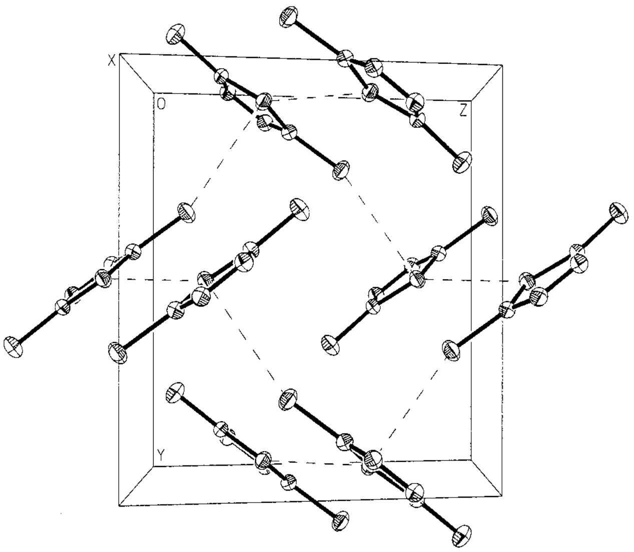


Figure 2. Packing of the molecules of compound **6** in the crystal.

atoms.There is also little reason to invoke *inter*molecular interaction, because the Si---S and S---S contacts are all larger than 3.78 and 3.63 Å, respectively, and thus in excess of the sum of the van der Waals radii. (The molecular packing is shown in Figure 2.) Remember also that the tetrahedral $-SiH_3$ groups show no sign of distortion. Only the conformation of the $-SiH_3$ groups, i.e., their twist against the ring plane, may be influenced by the packing forces.

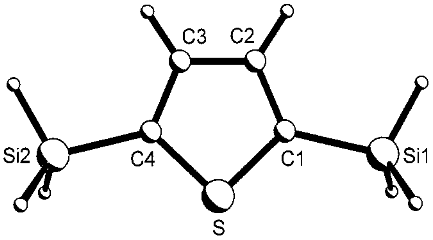


Figure 3. Molecular structure of 2,5-disilylthiophene (**6**) as calculated by ab initio quantum chemical methods (MP2/6-31G*). For geometrical dimensions see Table 3.

Ab Initio Quantum Chemical Calculations

Calculations on the MP2/6-31G* level lead to a molecular structure for disilylthiophene (**6**) which is in excellent agreement with the experimental data (Figure 3, Table 3). Interestingly, the only significant difference between the two structures is the conformation of the $-SiH_3$ group relative to the ring, which is eclipsed for Si−H and C−H bonds on each side of the ring for the calculated model. The calculated structure thus has the higher symmetry of point group C_{2v}, as compared to C_2 for the experimental data. The calculated energy differences between C_{2v} and C_s are very small, however, which suggests that the deviations may indeed be due only to packing forces in the crystal.

The ab initio calculations of the disilylated furan **2** lead to very similar results (Figure 4). The molecule is expected to have C_{2v} symmetry with geometrical parameters as listed in Table 3.

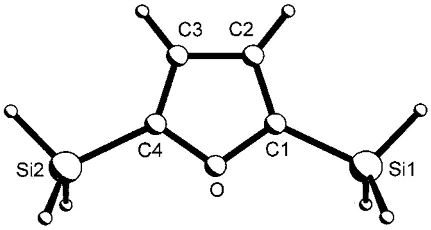


Figure 4. Molecular structure of 2,5-disilylfuran (**2**) as calculated by ab initio quantum chemical methods (MP2/6-31G*). For details see Table 3.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 2 and 6 (XRD and MP2/6-31G*)

6 (XRD, crystal data)	**6** (ab initio MP2/6-31G*)	**2** (ab initio MP2/6-31G*)
S−C1 = 1.718(9)	1.724	O−C1 = 1.379
S−C4 = 1.723(5)	1.724	O−C4 = 1.379
Si1−C1 = 1.857(4)	1.868	Si1−C1 = 1.867
Si2−C4 = 1.858(4)	1.868	Si2−C4 = 1.867
C1−S−C4 = 94.27(7)	94.02	C1−O−C4 = 108.29
S−C1−Si1 = 121.36(8)	124.13	O−C1−Si1 = 117.91
S−C4−Si2 = 122.08(8)	124.13	O−C4−Si2 = 117.91
C2−C1−Si1 = 129.54(12)	126.41	C2−C1−Si1 = 133.47
C3−C4−Si2 = 128.96(11)	126.41	C3−C4−Si2 = 133.47
C2−C1−S = 109.10(11)	109.46	C2−C1−O = 108.62
C3−C4−S = 108.96(11)	109.46	C3−C4−O = 108.62

A natural bond orbital analysis (NBO) has been performed on the basis of the molecular MP2/6-31 G* geometries of **6** and **2**. The results indicate that there is no significant interaction between the lone pairs (lp_S or lp_O) of the sulfur atom in the case of compound **6** (or the oxygen atom in case of compound **2**) and the σ^* orbitals of the Si−C/Si−H bonds of the exocyclic silyl functions (through space). Contributions of the type $lp_{O,S}$---σ^*_{C-C}(ring) seem to be more important.

Conclusions

The present complementary study of polysilylated heteroarenes presents new or improved strategies for the synthesis, which are also applicable to the fully hydrogenated members of the series. Most previous investigations had often considered only partially or fully alkylated homologues. The spectroscopic data of the products show no anomalies regarding structure and bonding as compared to related—and already known—alkylated or alkylsilylated species. The structural study of 2,5-disilylthiophene (**6**; by low-temperature X-ray diffraction) has revealed a molecular geometry with approximate C_2 symmetry, which differs only very slightly from the geometry calculated by state of the art ab initio quantum chemical calculations (C_{2v} symmetry). There is no indication for *intra*- or *inter*molecular donor/acceptor interactions between the sulfur and silicon atoms. The few “peculiarities” of the structure of **6** and also of the 2,5-disilylfuran **2** (such as the small angles $(H_3)Si-C-S/O$) resemble very closely the corresponding values in 2,5-di*methyl*thiophene/furan (i.e. the angles $(H_3)C-C-S/O$) and arise from the intrinsic geometry of the heteroarenes. The results, which rule out any specific “silicon effect”, are also in excellent agreement with the findings for polysilylated pyridines which have recently been revisited.[14]

Experimental Section

General Methods. All experiments were carried out under an atmosphere of dry nitrogen using Schlenk techniques.

Starting materials were commercially available; bromosilane was prepared and purified according to published procedures.[29] Solvents were appropriately dried, distilled, and saturated with dry nitrogen; glassware was dried in an oven and filled with nitrogen. All NMR spectra were recorded at 21 °C on a JEOL-JNM-GX 400 spectrometer (^{1}H at 399.78 MHz, ^{13}C at 100.54 MHz, ^{29}Si at 79.43 MHz) in sealed tubes with predried C_6D_6 as solvent, except where indicated otherwise. Mass spectra were recorded with an analytical GLC-MS Hewlett-Packard 5890 Series II chromatograph (column HP1, cross-linked methylsilicon gum 12 m/0.2 mm, thickness of film 0.33 μm) with an HP MS 5971 A mass-selective detector (EI-MS 70 eV). Microanalyses were performed by the Mikroanalytisches Laboratorium des Anorganisch-chemischen Instituts der Technischen Universität München.

2-Silylfuran (1). To a solution of *tert*-butyllithium (13.2 mL, 1.6 M, 0.021 mol) in hexane/diethyl ether at −78 °C was added a solution of furan (1.45 mL, 0.02 mol) in 15 mL of diethyl ether dropwise with stirring. After 1 h at −78 °C the reaction mixture was warmed to room temperature.The formation of a white solid was observed. The flask was connected to a STOCK-vacuum line and evacuated while cooling the mixture to −196 °C. A 2.22 g amount of bromosilane (0.020 mol) was condensed into the mixture at −196 °C, and the reaction mixture was warmed to −78 °C with vigorous stirring. After the mixture was stirred for 40 min at −78 °C, the formation of a white solid was observed. Subsequently, the mixture was warmed to room temperature. After all volatile products were condensed off from the salts, the product was isolated by fractional distillation as a colorless liquid (bp 72 °C, yield 0.61 g, 31%). ^{1}H NMR: δ 4.11 (s, $^1J_{SiH} = 209$ Hz, 3H, SiH_3), 6.03 (d, 1H, furyl-H_4, $^3J_{HH} = 3.5$ Hz), 6.55 (d, 1H, furyl-H_3, $^3J_{HH} = 3.5$ Hz), 7.30 (d, 1H, furyl-H_5). $^{13}C\{^1H\}$ NMR: δ 150.8 (C_2 ipso), 149.2 (C_5), 125.3 (C_3), 109.8 (C_4). ^{29}Si VT NMR (DEPT): δ −76.0 (20 °C, q, $^1J_{SiH} = 209$ Hz), −75.3 (−50 °C), −74.9 (−80 °C). MS (EI, 70 eV): *m/z* 98 [M^+, 100%], 97 [$M^+ - H$], 68 [$M^+ - SiH_3$], 67 [$M^+ - H - SiH_3$], 65, 59, 53, 51. Anal. Found for C_4H_6SiO (98.2): C, 48.9; H, 6.2. Calcd: C, 48.6; H, 5.9.

2,5-Disilylfuran (2). A procedure analogous to that described for 2-silylfuran (**1**) was used, with 1 equiv of furan (1.45 mL, 0.02 mol) and 2 equiv of *tert*-butyllithium (26.3 mL, 1.6 M, 0.042 mol) and bromosilane (4.44 g, 0.040 mol). The reaction time for the deprotonation was optimized to 1.5 h (determined by quenching of small amounts with trimethylchlorosilane and GC-MS analysis). The product **2** was separated by fractional distillation (bp 108 °C, yield 0.38 g, 15%). ^{1}H NMR: δ 4.08 (s, $^1J_{SiH} = 211$ Hz, 6H, SiH_3), 6.68 (s, 2H, furyl-$H_{3,4}$). ^{29}Si VT NMR (DEPT): δ −76.3 (20 °C, q, $^1J_{SiH} = 209$ Hz), −75.7 (−50 °C), −75.1 (−80 °C). MS (EI, 70 eV): *m/z* 129 [M^+], 128 [$M^+ - H$, 100%], 98 [$M^+ - SiH_3$], 97 [$M^+ - H - SiH_3$], 69 [$M^+ - 2SiH_3$] 53, 51.

Di-2-furylsilane (3) and Tri-2-furylsilane (4). A solution of *n*-butyllithium in hexane (77.5 mL, 1.6 M, 0.124 mol) was dissolved in 75 mL of dry diethyl ether and cooled to −78 °C. A precooled solution of furan (9.0 mL, 8.44 g, 0,124 mol) in 30 mL of thf was added slowly with stirring, and after 15 min the mixture was warmed to +50 °C. A pale brown precipitate formed. The mixture was stirred at room temperature until the formation of butane gas ceased. A solution of tetramethoxysilane (9.43 g, 0.062 mol) was then added, and stirring continued for 2 h. A 200 mL portion of pentane was added, the suspension was filtered, and the solvents were removed in vacuo. The remaining oil was fractionally distilled to give di-2-furyldimethoxysilane as a colorless oil (**3a**, bp 90 °C at 0.05 mbar, 78% (GC-MS analysis)). The major byproduct was tri-2-furylmethoxysilane (**4a**). ^{1}H NMR: δ 3.51 (s, 6H, Si-$(OMe)_2$), 6.11 (m, 1H, furyl-H_4), 6.94 (d, 1H, $^3J_{HH} = 3.5$ Hz, furyl-H_3), 7.42 (d, 1H, $^3J_{HH} = 1.5$ Hz, furyl-H_5). $^{29}Si\{^1H\}$ NMR: δ −47.5 (**3a**, s, $Si(OMe)_2$), −36.3 (**4a**, s, Si(OMe)). MS (**3a**, EI, 70 eV): *m/z* 227 [$M^+ + 2$], 225 [M^+], 196 [$M^+ - OCH_3$, 100%], 167 [$M^+ - 2\ OCH_3$], 128 [$M^+ - C_4H_3O - OCH_3$], 98 [$M^+ - C_4H_3O - 2\ OCH_3$] 91, 77, 51. MS (**4a**, EI, 70 eV): *m/z* 261 [$M^+ + 1$], 260 [M^+], 229 [$M^+ - OCH_3$], 193 [$M^+ - C_4H_3O$, 100%], 126 [$M^+ - 2\ C_4H_3O$], 95 [$M^+ - 2\ C_4H_3O - OCH_3$] 91, 61, 59.

Without further separation the mixture of **3a** and **4a** was dissolved in diethyl ether and added to a cooled and stirred suspension (−78 °C) of $LiAlH_4$ in diethyl ether. Stirring was continued until the temperature reached 20 °C. After 2 h the suspension was filtered, the solvents were condensed into a −196 °C trap, and the residue was distilled. The products are colorless oils (**3**, bp 39 °C at 0.5 mbar, 20%; **4**, bp 126 °C at 2 mbar, 10%). ^{1}H NMR **(3)**: δ 4.95 (s, $^1J_{SiH} = 215$ Hz, 2H, SiH_2), 6.07 (m, 1H, furyl-H_4), 6.69 (d, 1H, $^3J_{HH} = 3.5$ Hz, furyl-H_3), 7.31 (d, 1H, $^3J_{HH} = 1.5$ Hz, furyl-H_5). ^{1}H NMR **(4)**: δ 5.69 (s, $^1J_{SiH} = 214$ Hz, 1H, SiH), 6.05 (m, 1H, furyl-H_4), 6.84 (d, 1H, $^3J_{HH} = 3.5$ Hz, furyl-H_3), 7.34 (d, 1H, $^3J_{HH} = 1.5$ Hz, furyl-H_5). $^{13}C\{^1H\}$ NMR **(3)**: δ 150.5 (C_5), 149.2 (C_2 ipso), 124.7 (C_3), 110.2 (C_4). $^{13}C\{^1H\}$ NMR **(4)**: δ 151.0 (C_5), 150.2 (C_2 ipso), 124.3 (C_3), 109.8 (C_4) ^{29}Si NMR (**3**, DEPT): δ −63.9 (t, $^1J_{SiH} = 215$ Hz, SiH_2). ^{29}Si NMR (**4**, DEPT): δ −58.0 (d, $^1J_{SiH} = 216$ Hz, SiH). MS (**3**, EI, 70 eV): *m/z* 165 [$M^+ + 1$], 164 [M^+], 95 [$M^+ - C_4H_3O$], 119, 57. MS (**4**, EI, 70 eV): *m/z* 231 [$M^+ + 1$], 230 [M^+], 164 [$M^+ - C_4H_3O$], 119, 91, 57.

2-Silylthiophene (5). The synthesis followed the literature procedure,[12,16] and the product **5** was isolated by fractional distillation as a colorless liquid (yield 45%, bp 112 °C). ^{29}Si NMR (DEPT): δ −69.7 [q, $^1J_{SiH} = 207$ Hz].

2,5-Bis(trimethoxysilyl)thiophene (6a). The method employed was the same as that described for 2,5-bis(triethoxysilyl)thiophene.[17] Magnesium chips (9.04 g, 372 mmol) were suspended in dry thf (300 mL) and activated with dibromoethane. Freshly distilled tetramethoxysilane (169.88 g, 1.12 mol) was then added with stirring, followed by a solution of 2,5-dibromothiophene (30.00 g, 124 mmol) in 100 mL of thf. When 10% of the solution was added, the addition was stopped and stirring continued until an exothermic reaction set in (ca. 30 min). The addition was continued to maintain reflux of the solvent, and the mixture was refluxed for an additional 1 h until the formation of a yellow solid could be observed. After the thf solvent was removed, 100 mL of pentane was added, the suspension was filtered, and the solvent and the remaining tetramethoxysilane were removed in vacuo. The remaining yellow oil was fractionally distilled to give a colorless oil (yield 32%, 12.9 g, bp 110 °C at 0.05 mbar). ^{1}H NMR: δ 3.47 (s, 18H, OCH_3), 7.62 (s, 2H, thiophene-$H_{3,4}$). $^{13}C\{^1H\}$ NMR: δ 59.2 (OCH_3), 137.6 ($C_{2,5}$ ipso), 137.8 ($C_{3,4}$). $^{29}Si\{^1H\}$ NMR: $\delta = -58.3$ (s). MS (EI, 70 eV): *m/z* 324 [M^+], 293 [$M^+ - OCH_3$], 262 [M^+

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− 2 OCH_3], 230 [M^+ − 3 OCH_3], 200 [M^+ − $Si(OCH_3)_3$, 100%], 173 [M^+ − $Si(OCH_3)_3$ − 2 CH_3], 143 [M^+ − $Si(OCH_3)_3$ − OCH_3 − 2 CH_3], 121, 91, 59.

2,5-Disilylthiophene (6). A solution of 2,5-bis(trimethoxysilyl)thiophene (**6a**) (12.9 g, 39.75 mmol) in diethyl ether (30 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (2.82 g, 74.44 mmol) in diethyl ether (150 mL) at −78 °C. After the addition stirring was continued for 1 h and the mixture heated to room temperature.The formation of a white precipitate was observed. The reaction mixture was stirred for an additional 2 h at ambient temperature until the peak of the reactant **6a** disappeared in the GC-MS. A 150 mL portion of pentane was added, the mixture was filtered, and the solvents were removed in vacuo. The colorless liquid **6** was isolated by fractional distillation (40%, 2.28 g, bp 43 °C at 0.1 mbar, mp −57 °C). ^1H NMR: δ 4.21 (s, $^1J_{SiH}$ = 209 Hz, 6H, SiH_3), 7.12 (s, 2H, thiophene-$H_{3,4}$). $^{13}C\{^1H\}$ NMR: δ 133.4 ($C_{2,5}$ ipso), 140.0 ($C_{3,4}$). ^{29}Si NMR (DEPT): δ −70.3 (qm, $^1J_{SiH}$ = 209 Hz, $^3J_{SiH}$ = 1.7 Hz). MS (EI, 70 eV): *m/z* 144 [M^+], 143 [M^+ − H], 113 [M^+ − SiH_3, 100%], 82 [M^+ − 2 SiH_3], 77, 67, 58, 53. Anal. Found for $C_4H_8Si_2S$ (144.2): C, 35.3; H, 6.0. Calcd: C, 33.3; H, 5.6.

Crystal Structure Determination. A solid−liquid equilibrum was established at 216 K in a sample of **6** held in a capillary. A single crystal grew on cooling at 1 K h^{-1}. The specimen was used for measurement of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. The structure was solved by direct methods (SHELXS-86[19]) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93[20]). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms of **6** were found and refined with isotropic contributions. Further information on crystal data, data collection, and structure refinement are summarized in Table 2. Important interatomic distances and angles are given in Table 3. For further details, see the Supporting Information. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. The data are available on request on quoting CCDC No. 11 88 75.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[21] Geometry optimizations (SCF and MP2 level of theory) and vibrational frequency calculations (up to SCF/6-31G*) were performed from analytical first and second derivatives. Calculations were undertaken at the SCF level using the standard 3-21G*[22,23] and 6-31G*[24−26] basis sets, the larger basis sets being used for calculations at the MP2 level of theory. NBO calculations were undertaken with the NBO 3.0 facilities built into Gaussian 94.[27,28]

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Supporting Information Available: Tables giving details of crystal data, data collection and structure refinement, atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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