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Synthesis and Properties of the First 1-Silanaphthalene

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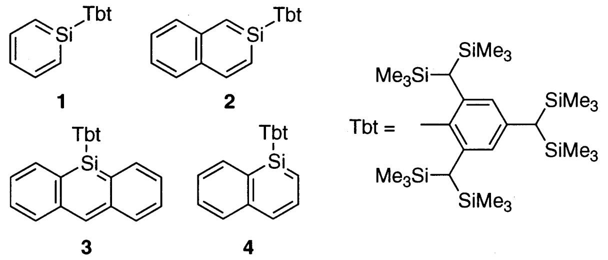
Summary: The first 1-silanaphthalene, ***4****, was successfully synthesized by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), and the aromaticity of* ***4*** *was discussed on the basis of its* ^1H*,* ^{13}C*, and* ^{29}Si *NMR, Raman, and UV/vis spectra together with theoretical calculations. In contrast to the thermal stability of the Tbt-substituted 2-silanaphthalene* ***2****, 1-Tbt-1-silanaphthalene (****4****) undergoes a ready [2 + 4] dimerization reaction in solution even at room temperature, despite its stability in the solid state.*

Chart 1



In recent decades, much interest has been paid to the chemistry of silicon analogues of aromatic compounds: i.e., silaaromatic compounds.[1] Although some stable examples of anionic,[2] cationic,[3] and neutral[4] silaaromatic compounds have been synthesized recently, the properties of silaaromatic compounds have not been fully revealed yet because of the extreme instability of the low-coordinated silicon compounds. Very recently, we have succeeded in the synthesis of the first stable silabenzene **1**,[5,6] 2-silanaphthalene **2**,[7−9] and 9-silaanthracene **3**[10] (Chart 1) by taking advantage of an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).[11] The aromatic character of **1**−**3** has been revealed by the NMR, UV/vis, and Raman spectral data and the X-ray structural analyses of these stable silaaromatic compounds. Moreover, it was found that they undergo 1,2- and/or 1,4-addition reactions at their 1-silabuta-1,3-diene moiety with various reagents such as H_2O, MeOH, an alkene, an alkyne, and a nitrile oxide, reflecting the extremely high reactivity of Si=C double bonds. On the other hand, there has been no report on the synthesis of 1-silanaphthalene, which is a structural isomer of 2-silanaphthalene, although much attention has been focused on the similarities and differences between 1- and 2-silanaphthalenes. We have already revealed by calculating the NICS values[12] that the aromaticities of 1- and 2-silanaphthalenes are comparable to each other and slightly less than that of naphthalene.[7,8] In addition, calculations of isodesmic isomerization energies indicated that the aromatic stabilization energies of 1- and 2-silanaphthalenes are comparable with that of naphthalene.[8] In this paper, we present the successful synthesis and characterization of the 1-silanaphthalene **4**, bearing a Tbt group, together with its chemical properties.

Bromosilane **7**, a precursor of 1-silanaphthalene **4**, was synthesized by the treatment of compound **5**[13] with *tert*-butyllithium and successive addition of $TbtSiH_3$,[14] followed by bromination of the resulting hydrosilane **6** with *N*-bromosuccinimide (NBS) (Scheme 1). When a THF solution of **7** was treated with lithium diisopropylamide (LDA) (1.0 equiv) at −40 °C in a glovebox, the expected 1-silanaphthalene **4** was obtained as moisture-sensitive pale yellow crystals in 97% yield.

The structure of **4** was confirmed by ^1H, ^{13}C, and ^{29}Si NMR, Raman, UV/vis, and high-resolution mass spectroscopy,[15] although good crystals of **4** suitable for an X-ray structural analysis could not be obtained, unfortunately. In the ^{29}Si NMR spectrum, a low-field-shifted signal (δ_{Si} 91.7) characteristic of an sp^2 silicon was

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Scheme 1

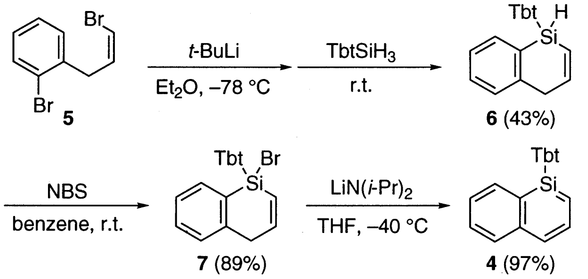


Table 1. Observed and Calculated ^{1}H, ^{29}Si, and ^{13}C NMR Chemical Shifts (δ in ppm) of 1-Silanaphthalenes

	4 (obsd)	**8a** (calcd)[a]	**8b** (calcd)[a]
H2	7.10	7.13	6.74
H3	8.07	7.77	7.79
H4	7.17	7.00	6.88
H5	7.73	7.56	7.54
H6	7.36	7.34	7.32
H7	7.15	6.98	6.97
H8	8.22	7.85	8.12
Si1	91.6	84.7	104.1
C2	116.7	121.4	110.6
C3	138.0	137.1	137.3
C4	116.9	118.2	115.9
C5	131.4	130.7	130.5
C6	128.8	127.7	127.3
C7	120.6	119.8	119.5
C8	133.2	130.8	130.4
C9	131.5	135.6	130.1
C10	145.3	145.0	145.4

[a] Calculated at the GIAO-B3LYP/6-311G(d)(6-311G(3d) for Si)//B3LYP/6-31G(d) level.[16]

observed, as in the cases of **1** (δ_{Si} 93.6),[5] **2** (δ_{Si} 87.3),[7] and **3** (δ_{Si} 87.2).[10] All the ^{1}H and ^{13}C NMR signals of the 1-silanaphthalene ring, which were assigned by 2D NMR techniques, were observed in the aromatic region (Table 1). These results strongly suggest the aromaticity of 1-silanaphthalene **4**.

Theoretical calculations[16] showed that the optimized structures of the 1-silanaphthalene rings in 1-silanaphthalene (**8a**) and 1-phenyl-1-silanaphthalene (**8b**) (Chart 2) are completely planar, as are the experimentally observed silaaromatic rings of silabenzene **1**, 2-silanaphthalene **2**, and 9-silaanthracene **3**. In **8b**, the dihedral angles for the angle between the 1-silanaphthalene ring and the phenyl ring are in the range of 36−38°. The two Si−C bond lengths of the 1-silanaphthalene ring of **8b** lie between Si−C single- and double-bond lengths, and the Si1−C2 bond in **8b** is slightly shorter than the Si1−C9 bond (Figure 1). This higher double-bond character for the bond between the elements at the 1- and 2-positions is also recognized in the cases of 2-silanaphthalene[9] and naphthalene.[17] The calculated NMR chemical shifts for **8a** and **8b** were consistent with the observed values of **4**. This agreement indicates that the 1-silanaphthalene ring structure of **4** might be very similar to those of **8a** and **8b**.

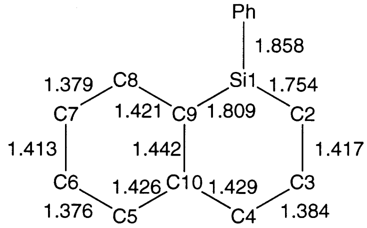
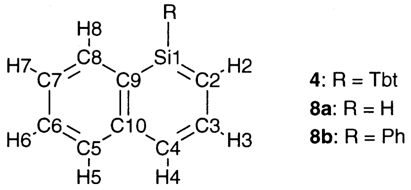


Figure 1. Optimized structure of **8b** (B3LYP/6-31G).

Chart 2



In the Raman spectrum, the pattern of strong lines of **4** was similar to those of **2** and naphthalene. Theoretical calculations for the vibrational frequencies of **8a** showed good agreement with the observed Raman shifts of **4**. It was considered that the strongest line of **4**, observed at 1340 cm^{-1}, corresponds to the most intense line of **8a** (1330 cm^{-1}, calculated at the B3LYP/6-31G(d) level and scaled by 0.96).[18] The calculated vibration mode of this line in **8a** is the skeletal vibration within the 1-silanaphthalene ring plane, which resembles those assigned to the most intense lines of **2** (1368 cm^{-1})[7,8] and naphthalene (1382 cm^{-1}). These results indicate that 1-silanaphthalene **4** has a ring skeleton similar to those of 2-silanaphthalene **2** and naphthalene.

The UV/vis spectrum of **4** showed absorption maxima (nm; ϵ values in M^{-1} cm^{-1}) at 254 ($\epsilon = 4 \times 10^4$), 354 ($\epsilon = 2 \times 10^4$), 364 ($\epsilon = 2 \times 10^4$), and 378 ($\epsilon = 1 \times 10^4$). Although these maxima are shifted to a longer wavelength region than those of naphthalene,[19] as in the case of 2-silanaphthalene,[7,8] the maximum of the former species around 250 nm is most likely assigned to the ^{1}B band and those between 300 and 400 nm are ascribed to the $^{1}L_a$ and $^{1}L_b$ bands. These results indicate that the aromatic structure of 1-silanaphthalene **4** is supported by the UV/vis spectrum as well.

1-Silanaphthalene **4** was found to undergo gradual dimerization at room temperature in solution under an argon atmosphere to give the corresponding dimer **9** via [2 + 4] cycloaddition (Chart 3),[20] although **4** is stable in the solid state at room temperature more than 3

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(15) Spectral and other characterization data for **4**: pale yellow crystals, mp 127−132 °C dec; ^{1}H NMR (400 MHz, 10 °C, C_6D_6) δ 0.04 (s, 9H), 0.08 (s, 9H), 0.15 (s, 18H), 0.18 (s, 18H), 1.55 (s, 1H), 2.49 (br s, 1H), 2.57 (br s, 1H), 6.64 (br s, 1H), 6.77 (br s, 1H), 7.10 (d, $^{3}J = 11.6$ Hz, 1H), 7.15 (ddd, $^{3}J = 7.8$ Hz, $^{3}J = 6.9$ Hz, $^{4}J = 1.0$ Hz, 1H), 7.17 (d, $^{3}J = 9.2$ Hz, 1H), 7.36 (ddd, $^{3}J = 8.2$ Hz, $^{3}J = 6.9$ Hz, $^{4}J = 1.5$ Hz, 1H), 7.73 (dd, $^{3}J = 8.2$ Hz, $^{4}J = 1.0$ Hz, 1H), 8.07 (dd, $^{3}J = 11.6$ Hz, $^{3}J = 9.2$ Hz, 1H), 8.22 (dd, $^{3}J = 7.8$ Hz, $^{4}J = 1.5$ Hz, 1H); ^{13}C NMR (100 MHz, 10 °C, C_6D_6) δ 0.94 (q), 1.20 (q), 1.26 (q), 1.54 (q), 31.68 (d), 36.52 (d), 36.95 (d), 116.74 (d), 116.89 (d), 120.58 (d), 121.77 (d), 123.64 (s), 126.29 (d), 128.76 (d), 131.40 (d), 131.52 (s), 133.19 (d), 137.95 (d), 145.33 (s), 148.16 (s), 153.05 (s), 153.16 (s); ^{29}Si NMR (59 MHz, 10 °C, C_6D_6) δ 2.2, 2.5, 2.6, 3.3, 91.7; UV−vis (hexane; λ_{max} (ϵ (M^{-1} cm^{-1})) 228 (2×10^4), 254 (4×10^4), 354 (2×10^4), 364 (2×10^4), and 378 (1×10^4); high-resolution FAB-MS *m/z* calcd for $C_{36}H_{66}Si_7$ ($[M]^+$) 694.3549, found 694.3556 ($[M]^+$). Elemental analysis of **4** gave values in agreement with the calculated values for the corresponding hydrolyzed product, due to the high sensitivity of **4** to moisture. Anal. Calcd for $C_{72}H_{68}OSi_7$: C, 60.60; H, 9.61. Found: C, 60.41; H, 9.31.

(16) Calculations were carried out using the Gaussian 98 program.

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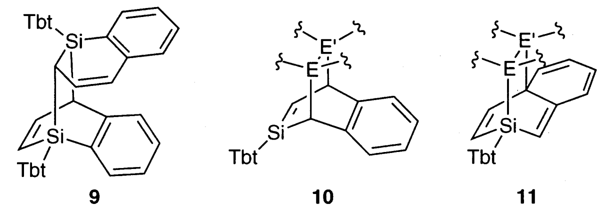
(20) Signals assigned to the dimers of **4** other than those of **9** could not be observed in the ^{1}H NMR spectrum of the crude products.

Chart 3



E, E ' = C or Si

weeks under an argon atmosphere. The structure of **9** was determined by its ^{1}H, ^{13}C, and ^{29}Si NMR spectra together with elemental analysis,[21] and the assignment of the stereochemistry was achieved by an X-ray structural analysis (Figure 2).[22] The dimerization reaction of **4** was completed by leaving its C_6D_6 solution at room temperature for 1 month and accelerated on heating. Heating of **4** in C_6D_6 at 100 °C for 12 h afforded the dimer **9** in 49% yield. This complete conversion of **4** into **9** indicates that **9** is thermodynamically more stable than **4** under these conditions. This thermal dimerization reaction of **4** in solution is in sharp contrast to the thermal stability of 2-silanaphthalene **2**, which is stable in C_6D_6 even on heating to 100 °C.[7,8] The difference in the thermal stability between **2** and **4** may be interpreted in terms of the thermodynamic instability of the conceivable dimers of **2** compared with that of **9**, as described below. Two types of structures, **10** and **11**, are expected as the dimerization products of **2**. Both dimers are presumably unstable, since **10** has an extremely unstable Si−C double bond and **11** has to lose the aromaticity of not only the two SiC_5 rings but also one of the C_6 rings. In contrast, **9** has no Si−C double bond and retains the aromaticity of both of the C_6 rings; therefore, dimer **9** is considered to be stable compared to the dimers **10** and **11**. On the other hand, silabenzene **1** also gives the corresponding [2 + 4] dimer when a C_6D_6 solution of the compound is left at room temperature for 4 months (ca. 50% conversion), and the dimer dissociates into **1** quantitatively by heating at 80 °C for 9 h.[23] In contrast to the case of **4**, these results indicate that **1** is thermodynamically more stable than its dimer under these conditions. This difference in the thermodynamic stability as compared to that of their dimers between **1** and **4** may be explained by the difference in the stabilities of their Si−C double bonds; that is, the partially localized Si1−C2 double bond of **4** is less stable than the completely delocalized Si−C double bonds of **1**. Thermolysis of **9** at 120 °C in C_6D_6 in the absence and presence of a trapping reagent such as benzophenone[24] did not cause any change, suggesting that the dimer **9** was thermally stable.

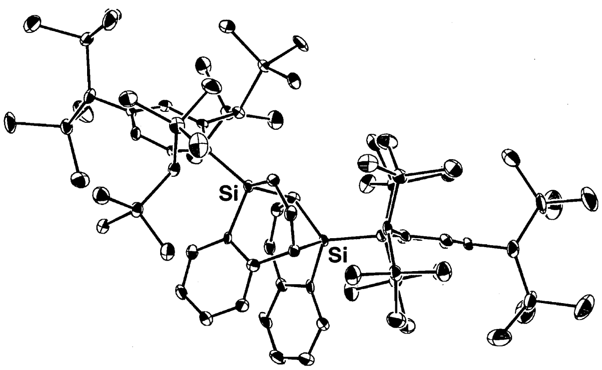


Figure 2. ORTEP drawing of **9** with thermal ellipsoid plots (50% probability). The fragment of a solvated chloroform was omitted for clarity.

In summary, we succeeded in the synthesis of the first 1-silanaphthalene, **4**, by taking advantage of the Tbt group. The ^{1}H, ^{13}C, and ^{29}Si NMR, Raman, and UV/vis spectra of **4** clearly indicated the aromaticity of **4**, as in the cases of naphthalene and 2-silanaphthalene **2**. In contrast to the thermal stability of **2**, 1-silanaphthalene **4** underwent ready dimerization via [2 + 4] cycloaddition, even at room temperature. This remarkable difference in the stability between the regioisomeric silanaphthalenes **2** and **4** is very interesting with regard to the chemistry of silaaromatic compounds. Further studies on the properties of **4** are currently in progress.

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Supporting Information Available: Text giving experimental procedures and characterization data for the reported new compounds and tables giving X-ray structural data for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Spectral and other characterization data for **9**: white powder, mp 144.3−147.8 °C; ^{1}H NMR (300 MHz, room temperature, $CDCl_3$) δ −0.25 (s, 9H), −0.22 (s, 9H), −0.18 (s, 18H), 0.04 (s, 27H), 0.08 (s, 9H), 0.09 (s, 18H), 0.18 (s, 9H), 0.21 (s, 9H), 1.28 (s, 1H), 1.35 (s, 1H), 2.10−2.16 (m, 2H), 4.02 (d, ^3J = 7 Hz, 1H), 5.89 (d, ^3J = 11 Hz, 1H), 6.10 (d, ^3J = 8 Hz, 1H), 6.26−6.48 (m, 6H), 6.57−6.59 (m, 1H), 6.77−6.79 (m, 1H), 6.81−6.84 (m, 2H), 6.95−6.98 (m, 1H), 7.57−7.64 (m, 1H); ^{13}C NMR (75 MHz, room temperature, $CDCl_3$) δ 0.61 (q), 0.73 (q), 0.81 (q), 0.91 (q), 0.98 (q), 0.99 (q), 1.14 (q), 1.27 (q), 1.37 (q), 1.49 (q), 1.69 (q), 1.75 (q), 2.06 (q), 2.12 (q), 15.36 (d), 27.11 (d), 27.21 (d), 28.48 (d × 2), 30.30 (d), 30.46 (d), 42.28 (d), 122.89 (d), 122.93 (d), 123.18 (d), 123.23 (s), 125.82 (d), 125.85 (d), 127.60 (d), 127.84 (d), 127.86 (d), 127.95 (d), 128.32 (s), 128.59 (d), 128.66 (d), 129.53 (d), 131.21 (d), 133.40 (d), 133.81 (d), 134.81 (s), 135.40 (s), 140.57 (s), 143.87 (s), 144.46 (s), 144.88 (s), 148.91 (d), 152.39 (s), 152.54 (s), 152.83 (s), 152.99 (s); ^{29}Si NMR (59 MHz, room temperature, $CDCl_3$) δ −33.2, −24.6, 1.67, 1.71, 1.9, 1.98, 2.04, 2.1, 2.2, 2.3, 2.7. Anal. Calcd for $C_{72}H_{132}Si_{14}$: C, 62.17; H, 9.56. Found: C, 61.85; H, 9.53.

(22) Crystal data for **9**·$CHCl_3$: Rigaku/MSC Mercury CCD, Mo Kα radiation, graphite monochromator, colorless crystals with 0.30 × 0.30 × 0.20 mm^3, wavelength 0.710 70 Å, T = 93 K, $2\theta_{max}$ = 50°, formula $C_{73}H_{133}Cl_3Si_{14}$, triclinic, space group $P\bar{1}$ (No. 2), a = 13.215(5) Å, b = 18.439(7) Å, c = 20.390(8) Å, α = 74.679(15)°, β = 79.450(18)°, γ = 78.132(17)°, V = 4645(3) Å^3, Z = 2, D_{calcd} = 1.080 g cm^{-3}, μ = 0.314 mm^{-1}, maximum/minimum residual electron density 0.797/−0.563 e Å^{-3}, GOF = 1.164, R1($I > 2\sigma(I)$) = 0.1006, wR2 (all data) = 0.2331 for 16 026 reflections, 921 parameters, and 61 restraints.

(23) Wakita, K. Ph.D. Thesis, The University of Tokyo, Tokyo, 1999. The details of the dimer−monomer equilibrium for **1** will be reported elsewhere as a full paper. The spectroscopic data and elemental analysis for the dimer are given in the Supporting Information.

(24) The reaction of **4** with benzophenone at room temperature gave the corresponding [4 + 2] cycloadduct, which was stable at 120 °C. The details of the reactivities of **4** will be reported elsewhere as a full paper.