

# The First Stable 9-Silaanthracene

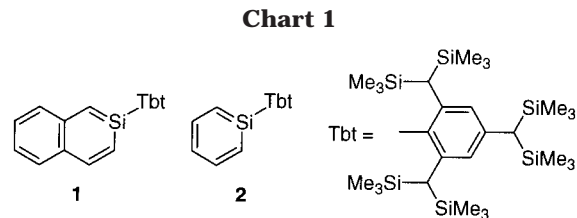
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**Summary:** The first stable 9-silaanthracene, **5**, bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), was successfully synthesized by the reaction of the corresponding silyl triflate, **7**, with a 1.0 M amount of lithium diisopropylamide. The aromaticity of **5** is discussed on the basis of the NMR, UV/vis, and Raman spectra, X-ray structural analysis, and theoretical calculations.

Aromatic compounds such as benzene, naphthalene, and anthracene play very important roles in organic chemistry. In recent decades, much attention has been paid to sila aromatics, i.e.,  $[4n+2]\pi$  electron ring systems containing at least one silicon atom as a ring member.<sup>1</sup> Since sila aromatic compounds are highly reactive and undergo ready dimerization and polymerization, there are few reports on the synthesis and isolation of sila aromatic compounds stable at room temperature. Recently, however, we have succeeded in the synthesis of the first stable 2-silanaphthalene, **1**,<sup>2,3</sup> and silabenzene, **2**,<sup>4,5</sup> by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).<sup>6</sup> In contrast, silaanthracenes, sila aromatic species having even more extended  $[4n+2]\pi$  electron ring systems than silanaphthalenes, have never been isolated as stable compounds, although there are some reports of the chemical trapping of intermediary silaanthracenes and of observation by UV/vis spectroscopy of unstable silanathracenes in matrixes at low temperature.<sup>7–9</sup> In this paper, we present the synthesis



and properties of the first stable 9-silaanthracene bearing a Tbt group.

9,10-Dihydro-9-silaanthracene, **3**, bearing a Tbt group on the silicon atom, was prepared by the reaction of  $\text{TbtSiH}_3$ <sup>10</sup> with bis(2-lithiophenyl)methane generated from bis(2-bromophenyl)methane and butyllithium.<sup>9</sup> Bromination of **3** with NBS (*N*-bromosuccinimide) gave the corresponding bromosilane **4**, which could in principle be a precursor of 9-silaanthracene, **5**. However, attempted dehydrobromination of **4** using LDA (lithium diisopropylamide), *n*-BuLi, or *t*-BuLi was unsuccessful, probably due to the low acidity of the proton at the 10-position.<sup>11</sup> Treatment of **4** with a “super base”, i.e., the 1:1 mixture of *t*-BuLi and *t*-BuOK,<sup>12</sup> and subsequent addition of MeOH resulted in the formation of a small amount of methoxysilane **6** (21%) most likely formed by the reaction of **5** with MeOH. Despite further investigation on the reaction conditions by changing solvents, bases, and reaction temperature, no increase in yield could be achieved. To bring about the ready deprotonation at the 10-position and rapid elimination of the leaving group from the silicon atom, a trifluoromethanesulfonyl group was introduced onto the silicon atom by the reaction of **4** with  $\text{AgOTf}$  ( $\text{Tf} = \text{SO}_2\text{CF}_3$ ). Optimization of the reaction conditions resulted in almost quantitative formation of 9-silaanthracene, **5**, by treatment of silyl triflate **7** with a 1.0 M amount of LDA in benzene at ambient temperature. Since 9-silaanthracene, **5**, is scarcely soluble in hexane, **5** was isolated (82%) by filtration of  $\text{LiOTf}$  from the reaction mixture, followed by the evaporation of the filtrate and the subsequent washing of the residue with dry hexane under argon atmosphere. The formation of **5** was confirmed by NMR, UV/vis, Raman, and high-resolution mass spectroscopy,<sup>13</sup> and the molecular structure of **5** was determined by X-ray structural analysis.

The <sup>29</sup>Si NMR spectrum of **5** in  $\text{C}_6\text{D}_6$  showed a signal assignable to the silicon atom of the 9-silaanthracene ring at 87.2 ppm, which is very similar to those for 2-silanaphthalene, **1** (87.3 ppm),<sup>2</sup> and silabenzene, **2**

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Scheme 1

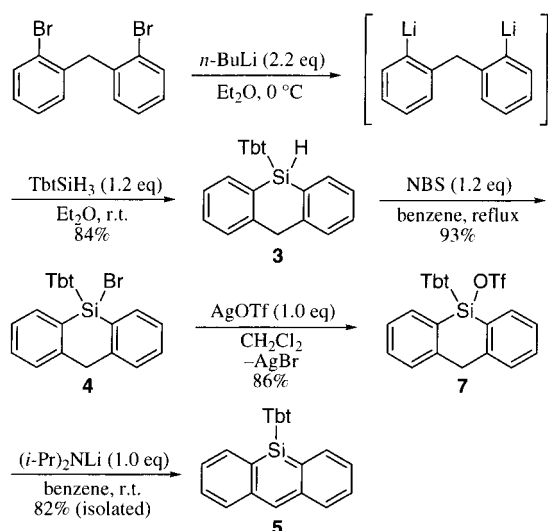
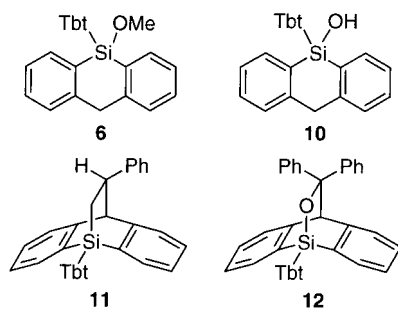


Chart 2



(93.6 ppm).<sup>4,5</sup> The <sup>29</sup>Si NMR chemical shift for **5** in 5:1 THF/C<sub>6</sub>D<sub>6</sub>, 86.8 ppm, was very little different, suggesting the absence of interaction with THF as a Lewis base. The <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated that the 9-silaanthracene ring of **5** has a C<sub>2</sub> axis passing through the Si1 and C8 atoms (Table 1), and this result indicates the delocalization of the double bonds in this ring system. The <sup>1</sup>H and <sup>13</sup>C signals from the 9-silaanthracene ring of **5** were assigned by the 2D NMR technique (Table 1), and all the signals were in the aromatic region. The <sup>1</sup>J<sub>SiC</sub> value (76 Hz, [D<sub>12</sub>]cyclohexane) observed for the Si–C bond in the 9-silaanthracene ring of **5** is larger than that of a Si–C single bond (e.g., 50 Hz for Me<sub>4</sub>Si)<sup>14</sup> and close to those for 2-silanaphthalene, **1** (92 and 76 Hz, C<sub>6</sub>D<sub>6</sub>),<sup>2</sup> and silabenzene, **2** (83 Hz, [D<sub>12</sub>]cyclohexane).<sup>4</sup> These results obtained from the <sup>29</sup>Si, <sup>1</sup>H, and <sup>13</sup>C NMR spectra strongly suggest the aromatic character of 9-silaanthracene, **5**, as in the case of 2-silanaphthalene, **1**<sup>2</sup> and silabenzene, **2**.<sup>4,5</sup> Theoretical calculations<sup>15</sup> for the model molecules 9-silaanthracene

(13) Spectral data for **5**: mp 178–183 °C (decomp); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.06 (s, 18H), 0.21 (s, 36H), 1.61 (s, 1H), 2.56 (br s, 1H), 2.66 (br s, 1H), 6.69 (br s, 1H), 6.83 (br s, 1H), 7.09 (ddd, <sup>3</sup>J<sub>HH</sub> = 15.0 Hz, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 2H), 7.34 (ddd, <sup>3</sup>J<sub>HH</sub> = 15.0 Hz, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 2H), 7.72 (s, 1H), 7.91 (dd, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 2H), 8.33 (dd, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.35 (q), 1.39 (q), 1.46 (q), 1.53 (q), 1.60 (q), 31.96 (d), 35.73 (d), 35.98 (d), 116.13 (d), 118.53 (d), 121.78 (s), 122.41 (d), 127.09 (d), 127.62 (d), 128.50 (s), 131.89 (d), 133.10 (d), 142.18 (s), 148.66 (s), 153.94 (s); <sup>29</sup>Si NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.5, 2.6, 87.2; UV/vis (hexane) λ<sub>max</sub> 278 (ε 2 × 10<sup>4</sup>), 386 (3 × 10<sup>3</sup>), 408 (7 × 10<sup>3</sup>), 453 (2 × 10<sup>3</sup>), 474 (3 × 10<sup>3</sup>), and 503 nm (2 × 10<sup>3</sup>); high-resolution FAB-MS *m/z* calcd for C<sub>40</sub>H<sub>68</sub>Si<sub>7</sub> 744.3706, found 744.3704.

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Table 1. Observed and Calculated <sup>1</sup>H, <sup>29</sup>Si, and <sup>13</sup>C NMR Chemical Shifts of Silaanthracenes

	<b>5</b> (obsd)	<b>8</b> (calcd) <sup>a</sup>	<b>9</b> (calcd) <sup>a</sup>
H3, H13	8.33	8.00	7.71
H4, H12	7.09	6.86	6.73
H5, H11	7.34	7.30	7.24
H6, H10	7.91	7.74	7.68
H1		6.93	
H8	7.72	7.50	7.43
Si1	87.2	81.5	104.9
C2, C14	128.5	134.8	129.8
C3, C13	133.1	130.2	130.6
C4, C12	118.5	118.1	117.3
C5, C11	127.6	126.8	126.5
C6, C10	131.9	131.5	130.5
C7, C9	142.2	141.6	141.4
C8	116.1	117.1	114.7

<sup>a</sup> Calculated by GIAO-B3LYP/6-311G(d)/6-311G(3d) for Si//B3LYP/6-31G(d) level. See ref 16.

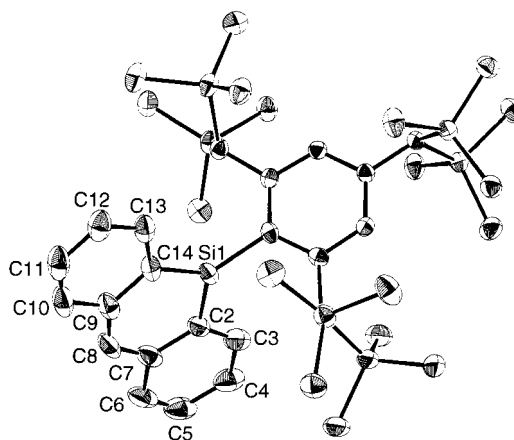
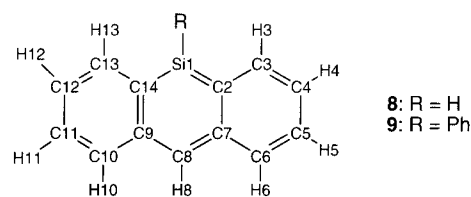


Figure 1. ORTEP drawing of 9-silaanthracene, **5**, with a thermal ellipsoid plot (50% probability).

Chart 3



(**8**; R = H) and 9-phenyl-9-silaanthracene (**9**; R = Ph) were carried out for comparison. The calculated chemical shifts of **8** and **9**<sup>16</sup> are in good agreement with the experimental data, suggesting only little perturbation by the Tbt substituent of the 9-silaanthracene system.

The X-ray structural analysis of 9-silaanthracene, **5**,<sup>17</sup> revealed that the 9-silaanthracene ring is completely planar and the silicon atom at the 9-position has a trigonal planar geometry (Figure 1 and Table 2). The dihedral angle between the 9-silaanthracene ring and

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

(16) The GIAO-B3LYP calculations were carried out with 6-311G(3d) for Si and 6-311G(d) for C and H. The geometries of **8** and **9** were optimized at the B3LYP/6-31G(d) level; the phenyl group of **9** was fixed perpendicular to the 9-silaanthracene ring.

(17) Crystal data of **5**: Formula C<sub>40</sub>H<sub>68</sub>Si<sub>7</sub>, *M<sub>r</sub>* = 745.57, triclinic, space group *P*1̄ (#2), *Z* = 2, *a* = 10.954(3) Å, *b* = 13.3077(18) Å, *c* = 17.683(3) Å, α = 67.639(6)°, β = 74.220(6)°, γ = 73.797(3)°, *V* = 2249.0(7) Å<sup>3</sup>, *D<sub>calcd</sub>* = 1.101 g/cm<sup>3</sup>, μ = 2.50 cm<sup>-1</sup>, 2θ<sub>max</sub> = 54.340°, *T* = 103 K, *R<sub>1</sub>* (*I* > 2σ(*I*)) = 0.0498, *wR<sub>2</sub>* (all data) = 0.1224, GOF = 1.047 for 9750 reflections and 442 parameters. Full details of the crystallographic analysis of **5** are described in the Supporting Information.

**Table 2. Observed and Calculated Bond Lengths (Å) of Silaanthracenes**

	5 (obsd)	8 (calcd) <sup>a</sup>	9 (calcd) <sup>a</sup>
Si1–C2, Si1–C14	1.787(3), 1.784(3)	1.782	1.786
C2–C3, C14–C13	1.419(4), 1.414(4)	1.425	1.427
C2–C7, C14–C9	1.442(4), 1.446(4)	1.449	1.451
C3–C4, C13–C12	1.371(4), 1.377(4)	1.371	1.373
C4–C5, C12–C11	1.401(4), 1.417(5)	1.421	1.422
C5–C6, C11–C10	1.345(5), 1.334(5)	1.368	1.370
C6–C7, C10–C9	1.444(4), 1.437(4)	1.434	1.436
C7–C8, C9–C8	1.398(4), 1.399(4)	1.408	1.409

<sup>a</sup> Calculated by B3LYP/6-31G(d) level.

the benzene ring of the Tbt group is about 70°. The two Si–C bond lengths in the 9-silaanthracene ring (1.787(3) and 1.784(3) Å) are almost the same and lie between the typical Si–C double and single bond lengths (1.70 and 1.89 Å, respectively).<sup>18</sup> As for the C–C bond lengths of the 9-silaanthracene ring (1.33–1.45 Å), considerable bond localization was observed for the fused benzene rings as well as the parent anthracene.<sup>19</sup> These experimental values strongly support the conjugation of the  $\pi$ -electrons in the 9-silaanthracene ring of **5**. The calculated bond lengths for the model molecules **8** and **9** are shown in Table 2,<sup>15</sup> and they showed an excellent agreement with the observed values of **5**. This indicates that the Tbt group substituted on the silicon atom little affects the bond lengths of the 9-silaanthracene ring.

The UV/vis spectrum of **5** [ $\lambda_{\max} = 278$  ( $\epsilon \times 10^4$ ), 386 ( $3 \times 10^3$ ), 408 ( $7 \times 10^3$ ), 453 ( $2 \times 10^3$ ), 474 ( $3 \times 10^3$ ), and 503 nm ( $2 \times 10^3$ )] shows a pattern very similar to that of anthracene, although the  $\lambda_{\max}$  values are red-shifted compared to those for anthracene.<sup>20</sup> The absorption maxima are almost the same as those of 9-silaanthracene, 9-phenyl-9-silaanthracene, and 9,10-diphenyl-9-silaanthracene, which have been observed under argon matrixes at 15 K by Maier et al.<sup>7</sup>

The Raman spectrum of **5** exhibited the most intense line at 1359  $\text{cm}^{-1}$ , while the most intense line for anthracene was observed at 1401  $\text{cm}^{-1}$ .<sup>21</sup> The vibrational frequency of the strongest line observed for **5** is in good agreement with those obtained by theoretical

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calculation (1338  $\text{cm}^{-1}$ , calculated at the B3LYP/6-31G-(d) level and scaled by 0.96).<sup>15,22</sup>

Although 9-silaanthracene, **5**, is thermally stable even at 100 °C in solution, treatment of **5** with H<sub>2</sub>O at room temperature resulted in the ready formation of silanol **10** (90%) via the 1,4-addition of water to the 9- and 10-positions. Furthermore, 9-silaanthracene, **5**, reacted with styrene and benzophenone at room temperature to give the corresponding [2+4] cycloadduct, **11** (93%) and **12** (81%), respectively.<sup>23</sup> It was revealed that **5** showed high reactivity toward various reagents despite its aromaticity as well as in the case of 2-silanaphthalene (**1**)<sup>2</sup> and silabenzene (**2**).<sup>4,5</sup> The occurrence of the addition to the 9- and 10-positions suggests the conjugation of  $\pi$ -electrons in this ring system.

In summary, we have succeeded in the synthesis of the first stable 9-silaanthracene, **5**, by taking advantage of kinetic stabilization afforded by an extremely bulky substituent, Tbt. The detailed analysis of the spectral data and the X-ray structural analysis revealed that 9-silaanthracene, **5**, is an aromatic compound despite its high reactivity. Further investigation on the 9-silaanthracene, **5**, is currently in progress.

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**Supporting Information Available:** Text giving experimental procedures and characterization data for the reported new compounds and X-ray structural report of **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(23) The regiochemistry of cycloadducts **11** and **12** was determined by spectroscopic data and X-ray crystallographic analysis. The details of the structural analysis will be reported elsewhere.