

A Stable Neutral Silaaromatic Compound, 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-2-silanaphthalene

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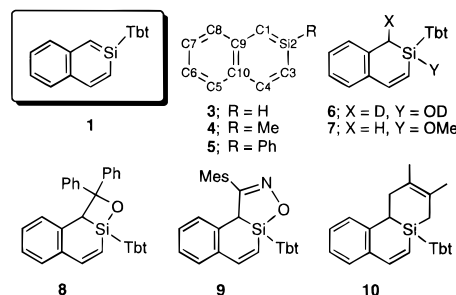
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Much attention has been focused on the chemistry of silaaromatic compounds, *i.e.*, Si-containing $[4n + 2]\pi$ ring systems, and a number of reports on the formation and reactions of transient silaaromatics such as sila- and disilabenzene have appeared in the past few decades.¹ Although some of them were characterized spectroscopically in low-temperature matrices,² no isolation has been reported due to their high reactivity. The exceptions, silole anions and dianions, reportedly have significantly delocalized electron density in their silole rings.^{3,4} As for a neutral silaaromatic compound, Märkl *et al.* have already reported the synthesis of a monomeric silabenzene, 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butylsilabenzene.⁵ However, it was observed only in solution (THF/Et₂O/petroleum ether, 4:1:1) below –100 °C, due apparently to stabilization by coordination of the solvent Lewis base judging by the relatively high field ²⁹Si NMR chemical shift ($\delta_{\text{Si}} = 26.8$) (*vide infra*). The only generation of a silanaphthalene ever reported, transient 2-methyl-2-silanaphthalene, was deduced by MeOD trapping of the reaction products in the flow pyrolysis of 2-allyl-2-methyl-1,2-dihydro-2-silanaphthalene.⁶ We have recently synthesized the first stable silanethione, Tbt(Tip)Si=S (Tip = 2,4,6-triisopropylphenyl),⁷ by taking advantage of a new and effective

bulky protecting group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt).⁸ Our successful application of the Tbt group to the kinetic stabilization of silaaromatic species has now led to the first isolation of 2-silanaphthalene **1**. The 2-silanaphthalene **1** was synthesized as a colorless, stable crystalline compound (mp 151–155 °C) in 80% yield by treatment of **2** with *t*-BuLi in hexane (Scheme 1).⁹



The structure of **1** was confirmed by its ¹H, ¹³C, and ²⁹Si NMR spectral data,¹⁰ which were in quite good agreement with chemical shifts computed for the parent and substituted 2-silanaphthalenes **3–5** (GIAO-B3LYP),¹¹ *e.g.*, δ_{H} for H(1) [**1**, 7.40; **3**, 7.74; **4**, 6.97; **5**, 7.32], H(3) [**1**, 7.24; **3**, 7.27; **4**, 7.03; **5**, 7.08], and H(4) [**1**, 8.48; **3**, 8.64; **4**, 8.50; **5**, 8.55], δ_{C} for C(1) [**1**, 116.01; **3**, 128.45; **4**, 120.43; **5**, 121.63], C(3) [**1**, 122.56; **3**, 125.13; **4**, 122.68; **5**, 123.56], and C(4) [**1**, 148.95; **3**, 153.38; **4**, 153.26; **5**, 152.45], and δ_{Si} for Si(2) [**1**, 87.35; **3**, 67.80; **4**, 100.97; **5**, 94.32]. The ²⁹Si NMR chemical shift ($\delta_{\text{Si}} = 87.35$) observed for the ring silicon of **1** is comparable to those for the previously reported sp² silicon compounds.^{1c} All the ¹H NMR signals of the ring protons (6.99–8.48 ppm) of **1** were observed in the aromatic region, and the ¹³C NMR signals of the ring carbons (116.01–148.95 ppm) were located in the sp² region. The coupling constants between the ring Si atom and the two adjacent ring carbons [92 Hz for $J_{\text{Si-C}(1)}$ and 76 Hz for $J_{\text{Si-C}(3)}$] both exceed normal values for C–Si(sp³) (~50 Hz)¹² and are similar to those reported for Si=C systems (83–85 Hz).^{1c} These results clearly indicate that the 2-silanaphthalene ring has delocalized double bonds.

The molecular structure of **1** was also established by X-ray crystallography (Figure 1).¹³ The silanaphthalene ring of **1** is almost planar and oriented perpendicular to the benzene ring of the Tbt group, suggesting essentially no conjugative interaction of the π -electrons of the Tbt group with those of the silanaphthalene ring. The 360° bond angle sum shows the completely planar trigonal geometry around the silicon atom.

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(9) The starting material, *i.e.*, 1,2,3,4-tetrahydro-2-silanaphthalene, was synthesized by LAH reduction of the corresponding dichlorosilane which was prepared by the reported procedures. (a) Zhdanov, A. A.; Andrianov, K. A.; Odinet, V. A.; Karpova, I. V. *Zh. Obshch. Khim.* **1966**, *36*, 521. (b) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Kuz'mina, T. M.; Kisin, A. V. *Zh. Obshch. Khim.* **1975**, *45*, 2227.

(10) The assignments of the ¹H signals of **1** were based on the NOE and decoupling experiments and those of the ¹³C NMR signals were accomplished by the analysis of the CH-COSY and HMBC spectra. Full details of the physical properties of **1** are described in the Supporting Information. (11) The GIAO-B3LYP calculations were carried out with 6-311G(3d) for Si and 6-311G(d) for C and H. The geometries of **3–5** were optimized at the B3LYP/6-31G(d) level, where the 2-phenyl group of **5** was fixed perpendicularly to the 2-silanaphthalene ring.

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(13) Crystallographic data for **1**: C₃₆H₆₆Si₇, MW = 695.52, monoclinic, space group P2₁/c, *a* = 12.762(6) Å, *b* = 9.91(1) Å, *c* = 34.67(1) Å, β = 96.58(3)°, *V* = 4356(4) Å³, *Z* = 4, *D_c* = 1.060 g cm⁻³, μ = 2.41 cm⁻¹, *R* (*R_w*) = 0.071(0.069). *T* = 193 K. Full details of the crystallographic analysis of **1** are described in the Supporting Information.

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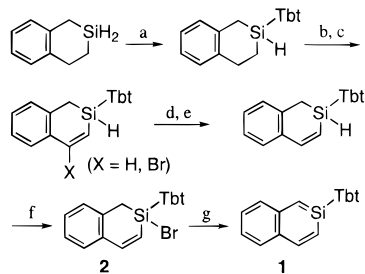
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Scheme 1^a

^a Conditions: (a) TbtLi, THF, $-78\text{ }^{\circ}\text{C}$, 34%; (b) NBS (3.7 equiv), BPO (cat.), benzene, reflux; (c) LiAlH₄ (10 equiv), THF, $0\text{ }^{\circ}\text{C}$, 29% (X = H) and 10% (X = Br) for two steps; (d) *t*-BuLi (2.0 equiv), THF, $-78\text{ }^{\circ}\text{C}$; (e) H₂O (excess), $-78\text{ }^{\circ}\text{C}$, 94% for two steps; (f) NBS (1.0 equiv), CCl₄, $0\text{ }^{\circ}\text{C}$, quant; (g) *t*-BuLi (1.0 equiv), hexane, rt, 80%.

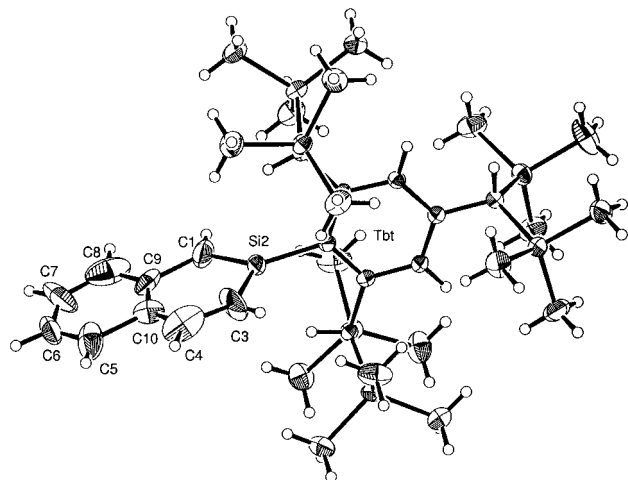


Figure 1. ORTEP drawing of Tbt-substituted 2-silanaphthalene (**1**) with a thermal ellipsoid plot (30% probability).

Although we are not able to discuss the X-ray distances because of the severely disordered 2-silanaphthalene ring of **1**,¹⁴ the SiC bond lengths computed at the uniform B3LYP/6-311+G** level for the parent 2-silanaphthalene (**3**) [1.747 Å for C(1)–Si(2) and 1.790 Å for Si(2)–C(3)] compared with silabenzene (1.771 Å), H₂C=SiH₂ (1.708 Å), and H₃C–SiH₃ (1.885 Å), suggest the delocalization of π -electrons in the 2-silanaphthalene ring system of **3** (Figure 2). These SiC bond length relationships are like those for the corresponding CC bonds in naphthalene, benzene, ethene, and ethane. These calculations, along with the NMR results just discussed, are indicative of the aromaticity of **3**, which is reinforced by the additional data below.

The Raman spectrum of **1** showed a strong line with a maximum intensity at 1368 cm^{-1} , compared with the most intense line of 1382 cm^{-1} for naphthalene. The strongest Raman shifts observed for **1** and naphthalene are in good agreement with the calculated vibrational frequencies (1377 cm^{-1} for **3**, 1378 cm^{-1} for **5**, and 1389 cm^{-1} for naphthalene, computed at the B3LYP/6-31G* level and scaled by 0.98).¹⁵ Furthermore, the calculated vibration modes of **5** showed a close resemblance to those of naphthalene, suggesting the aromatic character of **1**.

The UV–vis spectrum of **1** in hexane showed three absorption maxima [$267\text{ }(\epsilon\ 2 \times 10^4)$, $327\text{ }(\epsilon\ 7 \times 10^3)$, and $387\text{ }(\epsilon\ 2 \times 10^3)$ nm]

(14) The structural parameters for **1** reported here are still preliminary. All the data obtained at room temperature in several runs with different single crystals gave poorer results. Even from the data collected at low temperature we have not yet obtained satisfactory intramolecular parameters for the fused benzene ring moiety of **1** because of the severe disorder which is most likely caused by the fact that the benzene ring is located on the peripheral part of this big molecule. Although the final level has not yet been reached, we think the molecular geometry here obtained is significant enough to demonstrate the planarity in the silanaphthalene skeleton of **1**.

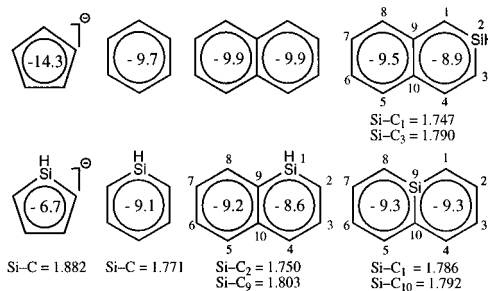


Figure 2. Calculated NICS (ppm) values (in the ring centers) for the possible silanaphthalenes and related aromatic systems at GIAO-SCF/6-31+G*. The optimized Si–C bond lengths (Å) are at the B3LYP/6-311+G** level.

most likely assignable to the *E*₁, *E*₂, and *B* bands. These are red shifted compared to those for naphthalene [$221\text{ }(\epsilon\ 1.33 \times 10^5)$, $286\text{ }(\epsilon\ 9.3 \times 10^3)$, and $312\text{ }(\epsilon\ 289)\text{ nm}$],¹⁶ suggesting the aromatic character of this conjugated ring system.

2-Silanaphthalene **1** was found to be very stable thermally even on heating in benzene at $100\text{ }^{\circ}\text{C}$ in a sealed tube in an inert atmosphere. No dimerization product was detected, although **1** is air- and moisture-sensitive due to its Si=C moiety. Its thermal stability, obviously due to the steric protecting ability of the Tbt group, is in sharp contrast to that of 1,4-di-*tert*-butylsilabenzene, which cannot be isolated as a monomer and undergoes facile dimerization even at $0\text{ }^{\circ}\text{C}$.¹⁷ Interestingly, **1** retains its high reactivity in spite of the thermal stability. Thus, **1** reacts with D₂O, methanol, benzophenone, mesitronitrile oxide, and 2,3-dimethyl-1,3-butadiene to give the corresponding adducts **6–10** across its Si=C moiety (59, 72, 62, 77, and 72% yields, respectively).¹⁸

The aromatic character of the 2-silanaphthalene ring system was evaluated by computing the NICSs (nucleus independent chemical shifts)¹⁹ of 2-silanaphthalene (**3**) together with the related sila-aromatic compounds and the parent hydrocarbons (Figure 2). The large negative NICS values obtained for the possible three silanaphthalenes, comparable to the parent naphthalene, suggest that the aromatic character will not be much reduced by the replacement of a ring carbon by a silicon atom, which agrees with the experimental evidence discussed above for **1**.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan, and at Erlangen by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are grateful to Professor Yukio Furukawa, The University of Tokyo, for the measurement of FT-Raman spectra. We also thank Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd., for the generous gift of chlorosilanes and alkyllithiums, respectively. Calculations were carried out with the Gaussian 94 program.

Supporting Information Available: Physical properties of compounds **1**, **2**, and **6–10**, crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1**, and a table for the observed Raman shifts for **1** and naphthalene (33 pages). See any current masthead page for ordering and Internet access instructions.

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(15) The geometry optimizations and vibrational frequency computations for **3**, **5**, and naphthalene were performed at the B3LYP/6-31G* level; the 2-phenyl group of **5** was fixed perpendicularly (*C_s* symmetry) to the 2-silanaphthalene ring. For the scaling factor of 0.98, see: Bauschlicher, Jr. C. W.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

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