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Crystal Structure of a Stable Silabenzene and Its Photochemical Valence Isomerization into the Corresponding Silabenzvalene

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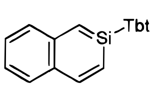
In contrast to the great developments in the chemistry of doubly bonded organosilicon compounds in the last two decades, silicon analogues of aromatic compounds are less studied except for charged systems.[1] Previous investigations on neutral silaaromatic compounds revealed their extremely high reactivity, although some of them were observed spectroscopically in the low-temperature matrices or in the gas phase.[1] The most stable silabenzene ever reported is 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butyl-1-silabenzene, but it reportedly survives only below −100 °C and is stabilized by the coordination of the solvent (THF/ether/petroleum ether = 4:1:1).[2]

Meanwhile, we have succeeded in the synthesis of the first stable 2-silanaphthalene **1** by protecting its reactive silicon center with a 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl} (Tbt) group.[3] More recently, a stable silabenzene **2** bearing a Tbt group was also synthesized by the reaction of the corresponding chlorosilane **3** with *t*-BuLi. Although silabenzene **2** was fully characterized by the ^{1}H, ^{13}C, and ^{29}Si NMR spectra and chemical trapping with benzophenone, the formation of an undesired byproduct **4** prevented the isolation of **2** in a pure form.[4] Here, we wish to report the effective synthesis and isolation of silabenzene **2** together with its crystallographic structural analysis and unique photochemical behavior.



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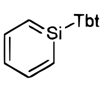
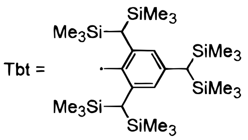


2



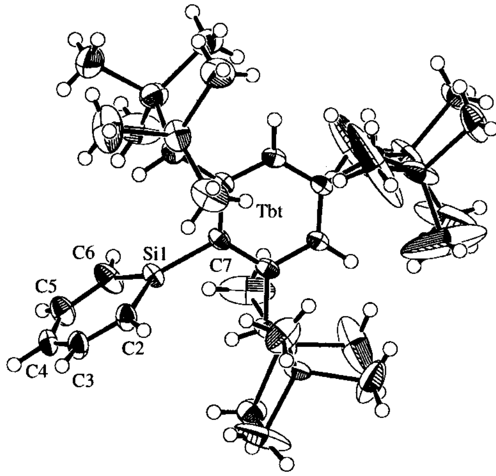
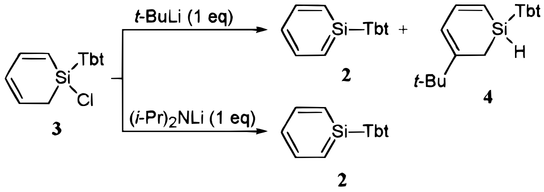


Figure 1. ORTEP drawing of silabenzene **2** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Si1−C2 1.765(4), C2−C3 1.391(6), C3−C4 1.399(6), C4−C5 1.381(6), C5−C6 1.394(7), C6−Si1 1.770(4), Si1−C7 1.853(4), C2−Si1−C6 107.8(2), C2−Si1−C7 127.2(2), C6−Si1−C7 124.9(2), Si1−C2−C3 117.7(3), C2−C3−C4 126.3(4), C3−C4−C5 124.1(4), C4−C5−C6 126.1(4), C5−C6−Si1 118.0(3).

After examination of several reaction conditions, the problem of the formation of the byproduct **4** was finally solved by using LDA as a base instead of *t*-BuLi. Reaction of chlorosilane **3** with 1 equiv of LDA in hexane at room temperature proceeded efficiently, and silabenzene **2** was obtained in 90% yield without any byproduct after the removal of inorganic salts.



The structure of silabenzene **2** was definitely determined by X-ray crystallographic analysis at −180 °C.[5] As shown in Figure 1, the planar geometry around the central silicon atom and silabenzene ring was clearly revealed.[7] The lengths of two Si−C bonds in the silabenzene ring were found to be essentially equal to each other (1.765(4) and 1.770(4) Å) and in the middle between those of Si−C double and single bonds (1.70 and 1.89 Å, respectively).[8] Furthermore, the C−C bond lengths (1.381(6)∼1.399(6) Å) in the silabenzene ring are almost equal to each other within the error of temperature factors, and also similar to the C−C length of benzene (1.39−1.40 Å).[9] Thus, it

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(1) For reviews of silaaromatic compounds, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 1102−1108. (c) Apeloig Y. ibid., pp 151−166. (d) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (e) Apeloig, Y.; Karni, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; , Vol. 2, Chapter 1.

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(3) (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336.

(4) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 634.

(5) Crystal data of **2**: Rigaku R-AXIS RAPID imaging plate area detector, Mo Kα radiation, graphite monochromator. The reflections were recorded at 93 K from a colorless prismatic crystal with dimensions 0.5 × 0.5 × 0.2 mm^3 to $2\theta_{\max} = 55$ °. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares procedures on F^2 (SHELX-97).[6] Formula $C_{32}H_{64}Si_7$, $M_r = 645.46$, monoclinic, space group $P2_1/a$, $Z = 4$, $a = 18.9186(3)$ Å, $b = 10.9969(2)$ Å, $c = 20.0757(4)$ Å, $\beta = 99.2711(6)°$, $V = 4122.1(1)$ Å^3, $\rho_{\mathrm{calcd}} = 1.040$ g cm^{-3}, $\mu = 2.50$ cm^{-1}; R_1 ($I > 2\sigma(I)$) = 0.097, wR_2 (all data) = 0.258 for 9446 reflections and 411 parameters.

(6) Sheldrick, G. M. *SHELX-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

(7) Sum of the bond angles around the central Si atom and that of the interior bond angles of the silabenzene ring are 359.8(3)° and 720.0(9)°, respectively.

(8) (a) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (b) Gutowsky, H. S.; Chen, J.; Hajduk, P. J.; Keen, J. D.; Chuang, C.; Emilsson, T. *J. Am. Chem. Soc.* **1991**, *113*, 4747.

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Table 1. Observed and Calculated Bond Lengths (Å) of Silabenzenes

	R	Si−C2	C2−C3	C3−C4
observed	Tbt	1.765(4)	1.391(6)	1.399(6)
		1.770(4)	1.394(7)	1.381(6)
calculated	H	1.773	1.400	1.403
	Ph	1.776	1.400	1.403
	Tbtx[b]	1.777	1.401	1.402

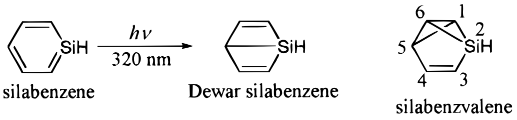
[a] B3LYP/6-31G(d). [b] All trimethylsilyl groups of Tbt are replaced by trihydrosilyl groups.

has experimentally been demonstrated that silabenzene has a delocalized 6π electron ring system similar to that of benzene.

Theoretical calculations for the model compounds of **2** ($RSiC_5H_5$; R = H, Ph, Tbtx) were also performed for comparison (Table 1).[10] Bond lengths of silabenzene rings are little affected by substituents on the silicon, and agreement between the experimental and theoretical values is excellent.

In the conversion from **3** to **2**, downfield shifts of the ring protons (∼1 ppm) were observed as in the case of 2-silanaphthalene **1**[3b] and support existence of the ring current effect of the silabenzene ring. In the UV spectrum **2** showed absorption maxima at ∼260 (sh), 301 ($\epsilon \sim 1 \times 10^3$), 323 ($\epsilon \sim 1 \times 10^3$), and 331 ($\epsilon \sim 2 \times 10^3$) nm, which are consistent with those recorded for two silabenzenes in low-temperature Ar matrices.[1a] The comparison of the UV spectra of benzene−silabenzene−1,4-disilabenzene series were already reported.[11]

Among the unique reactivities of silabenzene **2**, the photochemical reaction of **2** is worthy of special mention. It is well-known that the photolysis of benzene affords interesting isomers, such as Dewar benzene and benzvalene.[12] However, the photochemistry of silabenzene is less-studied since no stable silabenzene has ever been reported. Although the photochemical isomerization of the parent silabenzene to Dewar silabenzene has already been studied in an argon matrix,[13] the characterization of the Dewar silabenzene was only based on the shift of the Si−H stretching frequency in IR spectrum from that characteristic of an sp^2 to that characteristic of an sp^3 hybridized silicon.[13]



Photoirradiation of the stable silabenzene **2** resulted in the formation of a new compound,[14] which showed a ^{29}Si NMR signal of its central silicon atom at −71.6 ppm. This signal cannot be assignable to that of Dewar silabenzene, since it appears in a high field region characteristic of the three-membered ring silicon compounds.[15] Furthermore, separation of the mixture in the open air afforded silanol **6** having a three-membered ring.[16] Thus, the product of the photoirradiation of silabenzene **2** is not a Dewar silabenzene isomer but silabenzvalene **5**. ^{1}H and ^{13}C NMR spectra of **5** also supported the proposed silabenzvalene structure.[17]

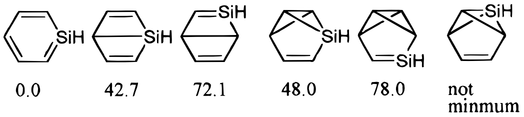
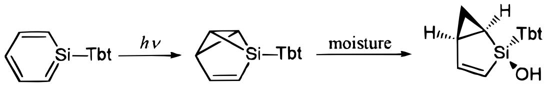


Figure 2. Calculated relative energies of silabenzene isomers (kcal/mol, B3LYP/6-31G(d)).



2 (δ_{Si} 93.6) **5** (δ_{Si} −71.6) **6**

Although a stable disilabenzvalene bearing four trimethylsilyl and two phenyl groups was recently reported by Ando et al.,[18] no silabenzvalene has been reported to the best of our knowledge. They indicated by theoretical calculations that the energy difference between the parent disilabenzvalene and its Dewar disilabenzene isomer is small. In contrast, previous theoretical studies on silabenzene isomers were concentrated only on Dewar silabenzene and the possibility of silabenzvalene was not taken into consideration.[19] We performed, therefore, B3LYP/6-31G(d) calculations on silabenzene isomers.[10] It has revealed that there is a small energy difference between Dewar silabenzene and silabenzvalene, while silabenzene is by far the most stable among the isomers (Figure 2).

In summary, the structure of silabenzene **2** was unequivocally determined by X-ray crystallography, and full delocalization of its ring π-electrons was clearly demonstrated. Moreover, interesting photochemical isomerization of **2** to the corresponding silabenzvalene was also disclosed. Further investigation to elucidate the characters of **2** is currently in progress.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (Nos. 08454197, 10440184, 11304045, and 11166250). We also thank Shin-etsu Chemical Co., Ltd. and Tosoh Akzo Co., Ltd. and Central Glass Co., Ltd. for the generous gifts of chlorosilanes, alkyllithiums, and tetrafluorosilane, respectively.

Supporting Information Available: X-ray structural report and spectral data of **2** and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Minkin, V. J.; Glukhovtsev, M. N.; Simkin, Y. B. *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994.

(10) Calculations were carried out using the Gaussian 98 program. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) Maier, G.; Schöttler, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 4079.

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(14) Photoreaction of silabenzene **2**: a C_6D_6 solution of **2** was sealed in a Pyrex NMR tube and irradiated by a 400 W high-pressure Hg lamp using a solution filter which is transparent at 290−350 nm (2 M $NiSO_4$/0.8 M $CoSO_4$/0.1 M $CuSO_4$ in 5% H_2SO_4). A 1:4 mixture of **2** and **5** was obtained after irradiation of 15 h. Longer time of irradiation gave polymeric products.

(15) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 536.

(16) The structure of **6** was determined by spectroscopic data and X-ray crystallographic analysis. Only this stereoisomer was obtained. See Supporting Information for details.

(17) NMR data of the silabenzvalene ring of **5**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.24 (m, 1H, H5), 2.50 (d, J = 5.1 Hz, 2H, H1,6), 5.82 (dd, J = 9.3, 2.0 Hz, 1H, H3), 7.41 (dd, J = 9.3, 3.5 Hz, 1H, H4). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 22.98 (C5), 39.81 (C1,6), 120.89 (C3), 161.19 (C4). ^{29}Si NMR (79 MHz, C_6D_6) δ −71.60. The complete data of **5** were not obtained since a small amount of silabenzene **2** (δ_{Si} = 93.64) remained after the irradiation (see ref 14).

(18) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3629. Two Si atoms of the disilabenzvalene resonated at −61.9 ppm. The disilabenzvalene was also air- and moisture-sensitive.

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