

Tetrasilane-Bridged Bicyclo[4.1.0]heptasil-1(6)-ene

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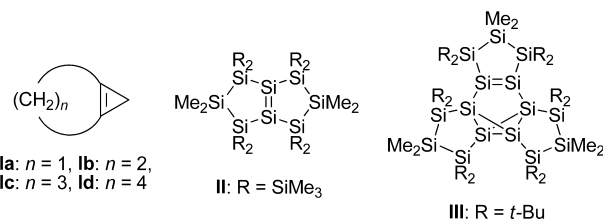
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S Supporting Information

ABSTRACT: Tetrasilane-bridged bicyclo[4.1.0]heptasil-1(6)-ene **1** was synthesized by the reduction of 1,1,2,2-tetrachlorocyclohexasilane **2** in 12% yield as red-orange crystals. The structure and properties of **1** were studied by spectroscopy, X-ray crystallography, and theoretical calculations. The linkage of the cyclotrisilene moiety with two tetrasilane chains with *tert*-butyl groups remarkably affects its structure and ²⁹Si NMR spectrum.

Highly strained hydrocarbons have attracted much attention from experimental and theoretical viewpoints.¹ Bicyclo[*n*.1.0]alk-1(*n*+2)-enes **Ia–d** are fused compounds consisting of cycloalkene and cyclopropene rings with a double bond at the bridgehead position (Chart 1), and they are

Chart 1



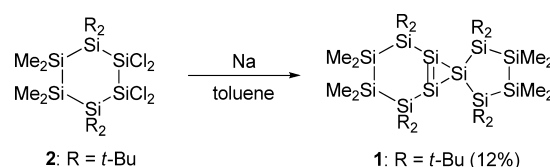
intriguing because of their unusual bonding properties and strain energies.² Theoretical calculations on **I** show that the structure around the C=C bond is pyramidal rather than planar.³ Although there are several reports on the generation of bicyclo[4.1.0]hept-1(6)-ene [1(6)-norcarene, **Id**],⁴ its isolation has not been reported because of its remarkably high reactivity.⁵

The chemistry of disilenes is a still growing research area since the first isolation of tetramesityldisilene in 1981.^{6,7} There have been reported not only acyclic but also cyclic disilenes such as cyclotrisilenes,⁸ cyclotetrasilenes,⁹ and a cyclopentasilene.¹⁰ Especially, spiropentasiladiene,¹¹ an isomer of hexasilabenzene,¹² and charge-separated cyclotetrasiladiene¹³ have recently been reported. Although a variety of disilenes have been known, disilenes with a fused Si=Si double bond are limited to bicyclo[3.3.0]octasil-1(5)-ene **II**¹⁴ and cyclopentasilane-fused hexasilabenzvalene **III** (Chart 1).¹⁵ To date, silicon analogues of **I** remain unknown. We report herein the first synthesis of bicyclo[4.1.0]heptasil-1(6)-ene **1** by the reduction of 1,1,2,2-tetrachlorocyclohexasilane **2**.

The reduction of **2** with 4 equiv of sodium dispersion in toluene under reflux for 4 h gave **1** in 12% yield as red-orange

crystals (Scheme 1). This compound is stable below 238 °C in the solid state under an argon atmosphere in a sealed tube.

Scheme 1. Synthesis of **1**



Apparently, **1** is the product of dimerization of **2**, but it is quite different from the expected cyclohexasilane-fused tetrasilatetrahdrene¹⁶ and cyclotetrasiladiene.¹³ In addition, one silicon atom is removed during the reduction of **2**. Similar examples have been reported in the formation of trisilaallene by the reduction of 1,1,1,2-tetrachlorodisilane¹⁷ and the formation of the Si₁₁ cluster by dimerization of an isomer of hexasilabenzene.¹⁸

X-ray crystallographic analysis showed that **1** contains 11 silicon atoms and comprises bicyclo[4.1.0]heptasil-1(6)-ene and cyclopentasilane rings that are connected at the spiro silicon atom (Figure 1). Both the cyclohexasilene and cyclopentasilane rings adopt the half-chair conformation. The 1,2-disilylcyclotrisilene moiety has a slightly trans-bent but nearly planar structure. The structural parameters of the 1,2-disilylcyclotrisilene moiety are comparable to those of the previously reported tetrasilylcyclotrisilenes **3a–c** (Chart 2 and Table S2 in the Supporting Information),^{8b–d} However, the exocyclic Si=Si–Si bond angles of 128.35(3)° (for Si3–Si2–Si7) and 131.73(3)° (for Si2–Si7–Si6) are considerably smaller than those in **3a–c** [144.74(4)–147.34(6)°].^{8b–d} These small bond angles are due to the effect of the fused cyclohexasilene ring. A small bond angle has also been reported in the optimized structure of **Id** (127.4–129.5°)^{4b} and is considered to be the origin of the low stability of **Id**.^{4a}

To investigate the intrinsic geometry around the Si=Si bond of bicyclo[4.1.0]heptasil-1(6)-ene, theoretical calculations on **1** (represented as **1**_{calc}) and model compounds **4a–c** and **5a–d** were carried out (Chart 2 and Table S4). The optimized structure of **1**_{calc} reproduces the X-ray structure well. Among the optimized structures, only **4c** and **5d** have nearly planar structures around the Si=Si bond as in **1**. On the other hand, **4a**, **4b**, and **5a–c** have cis-bent geometries with cis-bent angles¹⁹ of 8.3–37.2° (Table S4). Therefore, the planar

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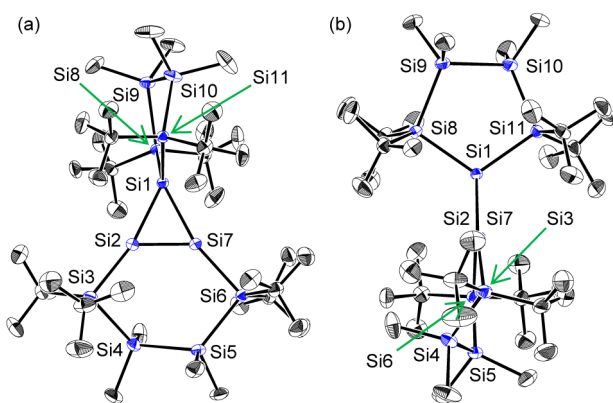
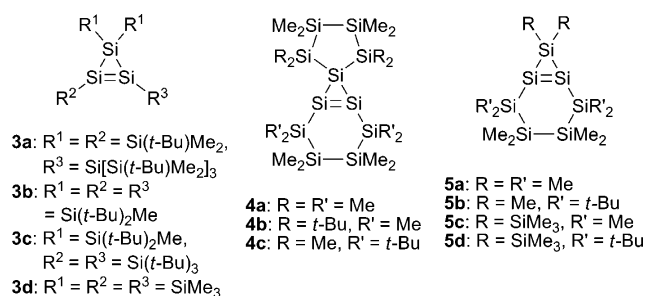


Figure 1. (a) Top view and (b) side view of the molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.3526(8), Si1–Si7 2.3744(7), Si2–Si3 2.3388(8), Si2–Si7 2.1473(8), Si6–Si7 2.3603(7); Si2–Si1–Si7 54.03(2), Si1–Si2–Si3 167.37(3), Si1–Si2–Si7 63.50(2), Si3–Si2–Si7 128.35(3), Si1–Si7–Si2 62.47(2), Si1–Si7–Si6 165.77(3), Si2–Si7–Si6 131.73(3); Si3–Si2–Si7–Si6 6.50(7).

Chart 2



structure of **1** is due to steric repulsion between the *tert*-butyl groups on the cyclohexasilene ring and the silyl groups on the spiro silicon atom. The inversion energies of the folded structures of **5a–c** are estimated to be 0.7, 0.4, and 1.4 kcal mol⁻¹, respectively (Tables S3 and S4). The energy barriers are similar to that of bicyclo[4.1.0]hept-1(6)-ene (~1 kcal mol⁻¹).^{4g}

The ²⁹Si NMR spectrum of **1** exhibits six signals at -85.4, -41.1, -31.5, -11.9, 15.0, and 147.1 ppm (Figure S3 in the Supporting Information). The signals at -85.4 and 147.1 ppm are assigned to the spiro silicon atom (Si1) and the Si=Si atoms (Si2 and Si7), respectively, which are considerably downfield relative to those of **3a–c** (-127.3 to -115.1 ppm and 81.9–99.8 ppm, respectively (Table S5)).^{8a,b,d,20} There are a few reports on unusually downfield ²⁹Si chemical shifts observed in silicon clusters.^{15,18,21} A possible explanation of the unusual downfield shifts may be given by the large paramagnetic term (σ_p) of Si1, Si2, and Si7. According to Ramsey's equation, σ_p is inversely proportional to the average of the transition energies between occupied and unoccupied molecular orbitals.^{22,23} Although the HOMOs and LUMOs of **3d**, **5d**, and **1**_{calc} are comparable to each other, the energies of the LUMO+1 and the LUMO+2 decrease considerably in the order of **3d**, **5d**, and **1**_{calc} as a result of the extension of the Si–Si σ^* orbitals of the cyclotrisilene ring by the cyclotetrasilane chain(s) (Figures S20 and S21). Therefore, the characteristic downfield shifts of **1** are caused by the linkage of the cyclotrisilene moiety with two tetrasilane chains.

The UV–vis spectrum of **1** shows complicated absorption tailing to ca. 550 nm (Figure 2). Two absorption maxima are

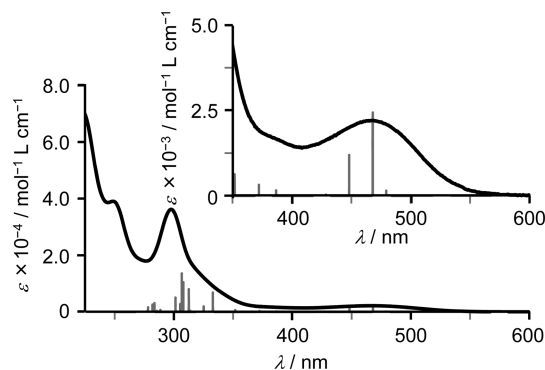


Figure 2. UV–vis spectrum of **1** in hexane at room temperature with transitions calculated using TD-DFT at the B3LYP/6-31+G(2d,p) level (gray bars).

observed at 468 nm ($\epsilon = 2200 \text{ M}^{-1} \text{ cm}^{-1}$) and 297 nm ($\epsilon = 36\,000 \text{ M}^{-1} \text{ cm}^{-1}$) together with two shoulders at 328 and 249 nm. The lowest-energy absorption maximum of **1** is comparable to those of **3a–c** ($\lambda_{\text{max}} = 466\text{--}482 \text{ nm}$)^{8a,b,d} and **II** ($\lambda_{\text{max}} = 468 \text{ nm}$).¹⁴ It is mainly due to the transition from the HOMO (Si=Si π) to the LUMO (Si=Si π^*) on the basis of time-dependent density functional theory (TD-DFT) calculations ($\lambda_{\text{calcd}} = 468.1 \text{ nm}$, $f = 0.0271$; Table S7).²⁴

ASSOCIATED CONTENT

Supporting Information

Details of the synthesis of **1**; X-ray crystallographic data for **1** and **2** (CIF); and theoretical calculations on **1**, **3d**, **4**, and **5** and homodesmotic reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(19) The definition of a cis-bent angle is shown in Table S4.

(20) The calculated ²⁹Si chemical shifts of the spiro silicon atoms of **3d**, **5d**, and **1** are -105.2, -74.8, and -54.2 ppm, respectively, and those of the Si=Si atoms are 102.9, 169.3, and 205.7 ppm, respectively (Table S5).

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(24) The strain energy of bicyclo[4.1.0]heptasil-1(6)-ene (37.3 kcal mol⁻¹) calculated using homodesmotic reactions is comparable to that of the parent cyclotrisilene (34.5 kcal mol⁻¹)¹¹ but much smaller than that of bicyclo[4.1.0]hept-1(6)-ene (63.2 kcal mol⁻¹). See the Supporting Information.