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Organosilicon Chemistry

An Organosilicon Cluster with an Octasilacuneane Core: A Missing Silicon Cage Motif**

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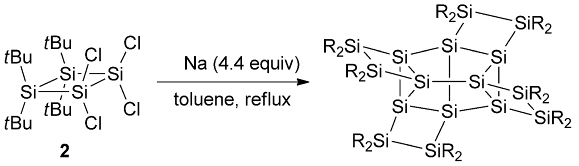
Organosilicon clusters (caged oligosilanes) are a fascinating class of molecules because 1) they can be regarded as partial structures of bulk crystalline or amorphous silicon and 2) the electronic properties of silicon clusters depend on silicon numbers and structural modification.[1] Therefore, synthetic studies on organosilicon clusters have been extensively developed. Persilapolyhedranes,[2–4] decasilaadamantane,[5] pentasila[1.1.1]propellane,[6] persila[*n*]staffane (catenated silicon cages),[7] and related siliconoids[8,9] have all been shown to possess unique electronic characteristics owing to developed σ conjugation among the caged Si–Si bonds. Octasilacuneane, a silicon analog of cuneane[10] (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane), is a missing saturated silicon cluster motif, but potentially important because octasilacuneane is an isomeric silicon cage of octasilacubane,[4] one of the most well-known silicon polyhedra. Moreover, through theoretical studies at the MP2/6-31G(d) + ZPE level, Versteeg and Koch have demonstrated that parent octasilacuneane (Si_8H_8) is only 3.3 kcal mol^{-1} less stable than the isomeric octasilacubane, which is in sharp contrast to the energetic relation between cubane and cuneane: cubane (C_8H_8) is much more unstable (by 43.7 kcal mol^{-1}) than cuneane in their calculations.[11] Cubanes readily isomerize to the corresponding cuneanes by metal-ion catalyzed skeletal rearrangements.[10a]

Herein, we report the synthesis, structure, and properties of cyclotetrasilane-fused persilacuneane (**1**), which consists of sixteen silicon atoms. Compound **1** was found in the course of our study on ladder oligosilanes.[12] As shown in Equation (1), the reductive tetramerization (formation of eight Si–Si bonds during the reaction) of tetrachlorocyclotetrasilane **2**[13] with sodium gave silicon cluster **1** as air-sensitive, thermally stable orange crystals in 15 % yield. No structural isomers of **1** were found in the reaction mixture. The ^{1}H NMR spectrum of the reaction mixture showed a set of eight singlet signals from the *tert*-butyl protons of **1** together with a very broad signal around 1–2 ppm, owing to an intractable polymeric mixture. Compound **1** was sparingly soluble in common organic solvents.



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1: R = *t*Bu (15 %)

The construction of the silicon cage could be ascribed to the formation of an energetically reasonable structure by successive bond formation during the reaction. To elucidate this idea, we estimated the relative energies of two fused persilacubanes and three fused persilacuneanes (**3**-D_{2d}, **3**-D_{4d}, **4**-C_2, **4**-C_{2v}, and **4**-C_s) by theoretical calculations at the B3LYP/6-31G(d) level, as shown in Figure 1.[14] Whereas parent persilacuneane is less stable than persilacubane by 3.3 kcal mol^{-1} at the MP2/6-31G(d) + ZPE level[11] (8.3 kcal mol^{-1} at the B3LYP/6-31G(d) level),[14] **4**-C_2, a model of **1**, is the most stable among the five isomers. The introduction of cyclotetrasilane units into the silicon cluster can change the relative energies of different silicon cages.

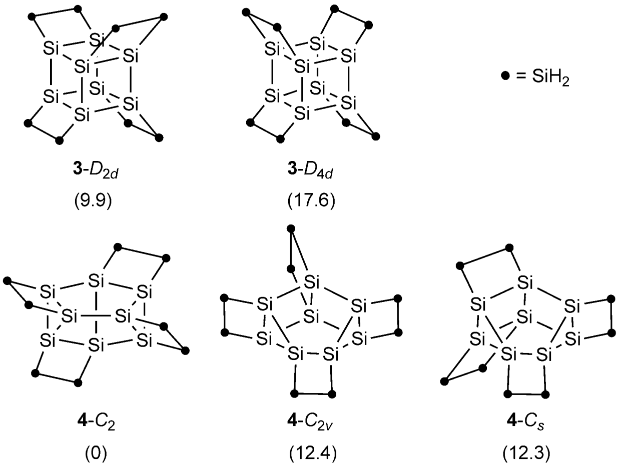

Figure 1. Relative energies (kcal mol^{-1}) of compounds **3** and **4**.

The molecular structure of **1** was determined by X-ray crystallography, as shown in Figure 2.[15] Compound **1** has crystallographic C_2 symmetry with the axis through the midpoints of the Si1–Si1* and Si5–Si5* bonds, and a well-developed network structure consisting of sixteen silicon

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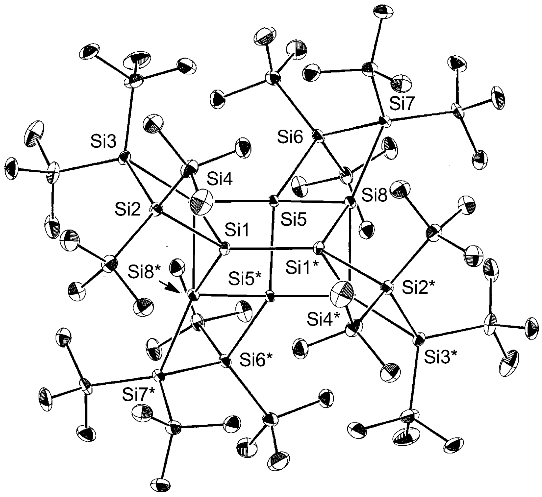


Figure 2. Molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [pm]: Si1–Si2 238.2(1), Si1–Si4 238.4(1), Si1–Si1* 238.0(2), Si1–Si8* 233.2(1), Si2–Si3 252.2(1), Si3–Si4 241.3(1), Si4–Si5 240.4(1), Si4–Si8* 235.4(1), Si5–Si6 241.8(1), Si5–Si8 236.1(1), Si5–Si5* 241.0(2), Si6–Si7 251.0(1), Si7–Si8 242.0(1).

atoms. The Si–Si bond lengths of peripheral cyclotetrasilane moieties (238.2(1)–252.2(1) pm) are slightly elongated because of steric hindrance from the *tert*-butyl groups.

Although the recently reported compound, pentasila-[1.1.1]propellane, has inverted tetrahedral silicon atoms with a significantly long bridgehead Si–Si bond (263.6(1) pm; its bonding character has been controversial)[6] the bridgehead Si–Si bond lengths of **1** (Si1–Si4 238.4(1) pm, Si5–Si8 236.1(1) pm) are within standard values.[16,17] However, the bridgehead silicon atoms (Si1, Si4, Si5, and Si8) have highly deformed trigonal monopyramidal structures, as illustrated in Figure 3. Each silicon atom has a planar structure, in which the sum of three Si–Si–Si bond angles is almost 360°. The remaining Si–Si bond is almost perpendicular to the plane in the cases of Si5 and Si8, whereas the remaining Si–Si bond is tilted to form a three-membered ring in the cases of Si1 and Si4. Similar trigonal monopyramidal silicon atoms have been found in the silicon clusters,[8,9d] tris(triisopropylsilyl)silane,[18] and unsolvated tris(di-*tert*-butylmethylsilyl)silyllithium.[19]

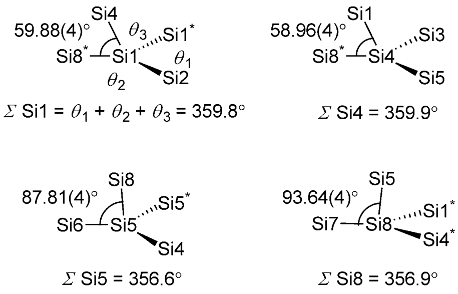


Figure 3. Geometries around the deformed silicon atoms of **1**.

Figure 4 shows the solid state ^{29}Si CP-MAS NMR spectrum of **1**. Eight signals were observed, which is consistent with the molecular structure in the solid state. These signals were essentially reproduced by GIAO calculation at the B3LYP/6-311+G(2d,p) level using the optimized structure, and can be assigned as follows: Three characteristic signals shifted upfield at −71.8, −62.4, and −56.6 ppm are due to the ^{29}Si nuclei of the cyclotrisilane rings (Si1, Si4, and Si8).[20,21] The signals at 25.0, 29.1, 35.4, and 39.0 ppm can be assigned to any of ^{29}Si nuclei of Si2, Si3, Si5, and Si6.[22,23]

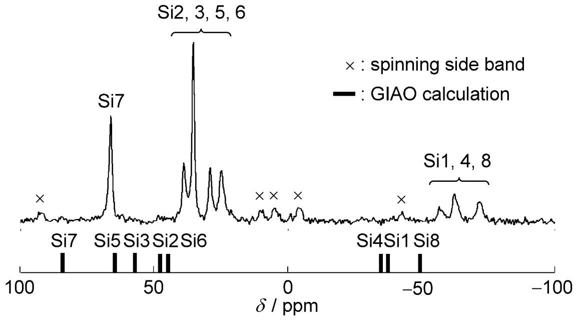
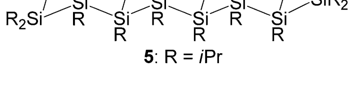


Figure 4. ^{29}Si cross polarization magic angle spinning (CP-MAS) NMR spectrum of **1** at room temperature with signals calculated by the GIAO method at the B3LYP/6-311+G(2d,p) level. Atom numbers correspond to those in Figure 2.

Notably, the ^{29}Si signal of Si7 at 66.4 ppm is shifted rather downfield. A possible explanation may be given by the large paramagnetic term (σ_p) of Si7. This term has a predominant effect on the chemical shift of ^{29}Si NMR. According to a theoretical equation,[24] σ_p is roughly inversely proportional to the averaged transition energy. The downfield shift of the ^{29}Si signal of Si7 is probably due to its contribution to the HOMO and the LUMO of **1**.

Theoretical calculations were carried out to obtain insight into the electronic characterization of **1**. Frontier orbitals are located on the silicon skeleton, indicating well-developed σ conjugation (see the Supporting Information). The major contribution of the HOMO is an out-of-phase interaction among the $\sigma_{\text{Si1–Si4}}$, $\sigma_{\text{Si1–Si8*}}$, and $\sigma_{\text{Si7*–Si8*}}$ orbitals and among the $\sigma_{\text{Si1*–Si4*}}$, $\sigma_{\text{Si1*–Si8}}$, and $\sigma_{\text{Si7–Si8}}$ orbitals. The major contribution of the LUMO consists of an out-of-phase interaction between the pseudo-π^* orbitals of two peripheral cyclotetrasilane rings (Si5-Si6-Si7-Si8 and Si5*-Si6*-Si7*-Si8* rings).

The UV/Vis spectra of **1** and our heptacyclic ladder oligosilane, iPr$_{20}$Si$_{16}$ (**5**),[25] both of which consist of sixteen silicon atoms, are compared in Figure 5. Compound **5** has well-developed σ conjugation along the long axis of the molecule and shows the lowest energy absorption as a distinctive band at 464 nm.[25] In contrast, the absorption of **1** does not show clear bands above 250 nm and tails to ca. 570 nm, except for some shoulders at 345 and 380 nm. The absorption tailing is characteristic of silicon polyhedral



5: R = iPr

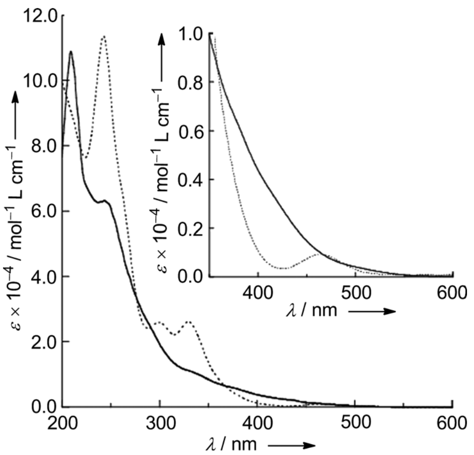


Figure 5. UV/Vis spectra of **1** in methylcyclohexane and **5** in hexane at room temperature. **1** (——), **5** (-----).

compounds: UV/Vis absorption of hexasilaprismane $(DipSi)_6$ (Dip = 2,6-diisopropylphenyl) tails to ca. 500 nm,[3] and those of octasilacubanes $(DepSi)_8$ (Dep = 2,6-diethylphenyl) and $[(t\mathrm{BuMe_2Si})\mathrm{Si}]_8$ tail to ca. 470 nm.[1c,4d] The absorption edge of **1** is remarkably red-shifted compared with those of these hexasilaprismane and octasilacubanes.

The characteristic tailing of **1** is probably due to close energy levels of molecular orbitals with a small band gap. The HOMO and the LUMO have energy levels close to other molecular orbitals, and therefore, absorption bands overlap to give a closely overlapped absorption curve without peaks. From these results, organosilicon cluster **1** may be regarded as an intermediate model between small organosilicon molecules and silicon semiconductors that have the band structures of orbitals.[26]

In summary, we have synthesized a cyclotetrasilane-fused octasilacuneane **1**, which consists of sixteen silicon atoms, by reductive tetramerization of tetrachlorocyclotetrasilane. X-ray crystallography, theoretical studies, and analysis by NMR and UV/Vis spectroscopy revealed the unique structural and electronic features of **1**, which are due to ring strain and developed σ conjugation. Investigations of the reactivity of **1** and the expansion of σ conjugation by introducing functional groups are now ongoing and will appear in the near future.

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Keywords: cluster compounds · cuneanes · organosilicon · propellanes · structure elucidation

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[13] Tetrachlorocyclotetrasilane **2** was prepared by the head-to-head reductive dimerization of 1,2-dichlorodisilane **S3** and subsequent dephenylchlorination. For details of the synthesis and X-ray crystal analyses of **1** and **2**, see the Supporting Information.

[14] We also calculated the energies of the parent cubane, cuneane, octasilacubane, and octasilacuneane at the B3LYP/6-31G(d) level. Our results were comparable to the previous report by Versteeg and Koch.[11] See the Supporting Information for details.

[15] CCDC 906219 (**S4**), 906220 (**2**), and 906221 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] The silicon skeleton of **1** contains hitherto unknown persila[3.2.1]- and [3.2.2]propellanes and spiro[3.3]- and [4.3]oligosilanes as substructures. Compound **1** also has a spiro[3.2]hexasilane moiety. Some spiro[3.2]hexasilane derivatives have been reported.[8,17d]

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