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Cyclopentasilane-Fused Hexasilabenzvalene

Akihiro Tsurusaki, Chisato Iizuka, Kyohei Otsuka, and Soichiro Kyushin*

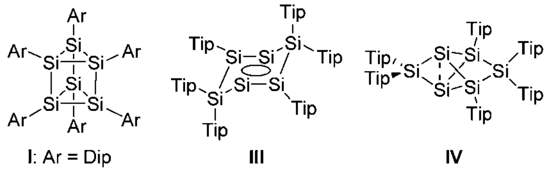
Division of Molecular Science, Faculty of Science and Technology, Gunma University, Kiryu, Gunma 376-8515, Japan

Supporting Information

ABSTRACT: Cyclopentasilane-fused hexasilabenzvalene **1** was synthesized by the reduction of tetrachlorocyclopentasilane **6** in 19% yield as a green powder. The molecular structure and properties of **1** were studied by spectroscopic and X-ray crystallographic analyses. Theoretical calculations of the model and real molecules of **1** and their structural isomers **12−16** suggest that the linkage of the central hexasilabenzvalene moiety with trisilane chains and the introduction of *tert*-butyl groups affect their relative energies.

Benzene has been known as the most stable compound among more than 200 isomers of C_6H_6.[1] The C_6H_6 isomers have fascinated chemists for a long time. Benzvalene[2] is a valence isomer of benzene and is of considerable interest together with other isomers, such as Dewar benzene,[3a] prismane,[3b] and bicyclopropenyl.[3c] Silicon analogues of these compounds are also synthetic targets in organosilicon chemistry. In recent years, much attention has been given to the structural isomers of Si_6R_6, including hexasilabenzene, from both experimental[4−7] and theoretical viewpoints.[8] Until now, there have been few reports on the synthesis and characterization of Si_6R_6 isomers (Scheme 1). Sakurai, Sekiguchi, and coworkers isolated 2,6-diisopropylphenyl-substituted hexasilaprismane **I** in 1993.[4] Very recently, Scheschkewitz and co-workers synthesized 2,4,6-triisopropylphenyl-substituted hexasilaprismane **II**.[5] They also reported the chairlike Si_6 siliconoid **III**[6] and the [1.1.1]propellane-like Si_6 siliconoid **IV**.[7] So far, hexasilabenzvalene, which consists of disilene[9] and bicyclo[1.1.0]tetrasilane[10] moieties, remains elusive although 2-silabenzvalene,[11] 2,5-disilabenzvalene,[12] and 1,2,5,6-tetrasilabenzobenzvalene[13] have been reported. Recent theoretical calculations of Si_6H_6 demonstrated that the isomer with the structure of **IV** is the most stable, and hexasilabenzvalene, hexasilaprismane, and hexasilabenzene are 32.7, 31.5, and 36.0 kcal mol^{-1} higher in energy at the B3LYP/6-311G** level.[8c]

Scheme 1. Isolated Si_6R_6 Isomers I−IV

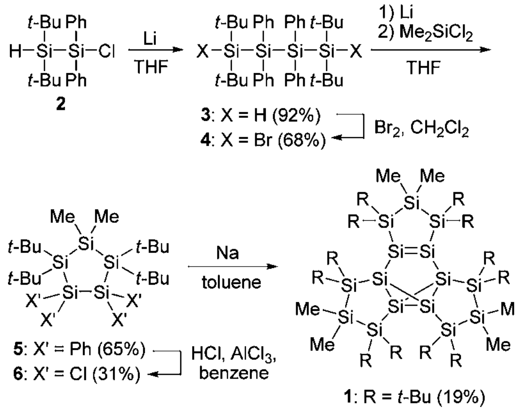


Dip = 2,6-(i-Pr)$_2$C$_6$H$_3$, Tip = 2,4,6-(i-Pr)$_3$C$_6$H$_2$

We recently reported the synthesis of cyclotetrasilane-fused octasilacuneane by the reductive tetramerization of tetrachlorocyclotetrasilane.[14] Octasilacuneane was a missing silicon cage motif in contrast to isomeric octasilacubane.[15] Theoretical calculations demonstrated that the linkage of the octasilacuneane framework with disilane chains changes the relative energies of octasilacubane and octasilacuneane. If tetrachlorocyclopentasilane were used as a precursor instead of tetrachlorocyclotetrasilane, the larger steric hindrance of the precursor would lead to trimerization to give a different type of the Si_6R_6 isomer. We report herein the synthesis, structure, and properties of cyclopentasilane-fused hexasilabenzvalene **1**, which was obtained by reductive trimerization of tetrachlorocyclopentasilane.

The synthetic route to **1** is outlined in Scheme 2. Bromination of dihydrotetrasilane **3**, which was obtained by the Wurtz-type coupling of chlorosilane **2**, gave dibromotetrasilane **4**. Reaction of **4** with lithium powder followed by addition of dichlorodimethylsilane afforded cyclopentasilane **5**. Chlorodephenylation of **5** with hydrogen chloride and aluminum chloride gave tetrachlorocyclopentasilane **6**. Finally, reduction of **6** with 4 equiv of sodium dispersion in toluene under reflux for 1 h gave **1** in 19% yield as a green powder, which becomes purple in crystals (Figure S28). The structure of **1** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectra, a high-resolution mass spectrum, and X-ray crystallography.[16] It is stable below 217 °C in the solid state under an argon atmosphere in a sealed tube and in refluxing toluene under an argon atmosphere, although **1** underwent decomposition in air

Scheme 2. Synthesis of 1



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in a few minutes to give an unidentified mixture. It is also stable on exposure to room light under an argon atmosphere.[17]

X-ray crystallographic analysis of **1** showed the hexasilabenzvalene moiety with three fused cyclopentasilane rings (Figure 1).[18] The Si−Si bond lengths of the peripheral cyclopentasilane moieties (2.362(2)−2.425(2) Å) are somewhat longer than those of the hexasilabenzvalene moiety (2.212(2)−2.368(2) Å).[19] The Si3−Si4 bond length (2.212(2) Å) is much shorter than the others, and it lies within the range of values of the reported tetrasilyldisilenes (2.180(3)−2.2598(18) Å),[9] indicating the double-bond character of the Si3−Si4 bond. In addition, **1** exhibits an unusual disilene geometry: (1) The Si3 and Si4 atoms show somewhat pyramidal structures with the sum of the three Si−Si−Si bond angles of 349.5 and 352.2°, respectively, in contrast to planar geometries of tetrasilyldisilenes (358.4−360°).[9] They also show (2) large *trans*-bent angles[20] (42.5° for Si3 and 36.5° for Si4) and (3) a large twist angle (16.2°).[21] These unique features are due to the fusion of the hexasilabenzvalene moiety with the cyclopentasilane rings and the introduction of *tert*-butyl groups on the cyclopentasilane rings (Table S3).[22] In fact, the Si10−Si3−Si4−Si12 torsion angle is 45.72(9)°, which is much larger than that observed in tetrachlorocyclopentasilane **6** (27.22(3) and 27.56(3)°, Figure S30).

The bridgehead Si1−Si6 bond length of **1** is 2.319(2) Å, which is shorter than those of hexasilylbicyclo[1.1.0]tetrasilane **7** (2.367(1) Å),[10e] 1,2,5,6-tetrasilabenzobenzvalene **8** (2.3462(14) Å),[13] and silicon clusters **9** (2.3430(9) and 2.3373(8) Å),[23] **10** (2.392(2) and 2.393(2) Å),[24] and **11** (2.357(10) and 2.362(9) Å) (Chart 1).[24b] The interflap angle[25] (110.07(8)°) is also smaller than that of **7** (129.25(4)°).[10e] Therefore, it is concluded that the bicyclo[1.1.0]tetrasilane moiety of **1** has the character of a short-bond isomer.[26]

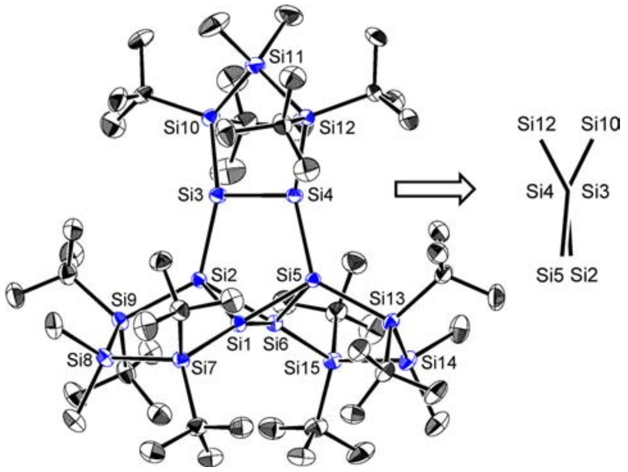
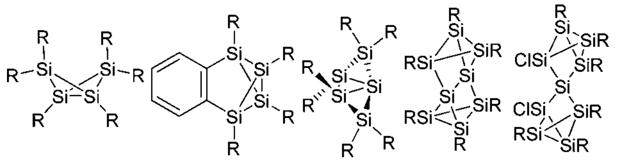


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Si2 2.360(2), Si1−Si5 2.351(2), Si1−Si6 2.319(2), Si2−Si3 2.357(2), Si2−Si6 2.359(2), Si3−Si4 2.212(2), Si4−Si5 2.349(2), Si5−Si6 2.368(2); Si2−Si3−Si4 104.32(7), Si2−Si3−Si10 140.99(7), Si4−Si3−Si10 104.16(7), Si3−Si4−Si5 104.09(7), Si3−Si4−Si12 106.74(7), Si5−Si4−Si12 141.40(7), Si6−Si1−Si7 148.32(7), Si1−Si6−Si15 146.52(7).

It is also noted that the Si1, Si2, Si5, and Si6 atoms exhibit deformed trigonal monopyramidal structures: the sums of the three Si−Si−Si bond angles of Si1, Si2, Si5, and Si6 are 358.0, 359.7, 359.5, and 357.7°, respectively (Figure S29). Similar structures have been reported in tris(triisopropylsilyl)silane,[27] unsolvated tris(di-*tert*-butylmethylsilyl)silyllithium,[28] and silicon clusters.[5,14,24]

Chart 1



7 8 9 10 11

R = SiMe$_2$(*t*-Bu) R = SiMe(*t*-Bu)$_2$ R = Tip R = Si(*t*-Bu)$_3$ R = Si(*t*-Bu)$_3$

In the ^{1}H and ^{13}C NMR spectra of **1**, three and six sets of signals assignable to methyl and *tert*-butyl signals were observed, respectively, indicating the C_2 symmetrical structure of **1** in solution. Although the ^{29}Si signals of only the peripheral silicon atoms (Si7−Si15 of Figure 1) were observed in the ^{29}Si NMR spectrum with the DEPT technique, the correlation between the ^{29}Si signals of the hexasilabenzvalene moiety and some of the *tert*-butyl signals was clearly observed in the 2D ^{29}Si/^{1}H correlation NMR spectra (Figure S4). A total of eight signals were observed, which is consistent with the structure of **1**. These signals were assigned with the aid of the GIAO calculations of **1**.[29] The signal of the disilene moiety was observed at 187.3 ppm, which is in the downfield region compared with those of the previously reported tetrasilyldisilene (132.4−167.4 ppm).[9] The signal at −54.2 ppm, assignable to the bridgehead silicon atoms of the bicyclo[1.1.0]tetrasilane moiety, is considerably downfield compared to those of **7** (−145.1 ppm)[10e] and **8** (−130.4 ppm).[13] On the other hand, the chemical shift of the bridge silicon signal of **1** (δ −84.6) is comparable to those of **7** (−90.6 ppm)[10e] and **8** (−92.2 ppm).[13] The characteristic downfield shifts may be caused by both the linkage of the bridge silicon atoms with the Si═Si bond and the fusion with the cyclopentasilane rings.[30] There are a few reports on the unusual ^{29}Si chemical shifts found in silicon clusters.[5,7,14,23,31]

In the UV−visible spectrum of **1** (Figure 2), a complicated absorption tailing around 650 nm was observed. The lowest energy absorption band at 585 nm (ε 1140) is assignable to the HOMO−LUMO transition based on the TD-DFT calculations (λ_{calcd} = 571.4 nm, f = 0.0129), where the HOMO and the LUMO exhibit the dominant contribution of the Si═Si π and π^* orbitals together with some contribution of the σ and σ^*

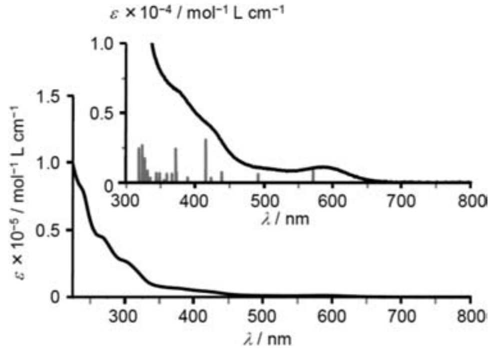
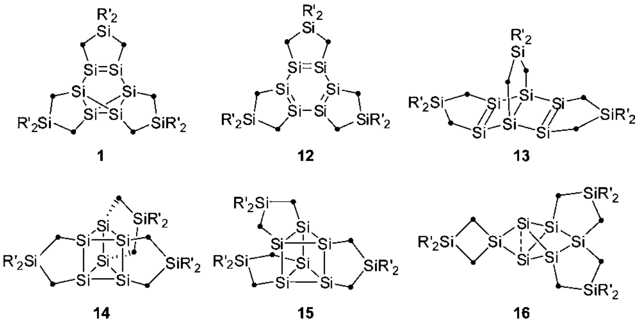


Figure 2. UV−visible spectrum of **1** in hexane at room temperature with transitions calculated at the B3LYP/6-31+G(2d,p) level (gray bars).

orbitals of bicyclo[1.1.0]tetrasilane, respectively (Figure S34).[32] This absorption band is in the longer wavelength region than those of silyl-substituted cyclic disilenes (λ_{max} = 448−482 nm)[9,33] and comparable to that of tetrakis(di-*tert*-butylmethylsilyl)disilene (λ_{max} = 612 nm).[34] The considerable bathochromic shift in **1** may be due to the interaction between the Si═Si π orbital and the σ orbitals of the bicyclo[1.1.0]-tetrasilane moiety together with the twisting of the Si═Si moiety. The calculated transitions at 491.5 (f = 0.0088) and 438.6 nm (f = 0.0106) are assigned to the HOMO−1 to LUMO and HOMO to LUMO+1 transitions, respectively. The relatively large absorption at 423 nm (λ_{calcd} = 415.4 nm, f = 0.0440) is due to the mixing of the HOMO−2 to LUMO and HOMO to LUMO+2 transitions. The molecular orbitals from the HOMO−1 to the HOMO−3 and from the LUMO+1 to the LUMO+3 consist of the σ orbitals of the bicyclo[1.1.0]-tetrasilane and peripheral rings (Figure S34). Therefore, the Si═Si π and π* orbitals and the Si−Si σ and σ* orbitals participate in the transitions.

To obtain further insight into the formation of **1**, theoretical calculations were carried out for both model (**a**,**b**) and real molecules (**c**) of cyclopentasilane-fused Si_6 isomers (hexasilabenzvalene **1**, hexasilabenzene **12**, Dewar hexasilabenzene **13**, two types of hexasilaprismanes **14** and **15**, and the global minimum structure of type IV, **16**). The relative energies are summarized in Table 1. In the model compounds with hydrogen (**a**) and methyl (**b**) substituents, **16a**,**b** are the most stable. Also, **12a**,**b** and **15a**,**b** are more stable than **1a**,**b**. It is noted that the differences among the relative energies of **16** and the others are small compared to those of Si_6H_6 (**d**).[35] The trend of the relative energies is drastically changed when the *tert*-butyl groups are introduced probably due to the steric hindrance of *tert*-butyl groups. Hexasilabenzvalene **1** (= **1c**) is the most stable among them, supporting the experimental results. Therefore, the fusion of the hexasilabenzvalene moiety with cyclopentasilane rings and the introduction of bulky *tert*-butyl groups promote the formation of hexasilabenzvalene **1**.

Table 1. Relative Energies (kcal mol^{-1}) of Cyclopentasilane-Fused Si_6 Isomers 1 and 12−16 Calculated at the B3LYP/6-31G(d) Level



• = SiR_2; **a**: R = R' = H, **b**: R = R' = Me, **c**: R = *t*-Bu, R' = Me

compd	**a**: R = R′ = H	**b**: R = R′ = Me	**c**: R = *t*-Bu, R′ = Me	**d**: Si_6H_6
1	0	0	0	0
12	−2.0	−6.3	12.2	−1.8
13	13.4	9.9	7.4	4.1
14	6.6	5.3	3.0	−7.5
15	−1.2	−3.5	19.0	–
16	−8.3	−10.4	29.2	−37.2

In summary, we have succeeded in the synthesis of cyclopentasilane-fused hexasilabenzvalene **1** by the reductive trimerization of tetrachlorocyclopentasilane **6**. Spectroscopy, X-ray crystallography, and DFT studies of **1** revealed the unique structure and properties of **1**, such as the highly strained silicon skeleton with the Si═Si and bicyclo[1.1.0]tetrasilane moieties and well-developed σ- and π-conjugations in the three-dimensional silicon cluster. Furthermore, theoretical calculations showed that the fusion of the hexasilabenzvalene moiety with cyclopentasilane rings and the introduction of *tert*-butyl groups bring about drastic changes in the relative energies of the Si_6R_6 isomers. The combination of these strategies provides the possibility of constructing silicon clusters with unknown skeletons. Further studies on the synthesis of such molecules are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the synthesis of **1**, X-ray crystallographic data for **1** and **6**, and theoretical calculations of **1** and **12**−**18**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

kyushin@gunma-u.ac.jp

Notes

The authors declare no competing financial interest.

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(16) Spectral data for **1**. Mp (under an argon atmosphere in a sealed tube): 217 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, 60 °C): δ 0.72 (s, 6H), 0.75 (s, 6H), 0.80 (s, 6H), 1.24 (s, 18H), 1.31 (s, 18H), 1.45 (s, 36H), 1.51 (s, 36H). ^{13}C NMR (151 MHz, C_6D_6, 60 °C): δ 5.8, 6.3, 7.2, 23.0, 24.2, 24.3, 24.9, 25.2, 26.8, 31.9, 32.2, 32.6, 33.0, 33.3, 33.7. ^{29}Si NMR (119 MHz, C_6D_6, 60 °C): δ −84.6, −54.2, −21.4, −14.5, 10.9, 16.5, 17.8, 187.3. UV−visible (hexane): λ_{max} 585 (ε 1140), 423 (sh, 4060), 378 nm (sh, 6500). HRMS (APCI): found 1194.63945 (M^+), calcd for $C_{54}H_{126}Si_{15}$ 1194.63930.

(17) Irradiation of **1** in a 3-methylpentane matrix at 77 K with a high-pressure mercury lamp with a filter (λ > 350 nm) was carried out. The UV−visible spectrum showed that only a small part (ca. 5%) of **1** decomposed after 1 h, but a new absorption band was not observed.

(18) For details, see the Supporting Information.

(19) Similar difference between the central and peripheral Si−Si bond lengths has been reported in cyclotetrasilane-fused octasilacuneane. See ref 14.

(20) A *trans*-bent angle for disilene $R_2Si{=}SiR_2$ is defined as the angle between the R_2Si plane and the Si═Si axis.

(21) A twist angle for disilene $R_2Si{=}SiR_2$ is defined as the angle between two R_2Si planes.

(22) Theoretical calculations of the model compounds indicate that the fusion of the hexasilabenzvalene moiety with the cyclopentasilane rings affects the twist angle, and the introduction of *tert*-butyl groups changes *trans*-bent angles and the sum of the bond angles. See the Supporting Information.

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(25) An interflap angle is defined as the dihedral angle between two three-membered rings.

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(29) The GIAO calculation of **1** at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level shows the ^{29}Si chemical shifts of the bridge and bridgehead silicon atoms of the bicyclo[1.1.0]tetrasilane moiety of **1** at −69.4 and −20.9 ppm, respectively. See the Supporting Information.

(30) The calculated ^{29}Si chemical shift of the bridgehead silicon atoms of hexakis(trimethylsilyl)hexasilabenzvalene (**17b**) at −75.6 ppm is in the middle of **1** at −20.9 ppm and the calculated hexakis(trimethylsilyl)bicyclo[1.1.0]tetrasilane (**18**) at −140.6 ppm. See the Supporting Information.

(31) Ito, Y.; Lee, V. Ya.; Gornitzka, H.; Goedecke, C.; Frenking, G.; Sekiguchi, A. *J. Am. Chem. Soc.* **2013**, *135*, 6770.

(32) For details of the molecular orbitals of **1**, see the Supporting Information.

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(35) Our results of the relative energies of the Si_6H_6 isomers calculated at the B3LYP/6-31G(d) level are comparable to the previous results. See ref 8.