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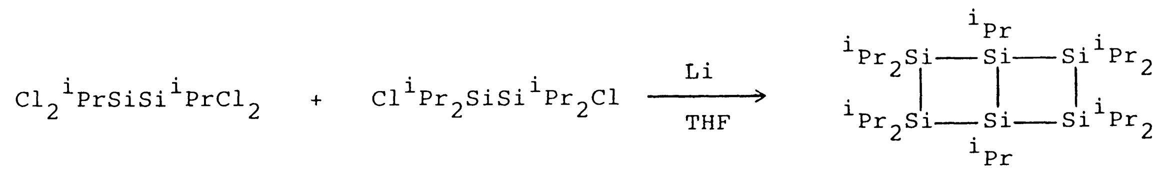
X-Ray Structure Analysis of a Bicyclo[2.2.0]hexasilane, Decaisopropylhexasilabicyclo[2.2.0]hexane

Hideyuki MATSUMOTO,* Hiroshi MIYAMOTO, Nobumoto KOJIMA, Yoichiro NAGAI,*
and Midori GOTO*†
Department of Chemistry, Gunma University, Kiryu, Gunma 376
†National Chemical Laboratory for Industry, Yatabecho, Tsukuba, Ibaraki 305

The X-ray analysis disclosed that the title compound has a cis-fused structure. The bicyclic skeleton is twisted and has C_2 symetry; the puckering of each four-membered ring is 21.8°. The central Si-Si bond distance, 239.6 pm, is comparable to those found for the peripheral Si-Si bonds, which range from 238.5 to 242.6 pm.

Bicyclopolysilanes consisting of small and strained rings are of considerable interest, since the annelated frameworks of silicon atoms are expected to exhibit unusual and even unprecedented physical and chemical properties. Recently, we found that a bicyclo[2.2.0]hexasilane, decaisopropylhexasilabicyclo[2.2.0]hexane (**1**), can be synthesized by the co-condensation of 1,1,2,2-tetrachlorodi-isopropyldisilane and 1,2-dichlorotetraisopropyldisilane with lithium (Eq. 1).¹⁾ This



1 (1)

compound is the first example of bicyclo[2.2.0]hexane structure based on the catenation of silicon atoms.²⁾ We report here the X-ray crystallography of **1**, which represents the first structure determination of a bicyclo[2.2.0]hexasilane system.³⁾

Single crystals of **1** were obtained by quite a slow evaporation of the solvent from an acetone solution at room temperature. They belong to monoclinic system, space group C2/c with cell constants a = 1063.3(2), b = 1803.5(5), c = 2049.7(5) pm, β = 94.36(2)°, V = 3.9229 X 10^{10} pm^3, and Z = 4.[4]

The molecular structure of 1 is illustrated in Fig. 1, which shows that the molecule has a cis-fused structure. There are several interesting features. The bicyclic skeleton is twisted and has C_2 symmetry with the two-fold axis of symmetry passing through the midpoint of the the central Si-Si bond;[5] the torsion angles (absolute values) for Si(2)-Si(1)-Si(1')-Si(3) and C(1)-Si(1)-Si(1')-C(1') are 15.2° and 14.8°, respectively. The extent of the puckering for each four-membered ring is gauged by the dihedral angle of 21.8° between the Si(1)-Si(2)-Si(3) and Si(3)-Si(1')-Si(1) planes.[6] By comparison, carbon analogue, bicyclo[2.2.0]hexane (2), has the puckering angle of 11.5°.[7] Furthermore, it is interesting to note that the observed dihedral angle in 1 is significantly smaller than that of the ring in the monocycle, octaisopropylcyclotetrasilane(3), where the corresponding angle is as large as 37.1°.[8] This may be the result of a compromise between a tendency to pucker, which alleviates isopropyl-isopropyl eclipsing interaction, and the steric constraint imposed by the cis fusion of the four-membered rings.

The central Si-Si bond distance (239.6 pm) falls into the longer range of the reported values for cyclopolysilanes (e.g., 237.3 pm in 3).[8,9] It is, however, worthy to note that the distance of this particular bond is comparable to those found for the peripheral Si-Si bonds which range between 238.5 and 242.6 pm (average value 240.1 pm)(Table 1).[10] This bonding pattern is contrast to carbon system 2, where the central bond is longer than the peripheral bonds (157.7 vs. 154.2-155.7 pm) (by electron diffraction).[7] Also noteworthy is the fact that the Si-Si-Si bond angles in the Si_4 ring vary from 87.2° to 90.6°, compared to monocycle 3 where all the Si-Si-Si bond angles are equal (87.0°).[8] The observed variation presumably reflects the steric congestion induced by accomodating six isopropyl groups around the fused Si_6 ring.

The packing scheme (Fig. 2) shows that molecules stack along b axis with high symmetry. An analysis of the crystal structure reveals that most of the intermolecular distances are more than the terminal methyl-methyl van der Waals contact distance of 400 pm. Therefore, crystal packing forces may have virtually little influence on the molecular geometry of 1.

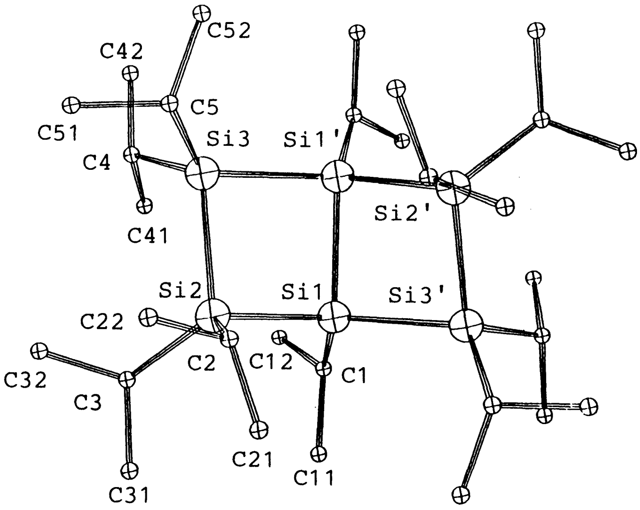


Fig. 1. Molecular Structure of **1**.

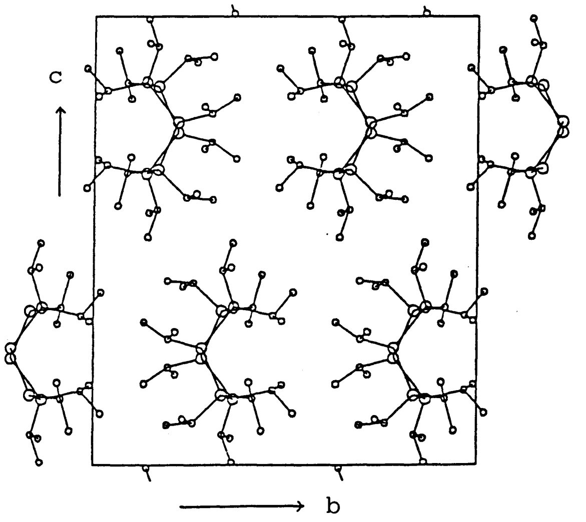


Fig. 2. Packing in **1**.

Table 1. Selected Interatomic Distances (pm) and Angles (°) for **1**

Si(1)-Si(1')	239.6(2)	Si(1)-Si(2)	242.6(2)	Si(2)-Si(3)	239.1(2)
Si(3)-Si(1')	238.5(2)	Si(1)-C(1)	191.4(9)	Si(2)-C(2)	190.3(8)
Si(2)-C(3)	191.3(7)	Si(3)-C(4)	191.7(7)	Si(3)-C(5)	190.8(7)
C(1)-C(12)	150(1)	C(2)-C(21)	152(1)	C(2)-C(22)	158(1)
C(3)-C(31)	153(1)	C(3)-C(32)	154(1)	C(1)-C(1')	457(1)
Si(1')-Si(1)-Si(2)	87.2(1)			Si(1)-Si(2)-Si(3)	89.8(1)
Si(2)-Si(3)-Si(1')	88.3(1)			Si(3)-Si(1')-Si(1)	90.6(1)
Si(1')-Si(1)-C(1)	124.4(3)			Si(1)-Si(2)-C(2)	114.4(2)
Si(1)-Si(2)-C(3)	112.9(2)			Si(3)-Si(2)-C(2)	110.9(3)
Si(3)-Si(2)-C(3)	115.3(2)			Si(1')-Si(3)-C(4)	112.3(2)
Si(1')-Si(3)-C(5)	120.0(2)			C(11)-C(1)-C(12)	116.5(2)
C(21)-C(2)-C(22)	108.7(7)			C(31)-C(3)-C(32)	109.1(1)
Si(2)-Si(1)-Si(3')	119.2(1)				

Table 2. Fractional Atomic Coordinates (X 10^4) and Equivalent Temperature Factors ($Å^2$) for **1**

atom	x	y	z	B(eq)	atom	x	y	z	B(eq)
Si(1)	1120(2)	2820(1)	2617(1)	3.72(4)	C(12)	1585(10)	1315(6)	3190(6)	10.4(4)
Si(2)	786(2)	3645(1)	3522(1)	3.89(4)	C(21)	2354(11)	4900(6)	3216(5)	11.5(4)
Si(3)	-1403(2)	3331(1)	3435(1)	3.89(4)	C(22)	515(9)	5194(5)	3839(6)	10.3(4)
C(1)	2106(8)	1951(5)	2820(5)	8.0 (3)	C(31)	3091(8)	3567(7)	4393(4)	9.8(4)
C(2)	1020(8)	4668(4)	3336(4)	6.8 (2)	C(32)	1062(8)	3601(6)	4935(3)	8.5(3)
C(3)	1695(7)	3349(4)	4321(3)	5.9 (2)	C(41)	-945(9)	1924(5)	4097(4)	7.4(3)
C(4)	-1817(7)	2590(4)	4054(3)	5.6 (2)	C(42)	-3190(8)	2331(5)	3971(4)	7.5(3)
C(5)	-2516(7)	4150(4)	3516(3)	5.3 (2)	C(51)	-2635(9)	4378(5)	4233(4)	8.6(3)
C(11)	3491(8)	2133(6)	2977(4)	8.6 (3)	C(52)	-3841(7)	4050(5)	3158(4)	7.4(3)

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2) Recently, Masamune et al. prepared a bicyclo[1.1.0]tetrasilane, 1,3-di-tert-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]butane, and determined its molecular structure, see: S. Masamune, Y. Kabe, S. Collins, D. J. Williams, and R. Jones, J. Am. Chem. Soc., 107, 5552 (1985); R. Jones, D. J. Williams, Y. Kabe, and S. Masamune, Angew. Chem., Int. Ed. Engl., 25, 173 (1986). For the synthesis of bicyclopolysilanes consisting of the medium rings (e.g., Si_5, Si_6, and Si_7 rings), see: (a) R. West and A. Indriksons, J. Am. Chem. Chem. Soc., 94, 6110 (1972); (b) M. Ishikawa, M. Watanabe, J. Iyoda, H. Ikeda, and M. Kumada, Organometallics, 1, 317 (1982).

3) Presented in part at 8th International Symposium on Organosilicon Chemistry, 7-12, June, 1987, St. Louis, Abstract No. B34.

4) Intenisty data ($2\theta_{max}$ 55°) were recorded on a Rigaku-Denki four-circle diffractometer (AFC-4) using graphite monochromated Mo-$K\alpha$ radiation and the ω-θ technique. 2850 unique reflections with $F > 3\sigma(|F_o|)$ were observed. The structure was solved by direct methods using Multan 78.[11] The hydrogen atoms were placed at calculated positions assuming a C-H bond distance of 110 pm and tetrahedral arrangement around carbon; terminal hydrogen atoms were assumed to be in gauche positions. Refinement by block-diagonal least-squares using the UNICS III program[12] with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for the hydrogen atoms led to R = 0.073.

5) The parent compound, bicyclo[2.2.0]hexasilane, has been found to be a minimum in C_{2v} symmetry with an central Si-Si bond distance of 239.9 pm and peripheral Si-Si bond distance of 238.0 pm using HF/6-31G* basis set (S. Nagase and T. Kudo, private communication).

6) The dihedral angle between Si(2)-Si(3)-Si(1') and Si(2)-Si(1)-Si(1') is 21.4°.

7) B. Anderson and R. Srinivasan, Acta. Chem. Scand., 26, 3468 (1972).

8) H. Watanabe, M. Kato, T. Okawa, Y. Kougo, Y. Nagai, and M. Goto, Appl. Organomet. Chem., 1, 157 (1987).

9) M. Weidenbruch, K.-L. Thom, S. Phol, and W. Saak, J. Organomet. Chem., 329, 151 (1987).

10) The result seems to be consistent with the observation that the central Si-Si bond is stable against the attacking reagents such as oxygen and water.[1]

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