Strain and Structures in the Silicon Analogues of Tetrahedrane, Prismane, and Cubane. A Theoretical Study

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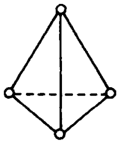
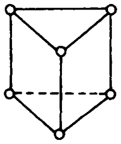
Ab initio calculations show that the strain energies of the silicon compounds, unlike the carbon case, decrease in the order tetrasilatetrahedrane > hexasilaprismane > octasilacubane, octasilacubane being markedly less strained than cubane.

Polyhedral alkanes $(CH)_n$ such as tetrahedrane (**1b**), prismane (**2b**), and cubane (**3b**) have long been of experimental[1] and theoretical[2] interest in view of their high strain, unusual geometries, and the fact that they form fascinating synthetic targets. There is currently growing interest in the preparation and characterization of the corresponding silicon compounds $(SiH)_n$. We have shown[3] that hexasilaprismane (**2a**) is a minimum on the Si_6H_6 potential energy surface and is the most stable valence isomer, this being in sharp contrast with the fact that in the carbon system prismane is much more unstable than the C_6H_6 isomers such as benzene, Dewar benzene, and benzvalene. In addition, Clabo and Schaefer have shown[4] that tetrasilatetrahedrane (**1a**) is a local minimum on the Si_4H_4 potential energy surface and may be experimentally observed.

We report here the first *ab initio* calculation for octasilacubane (**3a**) and compare the structures and ring strain of (**1**)—(**3**) at the same level of theory. Geometries were fully optimized at the Hartree–Fock (HF) level with the polarized 6–31G* basis set,[5] as shown in Figure 1. For comparison, we have also performed calculations on cyclotrisilane (**4a**) and cyclotetrasilane (**5a**), derivatives of which have been synthesized and isolated,[6] the silicon analogues of cyclopropane (**4b**) and cyclobutane (**5b**); see Figure 2.


(**1**)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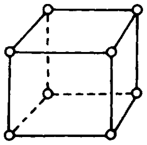
(**3**)

a; o = SiH, b; o = CH

As Figure 1 shows, (**1a**)—(**3a**) have equilibrium structures with T_d, D_{3h}, and O_h symmetry, respectively, as do the carbon compounds. The Si–Si bond lengths increase in the order (**1a**) (2.314 Å) < (**2a**) (2.359 and 2.375 Å) < (**3a**) (2.396 Å). Comparison of Figures 1 and 2 shows a general trend; the Si–Si bond lengths in the three-membered rings are shorter than the typical Si–Si single bond length of 2.352 Å in disilane, while those in the four-membered rings are longer. In addition, it is interesting that the Si–Si bond lengths in the three-membered rings become shorter in (**1a**) than in (**4a**), while those in the four-membered rings become longer in (**3a**) than in (**5a**). Thus, (**1a**) and (**3a**) have the shortest and longest Si–Si bond lengths, respectively, difference in these two bond lengths being as large as 0.082 Å.

Table 1 summarizes the strain energies of (**1**)—(**3**) calculated from the isodesmic (i) and homodesmic (ii) reactions,[1,7,8] where X = Si or C. The calculated strain energies of the carbon compounds from the homodesmic reaction (*i.e.*, the more severe matching of hybridization and bonding characteristics) agree well with the experimentally evaluated values.[9] Thus, comparable accuracy would be expected for the calculated values of the silicon compounds. As Table 1 shows, silicon (**1a**) and carbon (**1b**) compounds have almost equal ring strain. As the number of four-membered rings in the compounds increases, however, the strain is decreased in silicon compounds and increased in carbon compounds. Thus, (**2a**) is 32 kcal/mol less strained than (**2b**). It is particularly

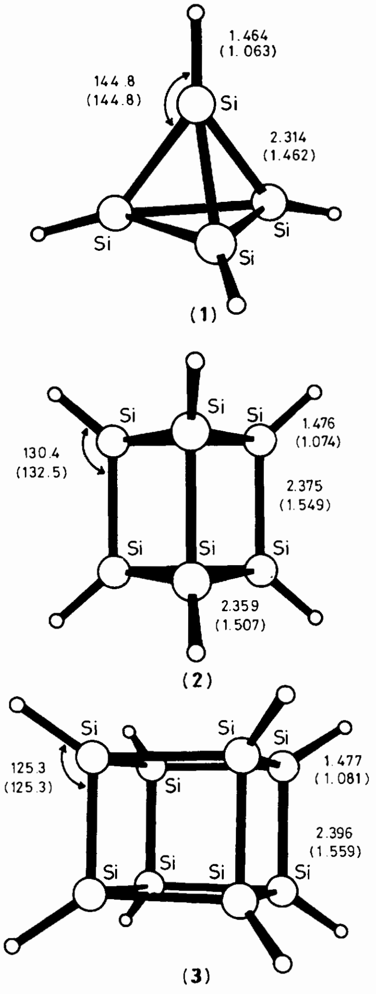

Figure 1. The HF/6–31G* optimized geometries of (**1**) (T_d), (**2**) (D_{3h}), and (**3**) (O_h) in Å and degrees. The values in parentheses are for the carbon compounds. The total energies of (**1**)—(**3**) are −1157.82123 (−153.59789), −1736.88739 (−230.50328), and −2315.94264 (−307.39391) Hartrees, respectively.

Table 1. Strain energies (kcal/mol; 1 cal = 4.184 J) calculated from isodesmic and homodesmic reactions at the HF/6–31G* level.[a]

Compound	Isodesmic	Homodesmic	Exp.[b]
(**1**) (T_d)	130.7 (133.7)	140.9 (141.4)	(140.0)
(**2**) (D_{3h})	98.4 (134.0)	113.8 (145.3)	
(**3**) (O_h)	73.0 (143.2)	93.5 (158.6)	(154.7)
(**4**) (D_{3h})	36.2 (26.3)	38.9 (28.7)	(27.5)
(**5**) (D_{2d})[c]	13.1 (23.3)	16.7 (26.7)	(26.5)

[a] Values in parentheses are for the carbon compounds. [b] Taken from ref. 9. [c] The square D_{4h} structures of (**5a**) and (**5b**) have one imaginary frequency and are 0.7 and 0.9 kcal/mol higher in energy, respectively.

noteworthy that the strain energy of the cubic (**3a**) is 65 kcal/mol smaller than that of (**3b**).

$$(XH)_n + 2nXH_4 \rightarrow (3n/2)H_3X\text{–}XH_3 \quad \text{(i)}$$
$$(XH)_n + (3n/2)H_3X\text{–}XH_3 \rightarrow n(XH_3)_3XH \quad \text{(ii)}$$

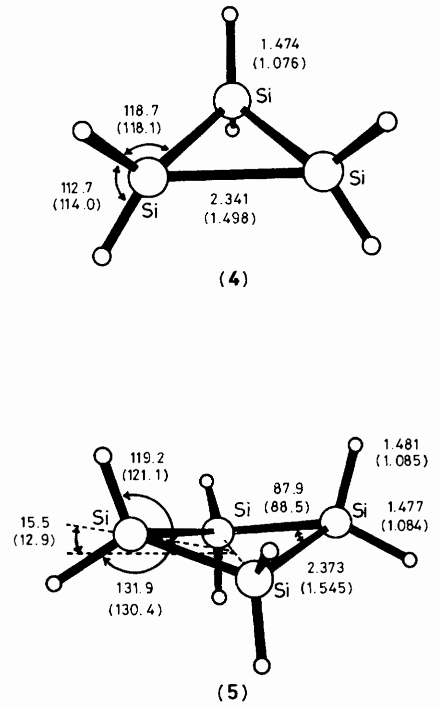

Figure 2. The HF/6–31G* optimized geometries of (**4**) (D_{3h}) and (**5**) (D_{2d}) in Å and degrees. The values in parentheses are for the carbon compounds. The total energies of (**4**) and (**5**) are −870.18218 (−117.05887) and −1160.29894 (−156.09720) Hartrees, respectively.

Table 1 also gives the strain energies of the monocyclic (**4**) and (**5**) calculated from the isodesmic (iii) and homodesmic (iv) reactions. Schoeller and Dabisch[10] have recently calculated from the isodesmic reaction that (**4a**) is as strained as (**4b**), and (**5a**) is almost free of strain. As Table 1 shows, this differs† significantly from our finding that (**4a**) is 10 kcal/mol more strained than (**4b**), and (**5a**) possesses the considerable strain of 17 kcal/mol. However, agreement is seen in the fact that the four-membered silicon ring in (**5a**) is less strained than the corresponding carbon ring in (**5b**).

$$(XH_2)_n + nXH_4 \rightarrow nH_3X\text{–}XH_3 \quad \text{(iii)}$$
$$(XH_2)_n + nH_3X\text{–}XH_3 \rightarrow nH_3X\text{–}XH_2\text{–}XH_3 \quad \text{(iv)}$$

The strain energies of the cubic (**3a**) (93.5 kcal/mol) and (**3b**) (158.6 kcal/mol) may be considered to represent the sum of the strains of six four-membered rings, *i.e.*, 15.6 kcal/mol per silicon ring and 26.4 kcal/mol per carbon ring. In fact, these two values per ring are comparable to the strain energies of (**5a**) (16.7 kcal/mol) and (**5b**) (26.7 kcal/mol), respectively. However, such additivity does not hold well in other compounds.

In conclusion, we think that the cubic silicon skeleton could be the most successful target for syntheses related to the current interest in polyhedral silicon compounds.

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† From the isodesmic energies calculated at the lower HF/3–21G level, however, we have also obtained trends similar to those reported by Schoeller and Dabisch.[10] The less sophisticated isodesmic energies are more sensitive to the levels of calculation.

All calculations were carried out at the Computer Center of the Institute for Molecular Science, by using the GAUSSIAN 82 program[11] in the library program package.

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