

Remarkable Substituent Effects on the Strain Energies of Polycyclic Silicon Compounds

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Ab initio calculations show that electropositive substituents such as silyl groups have a remarkable effect on the relief of strain from polycyclic silicon compounds, the same effects being predicted also for the still heavier polycycles.

Polycyclic compounds such as tetrahedrane, prismane and cubane are highly strained and have long formed interesting synthetic targets. We have recently calculated that the strain energies decrease significantly when the skeletal carbons are replaced by heavier homologues (Si, Ge, Sn and Pb);¹⁻³ this

decrease in strain is progressively enhanced as the replacement atoms become heavier and the number of four-membered rings increases.⁴ Thus, the heavier group 14 analogues of cubane⁵ and prismane⁶ as well as bicyclo[2.2.0]hexane⁷ have been synthesized which contain four-membered rings.⁸

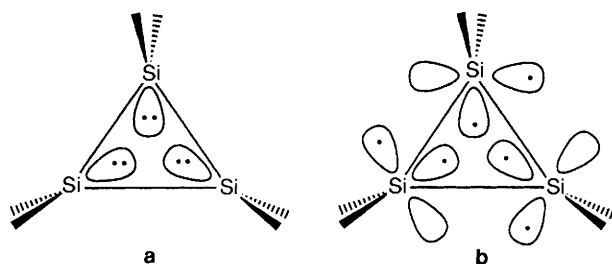


Fig. 1 Two interaction modes of three silylene units

In contrast, it is calculated that the heavier polycyclic compounds consisting of only three-membered rings still possess high strain and undergo bond-stretching or bond-breaking. For example, the heavier analogues of bicyclo[1.1.0]butane⁹ and [1.1.1]propellane¹⁰ undergo severe central bond-stretching, as verified by the X-ray study of a pentastanna[1.1.1]propellane derivative.¹¹ The heavier analogues of tetrahedrane collapse almost without resistance by breaking the two skeletal bonds to form an isomer with one four-membered ring.¹²

In an attempt to remove the disadvantage and enrich further the chemistry of the heavier polycycles, we report the *ab initio* calculations of the substituent effects on the strain energies of three-membered as well as four-membered rings; Me and SiH₃ groups were representatively investigated. All geometries were fully optimized at the Hartree-Fock (HF) level with the split-valence d-polarized 6-31G* basis set¹³ using the GAUSSIAN 88 program.¹⁴

Table 1 summarizes the strain energies of cyclotrisilanes (c-Si₃R₆) calculated from the homodesmotic reactions.¹⁵ For comparison, the strain energies of cyclopropane (c-C₃R₆) were calculated at the same level. The value of 28.7 kcal mol⁻¹ (1 cal = 4.184 J) calculated for c-C₃H₆ agrees well with the experimental value of 27.5 kcal mol⁻¹;¹⁶ comparable accuracy would be expected for silicon compounds where experimental data are not available, though the present interest is rather in the relative values.

As has been well documented, the strain energy (38.9 kcal mol⁻¹) of c-Si₃H₆ is *ca.* 10 kcal mol⁻¹ larger than that of c-C₃H₆.^{1,17} Upon substitution by the Me group, it is decreased only by 1.3 kcal mol⁻¹, though alkyl groups are usually employed as a representative substituent in silicon chemistry. In contrast, substitution by the SiH₃ group has a remarkable effect on the strain energy, c-Si₃(SiH₃)₆ becoming 10.8 kcal mol⁻¹ less strained than the parent c-Si₃H₆. Consequently, the strain energy of 28.1 kcal mol⁻¹ for c-Si₃(SiH₃)₆ is almost equal to that of 28.7 kcal mol⁻¹ for c-C₃H₆. In addition, it is 7.4 and 6.7 kcal mol⁻¹ smaller than the strain energies of c-C₃Me₆ and c-C₃(SiH₃)₆, respectively. These findings are noteworthy since three-membered silicon rings have been widely believed to be more strained than the corresponding carbon rings.^{1,17,18}

It is interesting to view cyclotrisilanes as resulting from the interaction of three silylenes (SiR₂) units. Two interaction modes (a and b) are shown in Fig. 1. As well-known, the parent SiH₂ has a closed-shell singlet ground state which is *ca.* 21 kcal mol⁻¹ more stable than the open-shell triplet state, in contrast to the triplet ground state of CH₂.¹⁸ Thus, mode a should be dominant in c-Si₃H₆ which leads to a closed-shell repulsion. The singlet-triplet energy difference is a little changed by the Me substitution. However, it becomes as small as *ca.* 4 kcal mol⁻¹ in Si(SiH₃)₂.¹⁹ This marked singlet-triplet closeness is favourable for open-shell interaction mode b and should lead to the stabilization of c-Si₃(SiH₃)₆. The energy closeness makes silicon atoms able to form hybrid orbitals with high p character; as pointed out, high p character is essential for a description of the bent bond orbitals in three-membered rings.^{17e}

Table 1 Strain energies, HOMO-LUMO levels, bond lengths between skeletal atoms, charge densities on skeletal atoms and total energies at the HF/6-31G* level

R	Strain /kcal mol ⁻¹	HOMO /eV	LUMO /eV	Length /Å	Charge	Total energy /au
Cyclopropane (c-C ₃ R ₆ ; D _{3h})						
H	28.7	-11.4	6.7	1.498	-0.358	-117.05887
Me	35.5	-9.9	5.8	1.519	-0.009	-351.25867
SiH ₃	34.8	-10.5	2.9	1.545	-0.530	-1857.47991
Cyclotrisilane (c-Si ₃ R ₆ ; D _{3h})						
H	38.9	-9.0	2.7	2.341	0.188	-870.18218
Me	37.6	-7.9	3.3	2.357	0.476	-1104.45059
SiH ₃	28.1	-8.6	2.3	2.359	-0.241	-2610.69921
Tetrasilatetrahedranes (Si ₄ R ₄ ; T _d)						
H	140.9	-7.0	2.2	2.314	0.034	-1157.82123
Me	134.6	-6.0	2.4	2.324	0.157	-1314.00156
SiH ₃	114.5	-6.8	2.2	2.319	-0.174	-2318.19917
Octasilacubanes (Si ₈ R ₈ ; O _h)						
H	93.5	-8.1	1.5	2.396	0.072	-2315.94264
Me	88.9	-7.0	1.8	2.404	0.215	-2628.29048
SiH ₃	77.9	-8.2	1.2	2.402	-0.157	-4636.63919

To confirm the remarkable substituent effects, the tetrahedrane system was investigated which consist of four three-membered rings. Tetrasilatetrahedrane (140.9 kcal mol⁻¹) is as highly strained as tetrahedrane (141.4 kcal mol⁻¹).¹ As Table 1 shows, substitution by the Me group decreases the strain energy by 6.3 kcal mol⁻¹, the effect being relatively small. On the other hand, the relief of strain becomes as large as 26.4 kcal mol⁻¹ upon SiH₃ substitution. This might suggest that the long-sought tetrasilatetrahedrane framework⁸ can be an interesting synthetic target with proper substituents.

Also shown in Table 1 are the strain energies of the cubane system. The strain energy (93.5 kcal mol⁻¹) of octasilacubane consisting of only four-membered rings is already 65 kcal mol⁻¹ smaller than that (158.6 kcal mol⁻¹) of cubane.¹ Upon substitution by the Me and SiH₃ groups, the strain energy is further decreased to 88.9 and 77.9 kcal mol⁻¹, respectively, the effect of the SiH₃ group being again larger. This reflects the fact that the strain energy (14.7 kcal mol⁻¹) of the silyl-substituted cyclotetrasilane [c-Si₄(SiH₃)₈] is smaller than that (16.7 kcal mol⁻¹) of the parent c-Si₄H₈; in fact, the strain energy of c-Si₄(SiH₃)₈ differs little from the strain energy per four-membered ring (13.0 kcal mol⁻¹) of Si₈(SiH₃)₈. The advantage of SiH₃ over Me substitution is true also for the prismane (Si₆R₆) system which contains both three-membered and four-membered rings: the strain energies decrease in the order 113.8 (R = H) > 105.6 (R = Me) > 95.7 (R = SiH₃) in kcal mol⁻¹.

As the charges on the skeletal atoms in Table 1 show, the SiH₃ group is a good electropositive substituent while the Me group is electronegative in silicon compounds. The Me group raises the HOMO level more highly than the SiH₃ group. It is interesting that the skeletal rings undergo little geometrical change upon substitution.

In summary, silyl groups are much more effective for the relief of strain than alkyl groups. 'Strain' and 'aromaticity' are two important concepts in chemistry. In this context, it should be mentioned that the aromaticity of hexasilabenzene is highly increased by the silyl substitution while it is rather decreased by the alkyl substitution.²⁰ The choice of substitution is also important for the stabilization of the still heavier Ge, Sn and Pb skeletons. According to the preliminary calculations at the HF/DZ level, the strain energies of octastannacubanes (Sn₈R₈) are 77.0 (R = H), 75.7 (R = Me), 65.0 (R = SiH₃), 62.0 (R = GeH₃) and 58.4 (R = SnH₃) kcal mol⁻¹. Although

these values tend to be overestimated by *ca.* 6 kcal mol⁻¹ because of the omission of d polarization functions, it appears that the effects of substituents are remarkable also for the tin skeleton; the more electropositive the substituents, the larger the effects. This was true also for the silicon skeleton: on going from Si₈(SiH₃)₈ to Si₈(SnH₃)₈ the strain energy is decreased by 5.2 kcal mol⁻¹ at the HF/DZ level.

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