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Ab Initio Study of the Effect of Heteroatoms and Bulky Substituents on the Strain Energies of Cyclosilanes

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In an attempt to estimate the strain energy of three-, four-, and five-membered cyclosilanes substituted with a heteroatom or group, $[R_2Si]_nX$ ($n = 2$, 3, and 4; $X = CH_2$, NCH_3, O, SiH_2, PCH_3, and S; R = H and *i*-Pr), we have performed high-level ab initio molecular orbital calculations, some involving the ONIOM method. It is found that the hetero group X with a third-row element brings about the release of ring strain compared to the second-row analogues and that the effect of bulky substituents R on the strain energy works differently in the cyclosilanes with lone-pair electrons than in those without them.

Introduction

Ring strain of cyclic hydrocarbons is one of the most important topics in organic chemistry and has been studied extensively for many years.[1] Therefore, it is not surprising that the strain energy of heavier 14 group analogues, such as cyclosilanes ($(RR'Si)_n$),[2] has been noted as a next research target after cycloalkanes. On the other hand, much less is known on the chemistry of heterosubstituted cyclosilanes ($[RR'Si]_nX$) and related compounds.[3,4] With recent establishment of synthesis and characterization, however, it is becoming possible to explore experimentally their properties.[4] Several ab initio theoretical studies on the structure and properties of unsubstituted cyclosilanes[2b−d,5] have already been published. Nevertheless, a comprehensive study for their properties including the strain energy of cyclosilanes substituted with a heteroatom (group) is not available except for our previous study[4] and a theoretical study for the three-membered compound $[H_2Si]_nX$.[6] In that study, we have mainly discussed experimental results in detail. Therefore, we here focus on theoretical studies for the strain energy of cyclosilanes with various heteroatoms (groups) ($[R_2Si]_nX$; $n = 2$, 3, and 4; $X = CH_2$, NCH_3, O, SiH_2, PCH_3, and S; R = H and *i*-Pr), which we performed with several levels of ab initio molecular orbital calculation.

Computational Methods

The geometries of all molecules of interest have been fully optimized at the B3LYP hybrid density functional levels of theory[7] using the 6-31G(d) basis set.[8] In addition, all structures were confirmed as minima on the potential surface by analytical vibrational frequency calculation. The vibrational frequencies obtained at this level were used for thermal correction in the strain energy below. Single-point energy calculations were carried out at the G2MS level, which is an additivity approximation for E[CCSD(T)/6-311+G(2df,2p)] and is expected to give energetics with an error of 2 kcal/mol or so:[9]

$$E[\mathrm{G2MS}] = E[\mathrm{CCSD(T)/6\text{-}31G(d)}] + E[\mathrm{MP2/6\text{-}311{+}G(2df,2p)}] - E[\mathrm{MP2/6\text{-}31G(d)}]$$

For the *i*-Pr-substituted species (R = *i*-Pr), the ONIOM method[10] was used as the molecular size becomes large

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(1) For example: (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1975**, *32*, 317. (c) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. (d) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 2588, and references therein. (e) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 3884.

(2) For example: (a) Watanabe. H.; Shimoyama, H.; Muraoka, T.; Okawa, T.; Kato, M.; Nagai, Y. *Chem. Lett.* **1986**, 1057. (b) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6569. (c) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329. (d) Nagase, S.; Kobayashi, K.; Nagashima, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1302.

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Table 1. Optimized Si−Si and Si−X Distances (Å) of $[R_2Si]_nX$ ($n = 2-4$) at the B3LYP/6-31G* Level

hetero group (X)		r(Si−Si)[a])			r(Si−X)		
		R = H	*i*-Pr	exptl[b]	H	*i*-Pr	exptl[a]
$n = 2$	O	2.212	2.236		1.718	1.725	
	NCH_3	2.248	2.271		1.747	1.762	
	CH_2	2.268	2.283		1.915	1.923	
	SiH_2	2.345	2.362		2.345	2.375	
	PCH_3	2.287	2.309		2.297	2.313	
	S	2.261	2.284		2.177	2.199	
$n = 3$	O	2.368	2.395	2.433	1.695	1.709	1.656
	NCH_3	2.354	2.387	2.37	1.761	1.779	1.757
	CH_2	2.366	2.399	2.394	1.918	1.927	1.889
	SiH_2	2.370	2.419	2.373	2.371	2.376	2.373
	PCH_3	2.358	2.403		2.292	2.3	
	S	2.359	2.402		2.188	2.203	
$n = 4$	O	2.369	2.432	2.392	1.674	1.688	1.646
	NCH_3	2.357	2.420	2.402	1.745	1.786	1.76
	CH_2	2.367	2.430	2.393	1.905	1.919	1.888
	SiH_2	2.368	2.450	2.422	2.364	2.38	2.422
	PCH_3	2.365	2.441		2.282	2.294	
	S	2.364	2.428		2.177	2.204	

[a] The average of two kinds of Si−Si bonds in the case of $n = 4$. [b] Ref 4 for R = ($n = 3$, X = O: *t*-$BuCH_2$; $n = 3$, X = NCH_3: *i*-Pr; $n = 3$, X = CH_2: *t*-$BuCH_2$; $n = 3$, X = SiH_2: *i*-Pr, $n = 4$, X = O: *i*-Pr; $n = 4$, X = NCH_3: *i*-Pr; $n = 4$, X = CH_2: *i*-Pr; $n = 4$, X = SiH_2: *i*-Pr).

especially for the five-membered rings. As a result of several *S*-value tests, we have decided to take G2MS as the "high" level for the frame of rings (Si atoms and the X group) and MP2/6-31G* as the "low" level for the other parts (the R group) of molecules; namely, we used ONIOM(G2MS:MP2/6-31G*) as the highest level of calculation for *i*-Pr-substituted compounds.

Finally, by using the single-point energies, their strain energy was estimated by the conventional homodesmotic reaction energy[1b] as shown in the following equation.

$$[R_2Si]_nX + (n-1)SiR_2H\text{-}SiR_2H + 2SiR_2H{-}XH \rightarrow SiR_2H{-}X{-}SiR_2H + (n-2)SiR_2H{-}SiR_2{-}SiR_2H + 2SiR_2H{-}SiR_2{-}XH$$

$$n = 2-4;\ -\Delta H = \text{strain energy}$$

All calculations were performed with Gaussian98 electronic structure codes.[11]

Result and Discussion

Geometry. In Tables 1−3 collected are some geometrical parameters of the cyclosilanes containing a heteroatom optimized at the B3LYP/6-31G* level together with the experimental values. All possible symmetries were considered on the geometry optimization. The *i*-Pr-substituted species tend to be nonsymmetric (C_1), while the H analogues have higher symmetry such as C_{2v} or C_s. In general, as the size of the ring becomes large and more flexible, the molecular symmetry becomes lower. Furthermore, compounds having the X group with lone-pair electrons tend to have nonsymmetric structure, while those without lone-pair electrons have a structure with symmetry higher than C_1.

As Table 1 shows, the Si−Si bond length for $n = 2$ and 3 is longer in the rings with the third-row elements than in the rings with the second-row elements. It is shortest in the oxygen compound while longest in the silicon compounds. For $n = 4$ (the average value of two kinds of Si−Si bonds), on the other hand, the Si−Si bond lengths of all species are rather similar. As n becomes larger, the Si−Si bond length becomes longer, but this trend is more obvious in the *i*-Pr compounds than in the H analogues, suggesting that the congestion caused by the bulky *i*-Pr groups becomes serious in the larger rings. Furthermore, both the Si−Si and Si−X bond lengths are elongated on the *i*-Pr substitution compared to those of the H analogues probably in order to avoid the serious steric repulsion between the bulky *i*-Pr groups.

The Si−X−Si bond angle, as seen in Table 2, is smaller in cyclosilanes with third-row elements than in those with second-row elements, suggesting that easier polarization of the former element can accommodate a smaller bond angle without accumulating strain energy, in contrast with the latter element. This trend is more enhanced for smaller n, where the bond angles are smaller, than for large n. The *i*-Pr substitution has nearly no effect on the Si−X−Si and Si−Si−X bond angles in the three-membered ($n = 2$) rings. For larger rings, however, the Si−X−Si angle in the *i*-Pr-substituted compounds is slightly larger than those in the H compounds, while the reverse is true in the Si−Si−X angle.

The Si−Si−Si bond angle becomes small with the *i*-Pr substitution in the five-membered ring. In contrast, the *i*-Pr−Si−*i*-Pr angle becomes larger by 0.2−2.7°compared with the H−Si−H angle. The bulky *i*-Pr groups on the same Si atom try to avoid each other by making the *i*-Pr−Si−*i*-Pr angle larger, which subsequently makes the Si−Si−Si as well as the Si−Si−X angles smaller. The bulky *i*-Pr groups also increase the deviation of the n-membered ring from the plane, especially for $n = 4$, as seen in Table 3.

Strain Energy. Table 4 shows the calculated strain energy (−ΔH) of all the cyclic molecules considered in the present work. As expected, as the ring size becomes larger, the strain energy becomes smaller. The effect of the heteroatom (group) is largest in the three-membered rings ($n = 2$), where the fraction of the heteroatom (group) in the ring is the largest. The strain energies of the three-membered rings with the H substituent are in good agreement with the isodemic reaction energy obtained at the MP2//HF/6-31G** level.[6] For all ring sizes and R substituents (except for the five-membered ring with *i*-Pr substituent), the oxygen compounds have the largest strain energy, while the strain energy of the sulfur compounds is smallest. The largest strain of the

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Table 2. Optimized Si−X−Si and Si−Si−X Bond Angles (deg) of $[R_2Si]_nX$ ($n = 2-4$) at the B3LYP/6-31G* Level

		Si−X−Si			Si−Si−X		
hetero group (X)		R = H	*i*-Pr	exptl[b]	H	*i*-Pr	exptl[b]
$n = 2$	O	80.2 (52.4)[a])	80.7 (50.0)		49.9	49.6	
	NCH_3	80.1 (63.8)	80.3 (64.7)		49.6	49.8	
	CH_2	72.6 (62.9)	72.8 (61.4)		53.7	53.6	
	SiH_2	60.0 (53.1)	60.1 (49.7)		60.0	59.9	
	PCH_3	59.7 (60.4)	59.9 (57.4)		60.2	60.0	
	S	62.6 (61.7)	62.6 (59.0)		58.7	58.7	
$n = 3$	O	108.5 (71.0)	109.7 (68.0)	111.1	90.2	89.5	90.3
	NCH_3	108.4 (86.4)	109.4 (88.2)	109.5	88.3	87.7	88.0
	CH_2	98.3 (85.2)	100.5 (84.8)	102.3	89.6	88.4	88.0
	SiH_2	87.7 (77.7)	90.0 (74.4)	87.0	87.7	86.0	87.0
	PCH_3	84.6 (85.5)	88.2 (84.6)		90.3	87.4	
	S	90.1 (88.8)	91.9 (86.6)		93.9	92.8	
$n = 4$	O	132.6 (86.7)	137.0 (84.9)	133.6	104.4	99.6	102.0
	NCH_3	127.1 (101)	124.1 (100.0)	125.6	105.4	100.9	106.1
	CH_2	112.3 (97.3)	117.6 (99.2)	117.7	105.4	100.8	102.7
	SiH_2	104.2 (92.3)	109.6 (90.6)	101.9	104.8	98.6	101.9
	PCH_3	96.2 (97.3)	104.8 (100.0)		105.5	98.4	
	S	101.2 (99.7)	109.5 (103.2)		107.6	102.8	

[a] The values in parentheses are {(Si−X−Si in $[R_2Si]_nX$)/(Si−X−Si in $[HR_2Si]_2X$)} × 100%. [b] Ref 4 for R = ($n = 3$, X = O: *t*-$BuCH_2$; $n = 3$, X = NCH_3: *i*-Pr; $n = 3$, X = CH_2: *t*-$BuCH_2$; $n = 3$, X = SiH_2: *i*-Pr, $n = 4$, X = O: *i*-Pr; $n = 4$, X = NCH_3: *i*-Pr; $n = 4$, X = CH_2: *i*-Pr; $n = 4$, X = SiH_2: *i*-Pr).

Table 3. Optimized Si−Si−Si Bond Angles and Dihedral Angles (torsion angle for $n = 4$) (deg) of $[R_2Si]_nX$ ($n = 3, 4$) at the B3LYP/6-31G* Level

		Si−Si−Si			dihedral or ring torsion angle		
heterogroup (X)		R = H	*i*-Pr	exptl[a]	H	*i*-Pr	exptl[a]
$n = 3$	O	71.0	71.4	68.2	0	0	3.0
	NCH_3	74.7	74.9	74.5	2.7	3.3	0
	CH_2	75.6	76.3	75.9	17.7	17.0	25.5
	SiH_2	87.7	88.0	87.0	22.6	23.0	37.0
	PCH_3	81.7	83.6		26.7	26.7	
	S	82.0	82.5		0	0	
$n = 4$	O	97.7	94.6	95.3	11.3 (6.2−15.6)[b]	23.6 (6.6−32.8)	23.0 (9.8−32.1)
	NCH_3	98.4	95.0	96.2	17.2 (9.2−24.6)	32.5 (14.8−47.2)	20.1 (8.3−27.3)
	CH_2	99.7	96.9	97.5	26.6 (0.0−43.6)	33.7 (7.8−52.2)	30.6 (7.3−47.1)
	SiH_2	105.1	102	101.9	25.0 (5.7−38.6)	27.6 (14.7−45.5)	
	PCH_3	102.6	100.0		32.5 (0.0−49.7)	38.1 (3.7−57.6)	
	S	102.2	98.6		27.4 (0.0−42.6)	33.7 (13.7−51.4)	

[a] Ref 4 for R = ($n = 3$, X = O: *t*-$BuCH_2$; $n = 3$, X = NCH_3: *i*-Pr; $n = 3$, X = CH_2: *t*-$BuCH_2$; $n = 3$, X = SiH_2: *i*-Pr, $n = 4$, X = O: *i*-Pr; n =4, X = NCH_3: *i*-Pr; $n = 4$, X = CH_2: *i*-Pr; $n = 4$, X = SiH_2: *i*-Pr). [b] The average and the range (in parentheses) of the ring torsion angles.

oxygen rings can be explained from the angle strain of the Si−X−Si bond angle. The values in parentheses in Table 2 show the ratio of the Si−X−Si bond angle in the ring to that in the corresponding acyclic compounds, $HSiR_2-X-SiR_2H$. The angle stain is expected to be larger if the value is smaller. Therefore, the oxygen compounds are likely to have the largest strain energy because of the angle strain. In addition, the short Si−O bond length may also enhance the large strain of the oxygen rings. It is obvious that the angle strain becomes small as the size of the ring approaches six-membered.

For the compounds with third-row elements such as SiH_2, PCH_3, and S, however, the angle strain seems to be rather large but the strain energy is small compared to the second-row analogues. As discussed above, the third-row elements are much more polarizable than the second-row, and a large angle strain can be easily accommodated without causing a large strain energy. In addition, as shown in Table 1, the ring strain may be less serious because of long Si−Si and Si−X bonds. The strain energy of $(SiH_2)_4$ and $(SiH_2)_5$ is calculated to be 14.0 and 3.4 kcal/mol, respectively, at the present G2MS//B3LYP/6-31G*+ZPC level (which incidentally is a little smaller than the experimental values of 23 and 6 kcal/mol[2a] or the MP4SDTQ/6-31G** values of 18.7 and 5.7 kcal/mol[5d]). The strain energy decreases in the

Table 4. Calculated Strain Energies (kcal/mol) of $[R_2Si]_nX$ ($n = 2-4$)[a]

hetero group (X)		R = H	*i*-Pr
$n = 2$	O	45.0	48.9
	NCH_3	37.1	40.2
	CH_2	38.6	38.6
	SiH_2	35.0	32.4
	PCH_3	28.1	30.5
	S	23.9	26.1
$n = 3$	O	18.6	17.7
	NCH_3	12.8	15.0
	CH_2	17.3	14.0
	SiH_2	14.0	6.6
	PCH_3	12.7	7.1
	S	10.1	7.2
$n = 4$	O	4.7	5.4
	NCH_3	2.8	6.2
	CH_2	4.5	3.4
	SiH_2	3.4	2.2
	PCH_3	2.7	3.8
	S	1.5	3.1

[a] Calculated at the G2MS+ZPC (for R = H) and ONIOM(G2MS: MP2/6-31G*)+ZPC (R = *i*-Pr) levels at B3LYP/6-31G* optimized geometries.

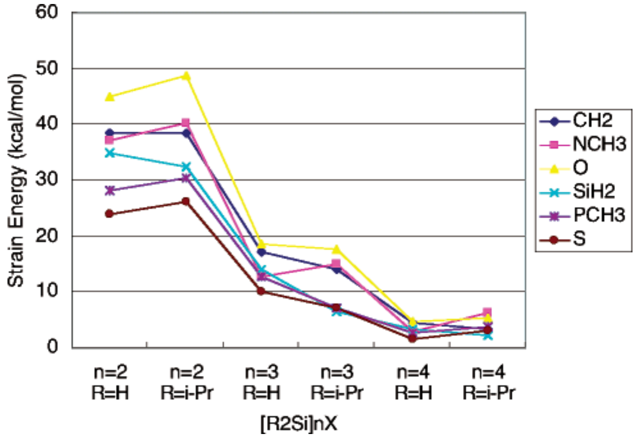

Figure 1. Strain energies of $[R_2Si]_nX$ calculated at the G2MS//B3LYP/6-31G*+ZPC and ONIOM(G2MS:MP2/6-31G*//B3LYP/6-31G*+ZPC) levels.

order X = SiH_2 (group 14) > PCH_3 (group 15) > S (group 16) for all sizes of the H-substituted rings ($[H_2Si]_nX$). This trend is similar to the order of strain energy of the carbon analogues substituted with a heteroatom (group), $[H_2C]_nX$: X = CH_2 (group 14) > NCH_3 (group 15) > O (group 16) for $n = 2-4$.[1e] These results may suggest some effect of atomic size on the strain energy of the rings constructed by the elements in the same periodic row.

As mentioned before, the ring is expanded upon substitution by the *i*-Pr group in all cases. Figure 1 shows some clear trend of the effects of the *i*-Pr group that the strain energy of the rings containing the group X with lone-pair electrons in general *increases* upon *i*-Pr substitution. There are some exceptions in the four-membered rings (X = O, S, and PCH_3), although the difference in strain energy between the H and *i*-Pr species is small in $[R_2Si]_3O$. This trend suggests the existence of steric repulsion between the bulky substituent and the lone-pair electrons despite the ring expansion. In contrast, the strain energy is decreased in $[R_2Si]_nCH_2$ ($n = 2-4$) and $[R_2Si]_nSiH_2$ ($n = 2-4$) without lone-pair electrons that cause repulsion with the *i*-Pr substituent. For $[R_2Si]_3S$ and $[R_2Si]_3PCH_3$, even though they have lone-pair electrons, the repulsion between the *i*-Pr groups and lone-pair electrons seems to be less important, as the Si−X and Si−Si bond lengths are much longer than those in the rings with the second-row elements.

The effect of the number of heteroatoms (groups) in the ring system is another interesting topic. Therefore, we have changed the number of CH_2's in tricyclosilane, $(SiH_2)_3$, and compared the strain energies. At the G2MS//B3LPY/6-31G*+ZPC level the strain energy increases from 35.0 kcal/mol for $(SiH_2)_3$ to 38.6 kcal/mol for $(H_2Si)_2CH_2$. After that, the strain energy decreases monotonically to 35.7 kcal/mol for $(H_2Si)(CH_2)_2$ and 27.4 kcal/mol for $(CH_2)_3$. This result suggests that hetero-mixed cyclic compounds have larger strain energies compared to the corresponding homo-rings, such as cyclopropane or cyclotrisilane. For the C/Si mixed rings, the strain energy of $(H_2Si)_2CH_2$ is larger than that of $(H_2Si)(CH_2)_2$, suggesting that the two silicon atoms with larger atomic size compared to the carbon atom bring about the larger strain energy. Therefore, the number of heteroatoms seems to have some effect on the strain energy of hetero-mixed rings. A more detailed study may be required for different ring sizes to generalize this conclusion.[12]

Concluding Remarks

It was found that the bond distances, bond angles, and lone-pair electrons play important roles with respect to the strain energy of cyclosilanes substituted with a heteroatom or group. The cyclosilanes substituted with third-row elements tend to have smaller strain energy compared to the second-row analogues. Upon substitution by bulky groups such as *i*-Pr on silicon atoms, the ring expands and the strain energy is released, but at the same time the existence of the bulky substituents brings about steric repulsion between lone-pair electrons on the heteroatom or group, which leads to increased strain energy.

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(12) We also have calculated the strain energy of the C/Si mixed four-membered rings at the same level of theory. The result was as follows: $(CH_2)_4 = 26.0$, $(CH_2)_3(SiH_2) = 22.4$, $(CH_2)_2(SiH_2)_2 = 39.6$ (C_s symmetry), $(CH_2)_2(SiH_2)_2 = 10.4$ (C_2 symmetry), $(CH_2)(SiH_2)_3 = 17.3$, and $(SiH_2)_4 = 14.0$ kcal/mol. It appears that other factors, the number of Si−Si bonds (stabilizing factor) and Si−C bonds (destabilizing factor) and the type of alignment, for example, rather than the atomic size play an important role in the larger ring.