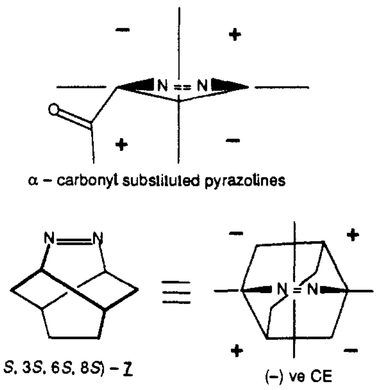
Scheme VII



bonyl compounds and saturated three-membered rings.

Owing to the fact that the $n_-\pi^*$ transition band of the diazirine chromophore is located in the long-wavelength range of the CD spectrum, this chromophore can be employed for studying the stereochemistry of compounds containing additional chromophores with absorption maxima less than 300 nm: >C=O, $-N_3$, >C=N–, Ar, and others. For example, in the CD spectrum of diazirine 5, the $n_-\pi^*$ transition of the diazirine chromophore is well separated from the $1L_b$ transition of the benzoate group, while in the case of 3-oxo-5α-androstan-17β-yl benzoate, overlapping of the absorption bands of the carbonyl and benzoate chromophores is observed (Figure 4).

The octant rule found for diazirines is certain to be applied in the case of the compounds containing a non-strained cis-azo group since the long-wavelength transition of both chromophores is of the same nature ($n_-\pi^*_{NN}$).[4] In fact, the above rule reliably predicts the sign of the long-wavelength band in the CD spectra of the known chiral cis-azo compounds. In the case of α-carbonyl-substituted pyrazolines,[4] the CE sign is mainly determined by the octant in which the carbonyl group enters. In the case of 4,5-diaza-twist-4-ene 7[6] similar to its carbonyl analogue 9-twistbrendanone,[15] the decisive contribution to the CE is made by the closer "outer" rings. Thus the general regional rule for studying the stereochemistry of chiral cis-azo compounds is proposed on the basis of studying of chiroptical properties of the diazirine chromophore.

Organosilicon Rings: Structures and Strain Energies

Douglas B. Kitchen, James E. Jackson, and Leland C. Allen*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. *Received April 7, 1987*

Abstract: Geometries, strain energies, and electronic structures for 23 organosilicon compounds have been determined. The species studied were those for which silicon successively replaced carbon in cyclopropane, bicyclobutane, and [1.1.1]propellane and in propane, cyclobutane, and bicyclo[1.1.1]pentane. Wave functions constructed from the recently developed compact effective core potentials and using a split-valence, d-polarized basis set were employed. Accurate strain energies, validated by extensive comparison with existing experimental data and ab initio calculations, were obtained from a series of homodesmic reactions. When the compounds investigated are displayed in a periodic table format (increasing number of silicon replacements down a column, increasing number of fused rings across rows) many useful interrelationships and bonding patterns manifest themselves. In spite of their considerable complexity in structure and properties, it proves possible to understand them in terms of electronegativity arguments and a simple two-orbital, three-atom, molecular orbital model. Our results also predict several interesting new organosilicon compounds, and an analysis of their synthetic accessibility suggests that these new species should be realizable.

Organosilicon chemistry is an exciting and rapidly growing field. Silicon compounds with Si_3 and Si_4 rings are now well represented in silicon chemistry[1] due in large part to recent intensive research on silicon double bonds and on silylenes.[2] Larger rings have also been studied extensively including cagelike species up to Si_9 and Si_{10}.[3] The advancements in these experimental studies have prompted considerable theoretical effort to understand Si–Si and Si–C double bonding.[4] A few theoretical studies on Si_3, Si_4, and Si_6 strained rings also have been undertaken.[5-8] Important results have been obtained, but it is not surprising that with these larger systems different levels of accuracy have made it difficult to discern trends and make comparisons.

In this work we present ab initio effective core potential electronic structure results[9] on silicon-containing strained rings generated from uniform basis sets using compact effective potentials to represent the core electrons. Results from these calculations are compared with experiment and with all-electron calculations and are found to provide accurate and consistent geometries and good estimates of strain energies. The efficiency of the recently developed compact effective core potentials employed here has enabled us to make comparisons with the well-known hydrocarbon literature[10-12] on strained ring systems and to extend our investigation to the corresponding mixed silicon–carbon ring systems and to the silanes. The large set of molecules treated has led to

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* Author to whom all correspondence should be addressed.

(1) Watanabe, H.; Nagai, Y. In *Organosilicon and Biorganosilicon Chemistry*; Sakurai, H., Ed.; Wiley: New York, 1985; p 107.

(2) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(3) West, R.; Carberry, E. *Science* **1975**, *189*, 179.

(4) (a) Sax, A. F. *J. Comp. Chem.* **1985**, *6*, 469. (b) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 3399. (c) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283. (d) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609. (e) Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 537.

(5) Rubio, J.; Illas, F. *J. Mol. Struct.* (*Theochem*) **1984**, *110*, 131.

(6) Sax, A.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651.

(7) Clabo, D. A.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 1664.

(8) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

(9) Although the many-electron formulation of our wave functions only includes the valence electrons, the basis sets, correlation corrections, and accuracies parallel traditional all-electron ab initio methods. We therefore follow the designation, ab initio effective core potential, established previously by Hay and Wadt (*J. Chem. Phys.* **1985**, *82*, 270).

(10) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

(11) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(12) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

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Table I. Comparisons of Geometries of Strained Hydrocarbon,[a] Silane, and Carbosilane Rings

(A) Strained Hydrocarbon Rings

	cyclopropane	bicyclobutane		propellane		bicyclopentane		cyclobutane	
	r(CC)	$r(C_1C_2)$	$r(C_1C_3)$	$r(C_1C_2)$	$r(C_1C_3)$	$r(C_1C_2)$	$r(C_1C_3)$	$r(C_1C_2)$	τ
exptl	1.514	1.498	1.497	1.525	1.596	1.545	1.84	1.548	155
CEP-31G*	1.519	1.504	1.489	1.517	1.574	1.555	1.88	1.504	153
6-31G*	1.498	1.489	1.466	1.502	1.543	1.546	1.87	1.489	165

(B) Strained Silane Rings

	Si_3 cyclopropane	Si_4 bicyclobutane		Si_4 cyclobutane	
	r(SiSi)	$r(\mathrm{Si_1S_2})$	$r(\mathrm{Si_1Si_3})$	$r(\mathrm{Si_1Si_2})$	τ^d
exptl[b]	2.375, 2.422	2.334	2.373	2.359	180
	2.425	2.336		2.367	
				2.308	
				2.311	
CEP-31G*	2.345	2.307	2.367	2.377	151.3
6-31G*	2.341			2.373	149.8
Rubio and Illas[c]	2.381			2.377	180

(C) Strained Carbosilane Rings

	1-silacyclopropane		1,3-disilacyclopropane		2,4-disilabicyclobutane			1,3-disilacyclobutane		
	r(SiC)	r(CC)	r(SiC)	r(SiSi)	r(SiC)	r(CC)	τ^f	r(SiC)	r(CC)	r(SiSi)
exptl[e]	1.865	1.643	1.886	2.272	1.832	1.781	121.8	1.923	2.766	2.699
	1.878		1.887		1.846			1.921		
CEP-31G*	1.855	1.571	1.913	2.258	1.830	1.692	126.1	1.912	2.738	2.667
6-31G*								1.911	2.739	2.667

[a] Distances in angstroms, angles in degrees; τ is the angle between the two planes formed by the four carbon atoms in the ring. Experimental and 6-31G* geometries are from: Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5649. Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227 and references contained therein. [b] Experimental results are from X-ray crystal structures of substituted compounds, see: Masamune, S.; Hanzawa, Y.; Murakami, S.; Bully, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. Jones, R.; Williams, J.; Kabe, Y.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 173. Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253. [c] Reference 5. [d] τ is the angle between the two planes formed by the four silicon atoms in the ring. [e] Experimental results are from X-ray crystal structures of substituted compounds, see: Ishikawa, M.; Matsuzawa, S.; Sugisawa, H.; Yano, F.; Kamitori, S.; Higuchi, T. *J. Am. Chem. Soc.* **1985**, *107*, 7706. Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776. Fritz, V. G.; Wartanessian, S.; Matern, E. *Z. Anorg. Allg. Chem.* **1981**, *475*, 87. Peters, K. v.; Peters, E.; Schnering, H. G. v. *Z. Anorg. Allg. Chem.* **1983**, *502*, 61. [f] τ is the angle between the two planes formed by the four silicon and carbon atoms in the ring.

the prediction of several new geometries and many new strain energies (including correction of probable errors). In addition, the systematic treatment of this set permits an assay of the relative synthetic accessibility of those as yet unknown.

Because of their high strain energies, hydrocarbons containing three- and four-membered rings have unusual properties and one might expect novel differences in electronic distributions when silicon is substituted for the carbon analogues. In particular, the interplay between σ and π bonding is interesting since carbon is known to π bond well whereas silicon is known to form only weak π bonds. As expected, the trends found in our chosen set of molecules are rather complex and it is a welcome surprise to find that most of them can be explained by electronegativity arguments and a simple two-orbital, three-atom-ring, molecular orbital model.

Methods, Validation and Predictions

Stevens, Basch, and Krauss[13] have recently developed a set of effective core potentials for the first two rows of the main group elements which have generally proved accurate and efficient. In the calculations reported here, a 31 contraction of their shared exponent, s,p basis set has been augmented by d orbital polarization functions. For carbon, an exponent of 0.80 was used and for silicon, an exponent of 0.45. All six Cartesian d orbitals were included. The hydrogen atom 31G basis is that developed by Pople and we designate the overall basis set CEP-31G*. All molecules were fully optimized at the SCF level with this basis set. Optimized all-electron results at the 6-31G*[14] level were carried out for comparisons because the hydrocarbon strain energies and heats of formation are known to be well reproduced with this basis.[15]

A. Geometries. Table I (reactions A, B, and C) lists experimental, CEP-31G*, and 6-31G* geometries for a variety of hydrocarbons, silanes, and mixed carbon–silicon compounds, respectively. Experimental structures for silane comparison are limited by the bulky substituents used and therefore X-ray crystal structures show Si–Si distances up to 5% longer. For example, in the 1-silacyclopropane ring, the bis(trimethylsilyl) and hydroxydimesitylsilyl groups on the carbons of the experimental reference compound[16] account for most of the difference between the long CC separation of 1.643 Å and the CEP-31G* value of 1.571 Å. Likewise the 2,4-disilabicyclobutane[17] has bulky trimethylsilyl groups which cause the 5% descrepency between the experimental CC distance of 1.781 Å and the calculated value of 1.692 Å. As noted in Table IB, Rubio and Illas[5] have carried out effective core potential calculations for the cyclotrisilane and cyclotetrasilane and obtained values comparable to CEP-31G* values. The discrepancy in the dihedral angles for tetrasilacyclobutane between theory and experiment is likely to be due to substitution on the silicons as well as the very shallow potential well (calculated to be 0.5 kcal/mol) which may necessitate very high levels of theory in order to accurately predict the puckering motions of these molecules. Likewise some of the differences between the calculated and experimental bond lengths may be due to electron correlation, but the substitutions on the compounds prevent any quantitative estimate of the amount of error due to lack of electron correlation.

It is apparent from Table I that CEP-31G* is yielding geometries quite close to experimental and notably superior to 6-31G* values. The fore-shortening of internuclear separations produced by 6-31G* is partly obviated by CEP-31G* because of its superior

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(13) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

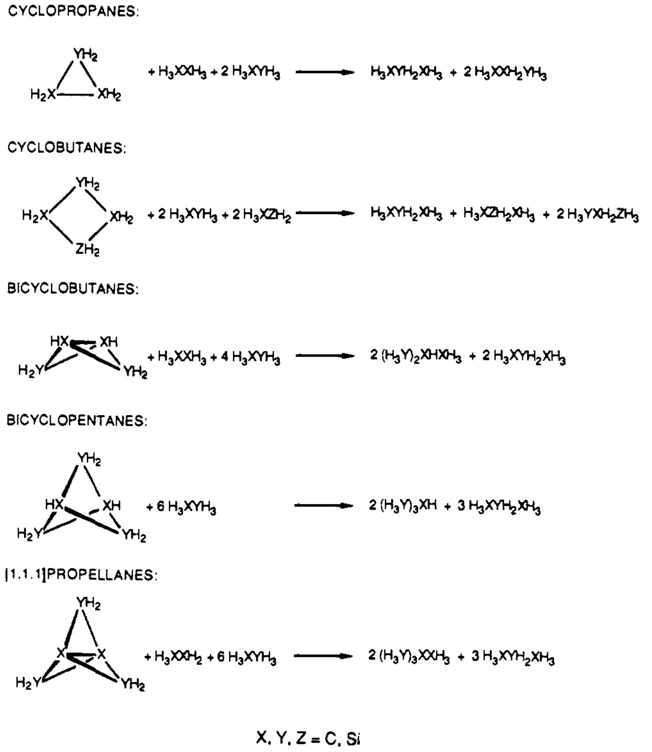
(14) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(15) (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. (b) Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679.

(16) Ishikawa, M.; Matsuzawa, S.; Sugisawa, H.; Yano, F.; Kamitori, S.; Higuchi, T. *J. Am. Chem. Soc.* **1985**, *107*, 7706.

(17) Fritz, V. G.; Wartanessian, S.; Matern, E.; Honle, W.; Schnering, H. G. v. *Z. Anorg. Allg. Chem.* **1981**, *475*, 87.

Scheme I



representation of the core electrons.

B. Strain Energies. The calculation of the strain energies in cyclic compounds may be accurately accomplished by the use of homodesmic reactions.[18] Those we employ are defined by Scheme I (the cyclobutane reactions follow the same pattern but are not shown). In this scheme the same number of each atom type and its bonding environment is preserved on both sides of the reactions. Accurate reaction energies are obtained because correlation and zero-point energy corrections largely cancel each other from the two sides of the reactions. The homodesmic approach is used here in preference to isodesmic reactions[19] (which derive their accuracy from a similar cancelation) because of its basic similarity to the traditional group equivalent method of obtaining strain energies.[20] Recently, Wiberg[21] and Schleyer[22] have up-graded the traditional group equivalent method by employing combinations of ab initio and experimental values to achieve high accuracy heats of formation from ab initio total energies. Wiberg's scheme has been applied to hydrocarbons with exceptional success. Schleyer's scheme also has been applied successfully to both hydrocarbons and heteroatomic compounds, but it necessitates a difficult division of total energy between different atoms. Neither Wiberg's nor Schleyer's procedure is applicable to organosilicon compounds because insufficient thermodynamic data exist. Homodesmic reactions largely overcome the need to use group equivalent averaging by employing whole molecules and because molecular total energies can be computed consistently for all species to many significant figures. In the present application, the "representative" C–C, Si–Si, and Si–C bonds are defined by ethane, disilane, and silaethane. When more experimental data become available it will be useful to check whether or not these reference values for single bonds in unstrained molecules should be averaged over molecules with larger end groups.

Table II lists strain energies computed for our chosen set of hydrocarbons, silanes, and organosilicon species at CEP-31G* and compares them with selected 6-31G* calculations and the available experimental data. The most complete and accurate experimental data are that for the hydrocarbons, and both CEP-31G* and 6-31G* give quite satisfactory agreement with them and with each other. The two experimental values available for the silanes[23] were obtained from rather uncertain spectroscopic estimates, but their agreement with CEP-31G* may still be regarded as reasonable. Experimental values for silacyclobutane and 1,3-disilacyclobutane were obtained from thermodynamic data on 1,1-dimethyl-1-silacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, respectively, using bond rather than group equivalent fragment definitions.[24] In Figure 1 calculated and experimental values for

Table II. Strain Energies of Cyclic Hydrocarbons and Silanes[a]

	homodesmic strain energy		exptl strain energy
	CEP-31G*	6-31G*	
C_3H_6	31.1	28.7	27.5
C_4H_6	71.0	68.9	63.9
C_4H_8	26.2	26.9	26.5
C_5H_6	103.0	104.3	98.0
C_5H_8	67.7	69.4	68.0
Si_3H_6	40.0	38.9	41
Si_4H_6	69.7		
Si_4H_8	16.5	16.6	23
Si_5H_6	71.3		
Si_5H_8	37.4		
CSi_2H_6	43.3		
C_2SiH_6	40.2		
1,3-$Si_2C_2H_6$	96.3		
2,4-$Si_2C_2H_6$	71.4		
SiC_3H_8	23.3		16.8
1,3-$Si_2C_2H_8$	20.6		24.6
Si_3CH_8	19.3		
1,3-$Si_2C_3H_6$	94.0		
1,3-$Si_2C_3H_8$	59.3		
2,4,5-$Si_3C_2H_6$	106.0		
2,4,5-$Si_3C_2H_8$	54.2		

[a] Strain Energies in kcal/mol. Experimental results from ref 9 for hydrocarbons, ref 20 for silanes, and ref 20 for organosilanes.

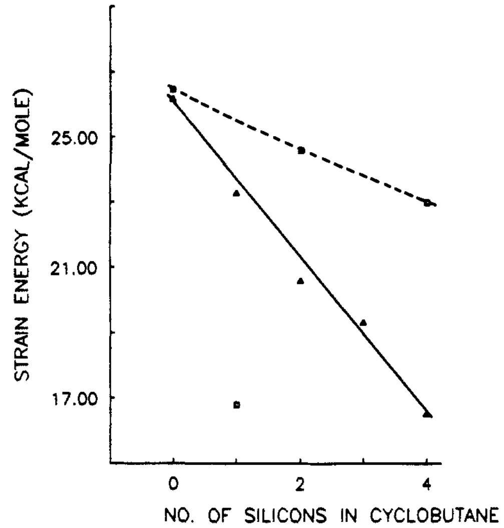


Figure 1. Strain energy versus the number of silicons in the set of silacyclobutanes ($C_nSi_{4-n}H_8$, n = 0–4): experimental points, □; theoretical points, △. The theoretical curve lies below the experimental curve because of steric strain between substituents on experimentally measured species. Note that the experimental point for 1-silacyclobutante appears to be incorrect.

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(18) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(19) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(20) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.

(21) Wiberg, K. B. *J. Comp. Chem.* **1984**, *5*, 197.

(22) Ibrahim, M. R.; Schleyer, P. v. R. *J. Comp. Chem.* **1985**, *6*, 157–167.

(23) Watanabe, H.; Shimoyama, H.; Muraoka, T.; Okawa, T. *Chem. Lett.* **1986**, 1057.

(24) O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* **1981**, *213*, 419.

(25) The optimized CEP-31G* SiSi distance in Si_2H_4 is 2.13 Å. From an X-ray crystal structure of a substituted disilene the SiSi distance is 2.14 Å.[26]

(26) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333.

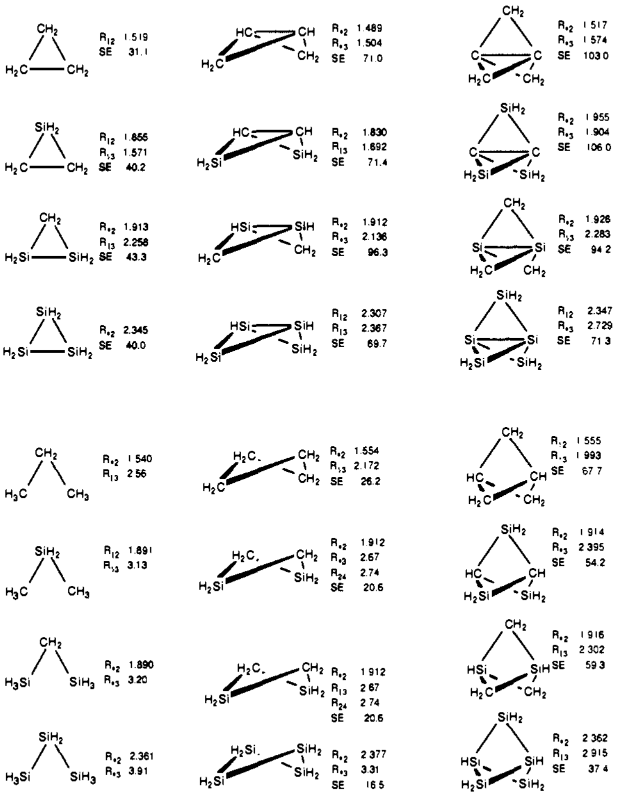

Figure 2. Geometries and strain energies versus the number of rings. Top half: cyclopropane, bicyclobutane, [1.1.1]propellane, and organosilicon analogues. Bottom half: propane, cyclobutane, bicyclo[1.1.1]pentane, and organosilicon analogues. R_{13} refers to bridgehead–bridgehed distance and R_{12} refers to bridgehead–bridge distance.

silicon-substituted cyclobutanes are plotted and these plots strongly suggest that the value for silacyclobutane is in error. We predict that for 1,1-dimethyl-1-silacyclobutane this value should be 25.5 kcal/mol. The dashed curve connecting experimental points and the calculated points correctly shows a parallel decrease with increasing silicon content because angle strain and eclipsing hydrogen repulsions are decreasing. The experimental curve may lie above the computed one because the experimental data derives from molecules with methylated silicons which introduce steric strain unrelated to the electronic ring strain determined by the theoretical calculations on the unmethylated species. It is interesting to note that the electronic ring strain appears to be an almost linear function of the number of silicon atoms in the ring.

C. Synthetic Opportunities. The data tabulated in Table II have important implications for experimental studies of organosilicon compounds. First, the low strain energy of Si_5 propellane indicates that it should be a reasonably stable molecule and since tetrasilabicyclo[1.1.0]butane has already been synthesized and its X-ray crystal structure determined, the propellane is a likely synthetic target. Second, these strained rings offer the advantage to the synthetic chemist that competing double bonded species are not likely to be very stable, unlike the hydrocarbon strained rings. Third, the polymerization possibilities do not appear to be very good for the Si propellanes since the decreased strain upon polymerization (as estimated by the decrease in strain energy upon hydrogenation) is no more than in the [1.1.1]propellane. In net, it appears that most of the strained species listed in Table II are likely to be reasonably stable and good candidates for synthesis.

Trends and Rationalizations

A summary of the geometry and strain energies of the compounds in this study is presented in Figure 2. For this discussion we will assume that normal C–C, Si–C, and Si–Si single bond lengths are 1.54, 1.89, and 2.36 Å, respectively, based on ethane, methylsilane, and disilane CEP-31G* optimized geometries. We will first consider the geometric trends within the top half of the table. The organizing principle for geometries is that bridging *carbons* shorten opposite silicon–silicon bonds and lengthen proximal silicon–carbon bonds. Bridging *silicons* lengthen opposite carbon–carbon bonds and shorten adjacent silicon–carbon bonds. Consider the cyclopropanes. The C–C bond length in cyclopropane is 1.519 Å but in 1-silacyclopropane the C–C bond length is stretched to 1.571 Å. The opposite trend holds for the cyclotrisilane and 1,2-disilacyclopropane where the bond length shrinks from 2.345 to 2.258 Å. Note that 2.258 Å is nearly half way between a Si–Si single and double bond length.[22] The results are true for the bicyclobutanes and propellanes as well. In fact, the trend for Si bridging of two carbon atoms is even more pronounced in 2,4-disilabicyclo[1.1.0]butane and 2,4,5-trisila[1.1.1]propellane where the C_1–C_3 distance is stretched to 1.692 and 1.904 Å, respectively (the long C–C distance in the 2,4-disilabicyclo[1.1.0]butane has been confirmed by X-ray crystal structure measurement[17]). The very short Si_1–Si_3 bond in the 1,3-disilabicyclo[1.1.0]butane is likewise indicative of Si–Si bond shortening due to bridging carbons (the Si_1–Si_3 bond length of 2.136 Å is nearly that of an Si–Si double bond).

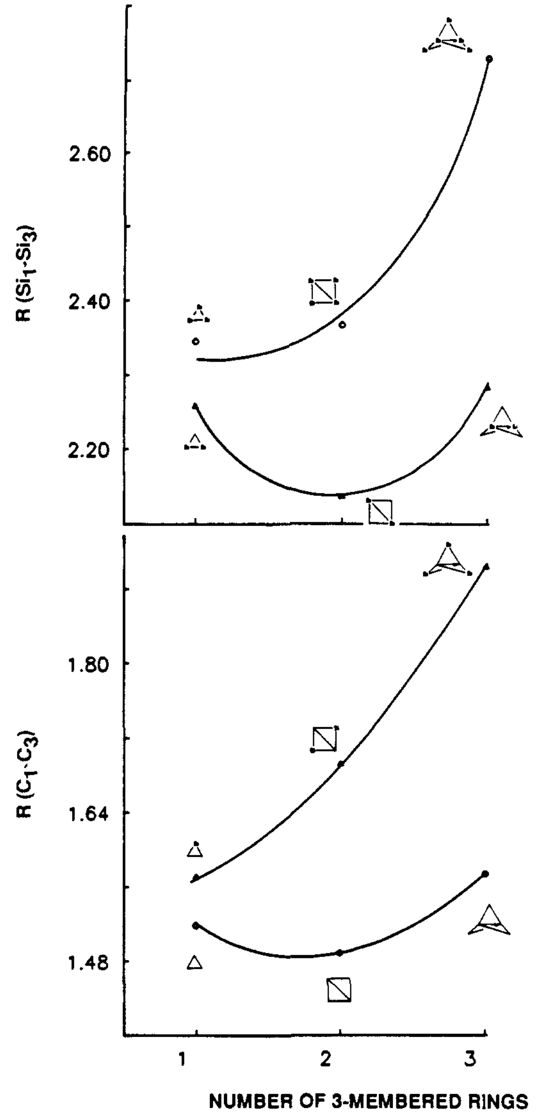

Figure 3. CC and SiSi bond lengths versus the number of fused 3-membered rings for hydrocarbons, organosilanes, and silanes.

Figure 3 plots C_1–C_3 and Si_1–Si_3 bond lengths versus the number of rings for the twelve molecules at the top of Figure 2 (for consistency we label the two silicons in disilacyclopropane as Si_1 and Si_3 henceforth). If we focus our attention along a vertical line (e.g., connecting the four molecules with one three-membered ring) through both the $R(C_1$–$C_3)$ and $R(Si_1$–$Si_3)$ graphs we find the well-ordered sequence of geometries discussed in the paragraph above. If we now focus on R_{13} as a function of the number of fused rings the trends fall into two sets. The C_1–C_3

and the Si_1–Si_3 distances clearly are dependent on the type of bridging atom (that is, the atom in the 2 position). If a methylene group is bridging, the opposite bond internuclear separation (for both Si–Si and C–C) follows a parabola as the type of molecule goes from cyclopropane to bicyclobutane to propellane. If a silylene group is bridging then the opposite bond internuclear separation (whether Si–Si or C–C) increases monotonically as the number of rings increases. One line of reasoning (see section on MO model) suggests that R_{13} should have decreased from the bicyclobutanes to the propellanes rather than the observed increase.

The trend of strain energies down vertical columns of Figure 2 is now considered. Among the cyclopropanes, the hydrocarbon has the least strain energy. The other three molecules have nearly the same strain energy within expected errors. At first glance, the higher strain energy values for cyclotrisilane, 1-silacyclopropane, and 1,2-disilacyclopropane appear counter-intuitive since ring strain is commonly explained in terms of angle bending force constants. Since all the silicon-containing cyclopropanes have higher strain energies relative to cyclopropane than would be expected based on the force constant model (angle bending around Si is known to have a lower force constant than that for C), other factors within the electronic structure must be at work in these systems. The low strain energy of cyclopropane with respect to other hydrocarbon rings has been well documented. A common rationalization has been that the ring is σ aromatic[11] or a nearly equivalent idea is that it has surface delocalization.[12] Within this column these hypotheses may be viable since, as shown for hexasilabenzene,[6] it is expected that silicon atoms are less able to delocalize electrons, thus cyclotrisilane has a significantly higher strain energy than cyclopropane. Alternatively, since Si–Si double bonds are known to be weaker than C–C double bonds, the weakness of Si–Si bent bonds would also be expected. The geometries of these two molecules also indicate a difference in the degree of delocalization (or at least in the degree of bent bonding): the C–C bond in cyclopropane is 2% shorter than a normal C–C bond length while the Si–Si bond length in cyclotrisilane is nearly equal to a normal Si–Si bond length. Strain energies for the Si_1 and Si_2 cyclopropanes yield a less obvious pattern. On the one hand strain energy should be proportional to the number of silicon atoms because of the expected decrease in electron delocalization as silicon atoms are added to the ring. On the other hand, silicon has smaller bending force constants than carbon. Both the electron delocalization and bent bond models predict shorter than normal bond distances in three-membered rings. In cyclopropane and cyclotrisilane in the bond distances, are short but in the 1-silacyclopropane and 1,3-disilacyclopropane the bond distances clearly do not follow this pattern. A long CC distance is found in 1-silacyclopropane and a somewhat short SiC distance. An opposite trend is found in the disilacyclopropane: a short SiSi distance and somewhat long SiC distances. These two molecules may be showing a lack of delocalization due to poor orbital energy and size matching which are both necessary for efficient delocalization. Thus the mixed cyclopropanes have less electron delocalization and therefore higher strain energies than either cyclopropane or cyclotrisilane.

In the bicyclobutanes and propellanes two other patterns of strain energies arise. In bicyclobutanes strain energies appear unrelated to bond lengths: bicyclo[1.1.0]butane, 2,4-disilabicyclo[1.1.0]butane, and tetrasilabicyclo[1.1.0]butane have nearly the same strain energies yet C_1–C_3 in bicyclo[1.1.0]butane is 0.203 Å shorter than in 2,4-disilabicyclobutane. The tetrasilabicyclo[1.1.0]butane has a nearly normal Si_1–Si_3 bond length yet its strain energy is smaller by 25 kcal/mol than 1,3-disilabicyclo[1.1.0]butane even though it has the shortest Si–Si bond of all the single bonded structures in this study. The propellanes are no less confusing: [1.1.1]propellane and 2,4,5-trisila[1.1.1]propellanes have nearly the same strain energy yet they possess strikingly different C_1–C_3 bond lengths. Bond lengths in the pentasila[1.1.1]propellane and 1,3-disila[1.1.1]propellane are 2.729 and 2.283 Å, respectively, which should reflect a very unstable pentasila[1.1.1]propellane species and a rather stable 1,3-disila[1.1.1]propellane, but strain energies reveal that the pentasila[1.1.1]propellane is by far the stablest of all four propellanes studied. Rationalization of these trends in strain energies is found by examining strain energy as a function of the number of fused rings.

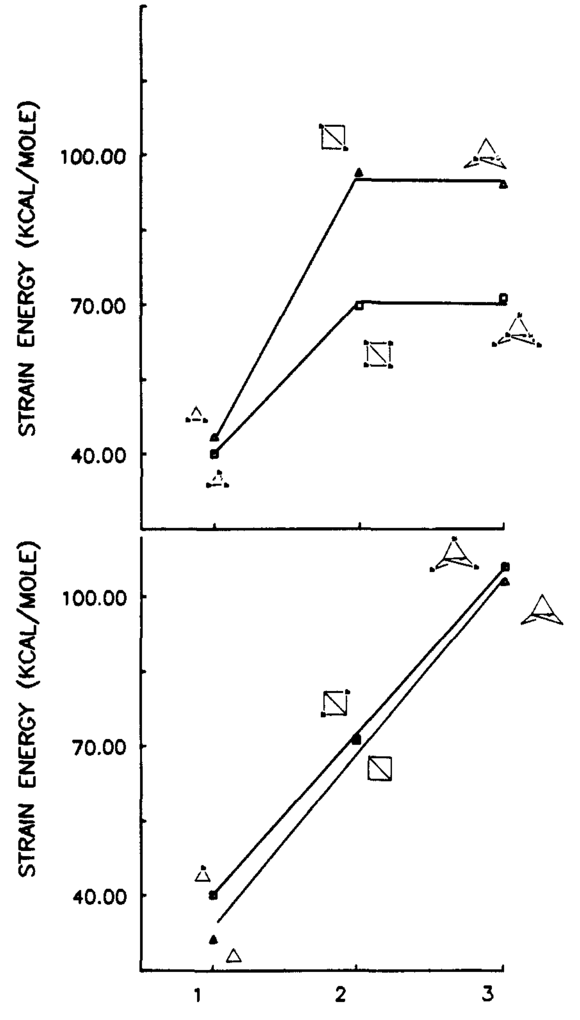

Figure 4. Strain energy versus the number of fused 3-membered rings for hydrocarbons, organosilanes, and silanes.

Figure 4 plots strain energy versus the number of rings. Again two sets of curves are apparent. Here the strain energy is dependent on the atoms at the bridgeheads. If carbon atoms are at the 1 and 3 positions strain energy increases nearly linearly from cyclopropane to bicyclobutane to propellane. On the other hand, if silicon atoms are at the 1 and 3 positions the strain energy curve shows saturation behavior as the number of rings is increased. We conclude from this that the strain energy is dependent upon the atoms making the central bond, but not on the bridging atoms (this is also true in the heterocyclic cyclopropanes, such as oxetane and aziridine, which have nearly the same strain energy as cyclopropane[12]). Janoschek has shown that silicon is less sensitive to hybridization changes than carbon due to its narrower s–p gap and its larger atomic size.[27] Thus, in the Si_nH_n polyhedranes strain energy decreases as n increases unlike the analogous hydrocarbons.[8] The silicon propellanes ($Si_2C_3H_6$ and Si_5H_6) are as stable as the silicon bicyclobutanes ($Si_2C_2H_6$ and Si_4H_6) again unlike the hydrocarbon case and 2,4,5-trisila[1.1.1]propellane where the strain energy continues rising.

The discussion in the paragraphs above has been concerned with the $X_nY_mH_6$ species, the top half of Figure 2. For the bottom half of the table, the hydrogenated forms, $X_nY_mH_8$, the most interesting trends fall into three categories. First, as in the dehydrogenated form, the distances opposite bridging carbons are

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[27] Janoschek, R. *Naturwiss. Rundsch.* **1984**, *37*, 486.

short nonbonded distances. The 1,3-disilacyclobutane nonbonded Si–Si distance, 2.67 Å, is shorter than the nonbonded C–C distance in this molecule and in $(CH_3)_2SiH_2$ and also shorter than the bonding Si_1–Si_3 distance in pentasila[1.1.1]propellane. The shorter SiSi distance means that in 1,3-disilacyclobutane carbon has a smaller bond angle than silicon in contrast to $(CH_3)_2SiH_2$ and $(SiH_3)_2CH_2$ and in disagreement with the force constant model of strain energies. This has been previously shown in other theoretical calculations[28] and in crystal structures.[29] An even shorter distance is found in the 1,3-disiladioxetane where the 2.40 Å Si–Si nonbonded distance is approaching that of a normal Si–Si bond.[29,30] We also note that the 1,3-disilabicyclo[1.1.1]pentane is only 0.019 Å longer than the corresponding propellane and in fact is shorter than an Si–Si bond. These results show the effect of bridging by a more electronegative atom on the opposite interatomic distance, even if it is not bonding. Second, in contrast to Figure 3, a plot of $R(C_1$–$C_3)$ and $R(Si_1$–$Si_3)$ for the bottom twelve molecules in Figure 2 yields a set of monotonically decreasing lines as the number of fused rings increases. This pattern is not surprising since an increase in the number of constraints placed on nonbonded R_{13} separations would be expected to successively shorten it. If the corresponding R_{13} values from the top half of Figure 2 are subtracted from these nonbonded R_{13} separations, the resulting R_{13} changes display a very strong dependence on the number of fused rings. The hydrogenation of the single rings results in an average R_{13} change (an increase) of 1.25 Å (40%), and those for two and three rings show changes that decrease geometrically in the ratio 5:3:1. Thus in the propellane structures there is relatively little difference between the 1–3 distances in nonbonded and bonded species suggesting that the region inside these molecules along the line between atoms 1 and 3 has much less charge than found in ordinary single bonds. Third, the larger 1–3 separations in the hydrogenated species obviously result in less angle and bond stretching strain (SE values in the bottom half of Figure 2 average 45 kcal/mol less than the top half). In contrast to Figure 4, strain energy versus the number of rings for the hydrogenated species rises approximately linearly in all four molecular sets. As expected, the line for the all-silicon molecules rises less steeply than the others because of their smaller angle bending force constants.

Electronegativity and Molecular Orbital Models

Given the complexity of the trends in geometries and strain energies catalogued above, it would clearly be useful to have a simple conceptual framework to explain and model the observed behavior. Partial equilization of electronegativity provides the simplest model. Bridging carbons absorb charge and become larger while bridging silicons become smaller. Thus bonds adjacent to carbons in silacyclopropane become longer than ordinary Si–C bonds and the bond opposite becomes shorter. The reverse trend is expected in the disilacyclopropane, the heterobicyclobutanes, and propellanes since the bridging atoms are more electronegative than the bridgeheads. A predictive mnemonic for the geometric trends is that adjacent atoms become more like each other in molecules: carbons become larger when near silicons and silicons become smaller when near carbons. The origin of this rule is found in molecular orbital arguments below.

From the molecular orbital viewpoint, there is certainly evidence for σ aromaticity, surface delocalization, and bent bonds in the cyclopropanes. But are there more general principles at work among all the fused ring systems? The collection of molecules we are treating starts with a single ring and successively fuses a second and third ring. Thus to a first approximation one may hope that many of the properties will be manifest in the orbitals of a single ring. We may expect to represent the trends we are interested in by examining orbital changes across the series C_3H_6, C_2SiH_6, CSi_2H_6, and Si_3H_6 using the highest common symmetry, C_{2v}. Others have shown[12,31] that the principal features of oxirane and 1-silacyclopropane could be analyzed as heteroatom-substituted cyclopropanes using only the two highest MOS: A_1 and B_2. We apply their approach, displaying the A_1 and B_2 MOs for our series in Figure 5. First, if a silicon is substituted for a carbon in cyclopropane there is a shift of charge in B_2 (a π* orbital) to the two remaining carbons from Si. This lengthens the CC bond and shortens Si–C. There is a concomitant reduction in the π-like character of the CC bond in the A_1 MO. One consequence is that H–C–H planes fold in toward each other. Second, if a carbon is substituted for a silicon in cyclotrisilane the more electronegative carbon withdraws charge from the Si–Si π* fragment (B_2 MO) shortening the Si–Si bond. Synergistically, the A_1 orbital becomes more π-like as is seen by comparing the A_1 orbital of 1,2-disilacyclopropane with the A_1 orbital of cyclotrisilane. In turn, the more π-like nature of the Si_2 fragment pushes the two H–Si–H planes away from each other decreasing the pyramidalization around the silicon atoms. The role of the A_1 orbitals is to delocalize electrons over three centers with use of a bridging group orbital.

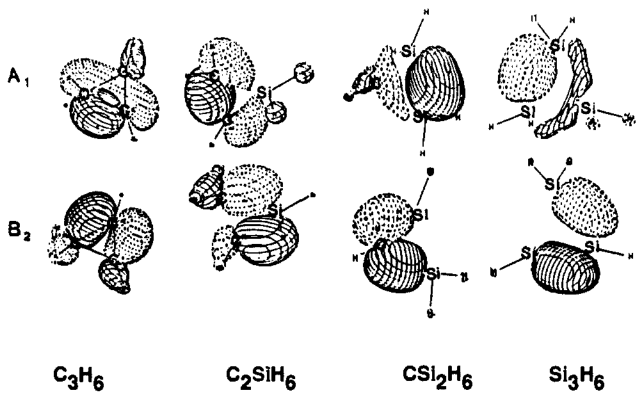

Figure 5. Two highest molecular orbitals in organosilicon cyclopropanes.

1,3-Disilabicyclo[1.1.0]butane has MOs like those in CSi_2H_6: a very high degree of π bonding between the Si atoms (the Si p orbitals in its HOMO are nearly parallel). As a consequence 1,3-disilabicyclo[1.1.0]butane has an extraordinarily short Si–Si separation (2.135 Å) and a very large Si_1Si_3H angle (164.1°). In contrast, 2,4-disilabicyclo[1.1.0]butane, a C_2SiH_6 analogue, has a CC distance of 1.692 Å and an HC_1C_3 angle of 122° (smaller than the 130.9° in C_4-bicyclobutane).

Similar MO arguments account for changes in R_{13} and strain energies for the propellanes. In [1.1.1]propellane the orbitals that bind C_1 to C_3 are an A_1-like degenerate pair that has been termed σ-bridged-π and previously described.[32] The 2,4,5-trisila-[1.1.1]propellane is a C_2SiH_6 analogue whose long C_1–C_3 separation results from a pair of orbitals like the B_2 orbital in silacyclopropane. In contrast, the Si_2 propellane is a CSi_2H_6 analogue with a short Si–Si separation of 2.28 Å (versus 2.35 Å in cyclotrisilane), arising because of a strong π interaction in the pair of orbitals like the A_1 MO in disilacyclopropane, and because of electron withdrawal from the π* Si_2 fragment of its B_2-like MOs. The most unusual propellane is Si_5H_6: its Si_1–Si_3 separation of 2.73 Å is 16% longer than the cyclotrisilane bond length, yet its string energy of 71.3 kcal/mol is less than twice that of cyclotrisilane. The bonding that extends over three centers in its A_1-like π orbitals is largely responsible for this remarkable combination of properties.

There is another important molecular orbital in the propellanes, not present in our three-atom model, which we have so far omitted. This is the σ MO between atoms 1 and 3 and in these species it is the HOMO. From Figure 3, R_{13} versus the number of rings, it is immediately apparent that there is an anomaly with respect to the 1–3 bond: for the sequence Si_2CH_6, $Si_2C_2H_6$, $Si_2C_3H_6$ a monotonic decrease in R_{13} is expected since formation of the

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[28] O'Keefe, M.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 4574.

[29] (a) Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253. (b) Peters, v. K.; Peters, E.-M.; Schnering, H.-G. v. *Anorg. Allg. Chem.* **1983**, *502*, 61.

[30] Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.

[31] Delker, G. L.; Wang, Y.; Stucky, G. D.; Lambert, R. L., Jr.; Haas, C. K.; Seyferth, D. *J. Am. Chem. Soc.* **1976**, *98*, 1779.

[32] Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.

1,3-disilapropellane adds one more electronegative bridge to the corresponding bicyclobutane. But, in fact, R_{13} increases from the bicyclobutanes to the propellanes in all cases (including the parallel sequence C_3H_6, C_4H_6, and C_5H_6). The origin of this propellane anomaly is easy to discern: the atoms 1 and 3 are inverted (all four of the σ bonds connected to atoms 1 and 3 are in one hemisphere). To understand the electronic charge distribution consequences of the inversion we start with a normal 1–3 σ bond, but initially imagine the 1–2, 1–4, and 1–5 bonds pointing away from the propellane cage in a normal tetrahedral arrangement. Now when the 1–2, 1–4, and 1–5 bonds are bent back to their positions along the sides of the propellane cage, the 1–3 bond will also invert and put its charge in a lone pair outside the cage, thereby maintaining approximate sp^3 hybridization around atoms 1 and 3. Thus the σ HOMOs in propellanes are more nearly lone pairs than bond pairs and do not appreciably contribute to the string energy or geometry of the propellanes.

Summary

1. Geometries and strain energies have been obtained for 23 organosilicon molecules representing successive replacement of C by Si in cyclopropane, bicyclobutane, and [1.1.1]propellane and the corresponding 1,3-dihydrogenated species. Wave functions were constructed by using the recently developed effective core potentials with the CEP-31G* basis set. This procedure was fully tested and validated against existing experimental data and existing ab initio calculations.

2. Many new or improved values for geometries and strain energies were determined and predictions were made for some as yet unknown silanes and silicon–carbon compounds.

3. Synthetic opportunities for realizing the predicted molecules were assessed relative to their strain energies, stability of competitive multiply bonded species, and polymerization likelihood and were found to be good candidates.

4. Geometries for the set of molecules investigated were compared by arranging them in the form of a periodic table. R_{13} trends down a family of molecules (corresponding to successive replacement of C by Si) are governed by the electronegativity of the bridging atoms. R_{13} across a row (corresponding to successive additions of fused rings) decreases for the 1,3 nonbonded (hydrogenated) species and generally increases for the 1,3 bonded species.

5. Strain energies were also arranged according in a periodic table format. Values in a given column were almost constant. Values across a row showed nearly linear increases. The two exceptions result from an unusually short R_{13} (yielding a high strain energy) and an unusually long R_{13} (yielding a low strain energy) and show up as saturation curves in the top graph of Figure 4.

6. A molecular orbital model comprising the two highest MOs of cyclopropane, silacyclopropane, disilacyclopropane, and cyclotrisilane was able to explain the geometric and strain energy data for all the multiple ring molecules as well as the single ring species. Many of the trends are also able to be rationalized by simple electronegativity differences and electronegativity equalization arguments.

Note Added in Proof. P. Schleyer, A. Sax, J. Kalcher, and R. Janoschels [*Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364] have computed structures for bicyclo[1.1.0]tetrasilanes at close to the same level as ours and obtain geometrical results almost identical to ours. Their work is directed toward the possibility of bond stretch isomerism in these molecules and we have another paper [*Bond Stretch Isomerism in Silabicyclobutanes.* Kitchen, D. B.; Allen, L. C. To be published] addressing this question. Nagase and Kudo (*Organometallics* **1987**, *6*, 2456) have calculated structures and strain energies for the pentasila[1.1.1]propellane and octasila[2.2.2]propellane at the HF/6-31G* levels. The former result is in agreement with the results of this work. The calculated bridgehead Si–Si distance of the [2.2.2]propellane and of the trioxa-substituted [1.1.1]propellane is consistent with predictions of this work on the nature of bonding in strained silicon systems.

A particularly important paper by D. Cremer, J. Gauss, and E. Cremer [*J. Mol. Struct.* (*Theochem*) **1988**, *169*, 531] has decomposed three-membered ring strain energies into bond angle strain (Baeyer strain), bond eclipsing strain (Pitzer strain), stretching strain, and nonbonded repulsion and related these to the degree of p character in the ring bond-forming hybrid orbitals for the same single ring carbon and silicon combinations we have treated. The strain energy analysis, which is contained in another recent article by D. Cremer and E. Kraka (Cremer) [*Structure and Reactivity*, Liebman, J. F., Greenberg, A., Eds.; VCH Publications: New York, 1988, Chapter 3, pp 65–137] is based on a new and sophisticated formulation of its basic principles and limitations. Their general conclusions concerning the bonding in these three-membered rings is entirely equivalent and complementary to ours. Their discussion of sp^n hybridization provides a useful new way of understanding three-membered rings, and they have concluded that the most important difference between the C and Si rings is that Si is unable to form sp^n hybrid orbitals with sufficiently high p character to guarantee flexible bent bond orbitals. As noted by Cremer, Gauss, and Cremer, the tendency of second-row atoms to employ less p character than first-row atoms has been well-established in a brilliant and thorough analysis of this problem by W. Kutzelnigg [*Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272]. Kutzelnigg showed that this resulted from the fact that 3s AOs are located significantly closer to the nucleus than 3p AOs while the reverse is true for first-row atoms. For Si we can quantify this difference by superposing the radial maximum positions of the C 2s on the Si 3s and determining the percent increase in elongation of the 3p radial maximum over that of the 2p radial maximum (for Hartree–Fock atomic orbitals) using the position of the C 2s radial maximum as reference. The Si 3p is 31% more elongated. A principal thrust of our work has been to understand the bonding patterns as one goes from the single silicon-containing rings to the larger systems containing two and three rings, and in the future we hope to make a detailed quantitative analysis of the p participation change in sp^n hybrids as the number of rings increases.

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Registry No. C_3H_6, 75-19-4; C_2SiH_6, 157-21-1; CSi_2H_6, 51130-21-3; Si_3H_6, 18548-76-0; $CH_3CH_2CH_3$, 74-98-6; $(CH_3)_2SiH_2$, 1111-74-6; $(H_3Si)_2CH_2$, 1759-88-2; Si_3H_8, 7783-26-8; C_4H_6, 157-33-5; 2,4-$Si_2C_2H_6$, 79647-93-1; 1,3-$Si_2C_2H_6$, 110797-75-6; Si_4H_6, 98721-26-7; C_4H_8, 287-23-0; 1,3-$Si_2C_2H_8$, 287-55-8; Si_4H_8, 287-69-4; C_5H_6, 35634-10-7; 2,4,5-$Si_3C_2H_6$, 110935-76-7; 1,3-$Si_2C_3H_6$, 110935-77-8; Si_5H_6, 110698-79-8; C_5H_8, 311-75-1; 2,4,5-$Si_3C_2H_8$, 110935-78-9; 1,3-$Si_2C_3H_8$, 103231-36-3; Si_5H_8, 110935-79-0.