MOLECULAR STRUCTURES OF SILACYCLOHEXANE AND SILACYCLOPENTANE AS DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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ABSTRACT

The molecular structures of silacyclopentane and silacyclohexane are determined by gas phase electron diffraction.

Silacyclohexane is found to exist in a modified chair conformation which is somewhat flattened (relative to cyclohexane) at the silicon atom and somewhat puckered at the C₄ position. The Si—C ($r_g = 1.885(3)$ Å) and C—C ($r_g = 1.550(3)$ Å) bond lengths were found to be comparable with those observed in more highly strained polycyclic molecules such as 1-methyl-1-silaadamantane and 1-methyl-1-silabicyclo(2.2.1)heptane. Valence angles for the ring were found to be: $\angle C_s SiC_1 = 104.2(1.4)^\circ$, $\angle SiC_1C_2 = 110.6(0.6)^\circ$, $\angle C_1C_2C_3 = 113.7(1.1)^\circ$ while the observed dihedral angles were: $\tau(Si-C) = 44.0(4.2)^\circ$, $\tau(C_1-C_2) = 57.3(2.0)^\circ$ and $\tau(C_2-C_3) = 67.5(2.0)^\circ$.

Combined analysis of electron diffraction and microwave spectroscopic data for silacyclopentane shows that the molecule exists in the C_2 or twist conformation with Si-C and average C-C bond lengths of 1.892(2) Å and 1.549(3) Å respectively. The valence angles obtained for the ring are: $\angle C_4 \operatorname{SiC}_1 = 96.3(0.3)^\circ$, $\angle \operatorname{SiC}_1 C_2 = 103.6(0.3)^\circ$ and $\angle C_1 C_2 C_3 = 108.4(0.7)^\circ$, while the ring dihedral angles are: $\tau(\operatorname{Si-C}) = 13.3(0.4)^\circ$, $\tau(C_1 - C_2) = 36.1(1.0)^\circ$ and $\tau(C_2 - C_3) = 49.7(1.4)^\circ$.

Molecular mechanics calculations are found to be helpful in interpreting the structures and conformations of these two molecules in terms of simple Bayer and Pitzer strain energy concepts.

INTRODUCTION

We have recently studied the structures of 1-methyl-1-silabicyclo(2.2.1)heptane [1] and 1-methyl-1-silaadamantane [2]. These molecules contain rather highly strained bridgehead silicon atoms, and the geometry at the bridgehead silicon has been shown to have a marked effect on the relative reactivities of these compounds [3]. For purposes of comparison with these highly strained polycyclic organosilanes, we also became interested in the structures of the simpler silacycloalkanes. With the single exception of silacyclobutane [4], complete structures of many of these compounds have not been determined by either microwave spectroscopy or gas phase electron diffraction. We therefore decided to undertake an investigation of the structures of silacyclopentane and silacyclohexane.

Silacyclopentane has been studied by a variety of spectroscopic methods. Laane [5] has investigated the hindered pseudorotational motion of silacyclopentane in the far IR. He concluded that silacyclopentane had a twofold pseudorotational potential function with a 4.04 kcal mole⁻¹ barrier and a potential minimum for the C_2 twist conformation. This was further reinforced by the complete vibrational assignment and far IR study of Durig and co-workers [6]. Philen, Chao and Laane [7] later determined a valence force field for silacyclopentane and two 1,1-dihalogenated silacyclopentanes. Durig, Lafferty and Kalasinsky [8] have also studied the microwave spectrum of silacyclopentane and two of its isotopically substituted forms; however, no attempt was made by these authors to determine a complete substitution structure for the molecule.

Very little is known about the structure or conformation of silacyclohexane. Two independent studies [9, 10] involving molecular mechanics calculations on silacyclohexane and substituted silacyclohexanes have been reported. Both studies have concluded that silacyclohexane exists in a chair conformation which is more flattened than cyclohexane in the region of the silicon atom and more puckered in the region of C₄. These calculations also predict about 4.5 kcal mole⁻¹ energy difference between the chair and skew-boat forms of the molecule.

We felt that a structural study of these two molecules would provide an interesting comparison with our previously published structures on the polycyclic organosilanes. Silacyclopentane was also of interest to us since it offered the possibility of a combined electron diffraction and microwave spectroscopic investigation which has several advantages over the more conventional analyses involving only electron diffraction data.

EXPERIMENTAL

Samples of silacyclopentane and silacyclohexane were prepared by reduction of their 1,1-dichloro- derivatives with $LiAlH_4$. The samples were purified by preparative gas chromatography, and were found to be > 98% pure by analytical gas chromatography.

Electron diffraction patterns were obtained using the Indiana University diffraction unit. Data were collected under identical conditions for both samples at 12 and 29 cm using a 40-keV accelerating potential. The samples were introduced into the scattering chamber through a stainless steel inlet system at 298 K, and carbon dioxide calibration photographs were used for s-scale calibrations as described elsewhere [1].

Three photographic plates for each camera distance were microphotometered on the Indiana University automated microdensitometer [11]. After applying the standard corrections for emulsion saturation, plate flatness and sector imperfections, the data were interpolated at integral $q(40/\pi \sin(\theta/2))$ intervals and averaged together for least-squares analysis. Least-squares analyses were performed on the spliced levelled intensity curves in the usual manner [12] using the elastic scattering factors of Schäfer, Yates and Bonham [13] along with the inelastic scattering factors calculated by Tavard et al. [14]. Tables of raw intensity data, backgrounds, and correlation and error matrices for both molecules are available as supplementary material from BLLD [15].

DATA ANALYSIS

Vibrational amplitudes and shrinkage correction parameters for both molecules were calculated using the general valence force field for silacyclopentane reported by Philen, Chao and Laane [7]. The only modification in this force field was to include a single torsional force constant of 0.055 mdyne Å for twisting about the Si–C and C–C bonds. This choice of torsional force constant gave calculated frequencies of 208 cm⁻¹ for the radial ring mode and 100 cm⁻¹ for the pseudorotational mode of silacyclopentane. These values are in reasonable agreement with the assigned frequencies of 264 cm⁻¹ and 101 cm⁻¹ for these two modes of vibration. During the least-squares analysis of both molecules, only a few amplitude parameters were varied while the remainder were constrained to their calculated values. Anharmonicity correction terms were assumed to be 2.0 Å⁻¹ for Si–C and C–C bonds and 2.5 Å⁻¹ for C–H and Si–H bonds.

The transferability of the silacyclopentane force field to silacyclohexane is somewhat questionable; however, it is our experience that amplitudes calculated from a transferred force field are reliable enough for most analyses. The basis for this assumption arises from the fact that experimental uncertainties in amplitudes determined from least-squares analyses of electron diffraction data are often much larger than the differences between observed amplitudes and those calculated from a transferred force field.

Silacyclohexane

The structural analysis of silacyclohexane was simplified by the introduction of the following assumptions:

1. Only one C_s chair type conformation was assumed to be present in any appreciable amount. This is consistent with the estimated chair-twist boat energy difference of 4.5 kcal mole⁻¹ predicted from molecular mechanics calculations.

2. Only one average C—C bond length was refined with no attempt to resolve the two different types dictated by symmetry.

3. The methylene hydrogens were all located by assuming a single average C-H bond length and one single \angle CCH angle. For the hydrogens attached to C₁ and C₅, the \angle SiCH and \angle CCH angles were presumed equal.

Independent parameters ^b		Dependent parameters ^c		
$Si-C$ $C-C_{av}$ $Si \cdots C_{2}$ $C_{1} \cdots C_{3}$ $C_{1} \cdots C_{5}$ $C_{2} \cdots C_{5}$ $Si-H$ $C-H_{av}$ $L CSiH$ $L CCH_{av}$ $= L SiCH$ $l_{C}-H$ $l_{C}-C$ $l_{Si}-C$ $l_{Si}-C_{2}$	$\begin{array}{c} 1.885(3)\\ 1.550(3)\\ 2.820(10)\\ 2.588(18)\\ 2.966(34)\\ 3.154(13)\\ 1.465(22)\\ 1.115(5)\\ 112.0(3.7)\\ 110.5(0.8)\\ 0.074(5)\\ 0.053(3)\\ 0.056(3)\\ 0.088(7)\\ 0.112(9)\\ \end{array}$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		
av.	0.11(0)			

Structural parameters for silacyclohexane obtained from least-squares analysis^a

^aDistances (Å) are reported as r_g values and angles (in degrees) are reported as r_{α} parameters which have been corrected for shrinkage. Reported errors are 3σ values obtained from the least-squares analysis. ^bIndependent parameters are those used to construct the model for the compound, and are therefore the parameters which were varied in the leastsquares analysis. ^cDependent parameters were calculated from the final model, and the reported errors were obtained by transferring the elements of the error matrix. ^d ϕ_1 is the obtuse dihedral flap angle between the plane containing C₁, C₂, C₄ and C₅. ^e ϕ_2 is the flap angle between the planes containing C₂, C₃ and C₄ and the plane containing C₁, C₂, C₄ and C₅.

The above assumptions reduce substantially the number of parameters required to specify the model. The parameter set chosen for the analysis is shown in Table 1, while Fig. 1 indicates the numbering system used in defining the parameters. A total of 10 geometrical parameters and 5 amplitude parameters were refined. Note that for the molecular skeleton, bonded and non-bonded distance parameters rather than angular parameters were used to construct the molecular model since their locations were somewhat easier to identify in the radial distribution curve.

The only major difficulty encountered in the analysis was the determination of a precise geometry for the SiH₂ moiety. This difficulty was to be expected since the Si-H and C-C distances are rather close together (1.465(22) Å and 1.550(3) Å respectively). This problem was further compounded by the fact that the C··H distance spanning the \angle CSiH angle was obscured by its proximity to the C₂··Si distance. For these reasons the uncertainties in the Si-H bond length and the \angle CSiH valence angle are quite large.

The final results of the least-squares analysis are indicated in Table 1, while the intensity curves and radial distribution curves for silacyclohexane are shown in Figs. 2 and 3 respectively.



Fig. 1. Atomic numbering for silacyclohexane.



Fig. 2. Levelled molecular intensity curves for silacyclohexane.

Silacyclopentane

It was anticipated at the outset of the analysis that silacyclopentane preferred the twisted C_2 conformation to the C_s envelope conformation. This was quite easily verified on the basis of the diffraction data alone by attempting a preliminary analysis of the C_s structure. It was possible to fit all of the bonded regions of the radial distribution; however, there were found to be large discrepancies in the longer non-bonded distances when a



Fig. 3. Radial distribution curves for silacyclohexane.

 C_s model was refined. C_2 symmetry was therefore assumed for the remainder of the analysis along with the following simplifying assumptions:

1. All C-H bond lengths were constrained to one common value.

2. All \angle CCH valence angles were constrained to a single parameter, and the \angle SiC₁H and \angle SiC₄H valence angles were also assumed to be equal to this parameter.

A preliminary analysis of the C_2 model consisting of 9 structural parameters and 4 amplitude parameters was conducted using only the electron diffraction data. The independent parameters chosen are listed in the top half of Table 2, and the labelling used in defining the parameters is shown in Fig. 4. Two problems were encountered when the structure was determined from the diffraction data alone. Firstly, as in the case of silacyclohexane, the geometry of the SiH₂ moiety was not well determined because of the proximity of the Si-H and $C_1 \cdot H_1$ distances to internuclear distances involving stronger scatterers. Secondly, it was not possible to obtain a reliable resolution of the two C-C distances using only electron diffraction data. Several attempts were made to refine the C_2 — C_3 distance independent of the $C_1 - C_2$ and $C_3 - C_4$ distances, but in all cases the uncertainties were large and the relative ordering of the distances indeterminant. The best least-squares structure for the molecule using the diffraction data alone is shown in Table 2 under the appropriate heading, and the intensity curves and radial distribution curves obtained from this analysis are shown in Figs. 5 and 6 respectively.

Incorporation of the microwave rotational constants into the experimental data set alleviated both of the problems mentioned above. Table 3 indicates the $B_z - B_0$ corrections which were applied to the microwave constants and the correction terms which were used to extrapolate the room temperature

Independen	t parameters ^b		Dependent parameters ^c		
	ED	ED + MW		ED	ED + MW
$Si-C$ $C-C_{av}$ C_1-C_2 C_2-C_3 $C_1\cdots C_3$ $Si-H$ $C-H_{av}$ $\angle CSiH$ $\angle SiCH$ $= \angle CCH_{av}$	1.893(2) 1.549(3) 2.510(8) 1.496(22) 1.118(5) 115.4(3.0) 111.3(0.9)	$\begin{array}{c} 1.892(2) \\ 1.550(2) \\ 1.535(5) \\ 1.580(5) \\ 2.516(8) \\ 1.497(8) \\ 1.112(6) \\ 113.2(0.3) \\ 110.1(0.8) \end{array}$	$ \mathcal{L} \operatorname{CSiC} $ $ \mathcal{L} \operatorname{SiCC} $ $ \mathcal{L} \operatorname{CCC} $ $ \mathcal{L} \operatorname{HSiH} $ $ \tau_{\operatorname{Si-C}} $ $ \tau_{\operatorname{G_1-C_2}} $	$\begin{array}{r} 96.0(0.3)\\ 103.7(0.3)\\ 108.7(0.6)\\ 100.1(10.6)\\ 12.8(0.5)\\ 35.7(1.4)\\ 25.5(1.1)\end{array}$	96.3(0.3) 103.6(0.3) 108.4(0.7) 112.3(2.9) 13.3(0.4) 36.1(1.0) 25.7(0.8)
$\tau_{C_2 - C_3}$ l_{C-H} $l_{C_1 \cdots C_3}$ $l_{Si \cdots C_2}$ $l_{Si \cdots C_2}$	48.8(1.9) 0.076(5) 0.063(6) 0.069(4) 0.056(3)	49.7(1.4) 0.080(6) 0.066(5) 0.069(3) 0.053(2)			

Structural parameters for silacyclopentane obtained from least-squares analysis^a

^a Distances (A) are reported as r_g parameters and angles (in degrees) are reported as r_{α} parameters. Quoted errors are 3σ values obtained from least-squares analysis. ^bED refers to analysis based on electron diffraction data alone while ED + MW refers to data analysis of the combined electron diffraction and microwave spectroscopic data sets. ^cErrors for dependent parameters were calculated from errors in independent parameters by transferring the elements of the error matrix. ^d ϕ is defined as the dihedral angle which the C_2 - C_3 bond makes with the C₄SiC₁ plane.



Fig. 4. Atomic numbering for silacyclopentane.



Fig. 5. Levelled molecular intensity curves for silacyclopentane.



Fig. 6. Radial distribution curves for silacyclopentane.

 r_{α} structure to 0 K. Also shown in Table 3 are the calculated rotational constants determined from the best least-squares fit to the combined electron diffraction and microwave spectroscopic data sets. Table 2 shows the results of the combined analysis in which a relative weight of 500 was applied to the 9 pieces of spectroscopic data. A comparison of the combined analysis with the analysis based on electron diffraction data alone reveals no significant differences in parameters, which were well determined from the diffraction data alone. The only significant differences are in the value of the \angle CSiH angle and in the resolution of the two C—C bond lengths. The uncertainties in the Si—H bond length and the \angle CSiH valence angle were also substantially

	$B_{0}(MHz)$	$B_z^{obs}(MHz)$	$B_z^{calc}(MHz)$	Difference (MHz)
(CH ₂) ₄ Si ²⁸ H ₂	5473.39	5477.70	5477.79	-0.09
	4137.01	4138.84	4137.86	+ 0.98
	2661.55	2661.26	2661.52	-0.26
$(CH_2)_4 Si^{28}D_2$	5308.25	5312.70	5312.94	-0.24
	3774.14	3775.98	3777.58	-1.60
	2542.43	2542.19	2542.73	-0.54
(CH ₂) ₄ Si ²⁹ H ₂	5473.42	5477.39	5477.76	-0.37
	4085.26	4087.00	4086.05	+ 0.95
	2639.99	2639.70	2639.97	-0.27

Observed and calculated rotational constants for silacyclopentane^a

r_z –	$-r_{\alpha}$	Corrections	to	bonded	distances	(X)	10 ⁵	Å)) b
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Distance	$(CH_2)_4Si^{28}H_2$	(CH ₂) ₄ Si ²⁸ D ₂	(CH ₂) ₄ Si ²⁹ H ₂	
<u>C,-C,</u>	98	95	98	
$C_1 - C_2$	609	594	608	
Si-C	345	359	342	
Si-H	1062	774	1062	
С—Н	694	687	694	

^a B_0 rotational constants taken from ref. 8. $B_z - B_0$ corrections calculated from the molecular force field in ref. 7. B_z ^{calc} is calculated from the least-squares r_z structure for silacyclopentane. ^b $r_z - r_\alpha$ corrections are calculated from the valence force field reported in ref. 7. These corrections include an extrapolation of the r_α structure from 298 K to 0 K plus a correction for isotopic substitution of the parent species.

reduced by incorporating the spectroscopic data. This is an excellent illustration of the complementary nature of the two types of experimental data.

MOLECULAR MECHANICS CALCULATIONS

It seems reasonable to expect that many of the conformational features of these two molecules could be accounted for in terms of Bayer (valence angle) and Pitzer (dihedral angle) strain energy considerations. For example, it should be possible to rationalize the relatively large deviations of the \angle CSiC valence angles from their normal sp^3 tetrahedral values on the basis of the relative lengths of the Si–C and C–C bonds, and the relative magnitudes of the \angle CSiC, \angle SiCC and \angle CCC bending force constants. In order to further explore this possibility, we decided to perform some rather simplified molecular mechanics calculations.

Two previous molecular mechanics studies on acyclic and cyclic organosilanes have been reported [9, 10]. Rather than use either of these previously reported force fields, however, we decided to use the diagonal valence force constants from Laane and co-workers' silacyclopentane force

Force field parameters used in molecular mechanics calculations

V	ale	nce	force	constan	ts
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K_{C-C}	632 (kcal A ⁻²)	r_{C-C}	1.540 (A)
K _{C-H}	669 (kcal A ⁻²)	$r_{\rm C-H}$	1.095 (Å)
K _{Si-C}	400 (kcal Å ⁻²)	r_{Si-C}°	1.880 (A)
K _{Si-H}	384 (kcal A ⁻²)	r _{si-H}	1,485 (A)
H _{HCH}	84.8 (kcal rad ⁻²)	HCCH	79.2 (kcal rad ⁻²)
HCCC	112.8 (kcal rad ⁻²)	H _{HSiH}	69.4 (kcal rad ⁻²)
H _{HSiC}	68.1 (kcal rad ⁻²)	HCSiC	109.2 (kcal rad ⁻²)
H _{CCSi}	131.1 (kcal rad ⁻²)	HHCSI	49.7 (kcal rad ⁻²)
V ₃ (C-C	C) 2.90 (kcal)	V_3 (Si-C	C) 1.65 (kcal)
		•	

Non-bonded potential functions

$V(r) = Ae^{-br} - C/r^6 \text{ (kcal)}$					
	A	Ъ	с	$r_{\omega}^{b}(A)$	
н.н	2376	4.0	49.2	2.4	
С…н	11858	4.0	125	2.9	
C··C	74822	4.0	325	3.4	
H∙∙Si	44493	3.8	430	3.3	
C…Si	139315	3.7	1105	3.6	

^aValence force constants are taken from ref. 7. r^0 parameters represent unstrained internuclear distances. α^0 parameters for all valence angles were assumed to be 109.47°. ${}^{b}r_{\omega}$ is the Van der Waals distance at which the non-bonded potential functions have their minima.

field [7] as a basis for our calculations. Calculations were performed on silacyclopentane and silacyclohexane as well as several of the acyclic compounds reported by Ouelette and co-workers [10]. The three-fold barriers to rotation about the Si—C and C—C bonds were chosen so as to roughly reproduce the rotational barriers in ethane and silaethane, and the unstrained r_0 distances were adjusted to give the best average values for all of the molecules studied. All of the unstrained valence angles (α_0 terms) were fixed at 109.47° so as not to prejudice the calculations for the ring systems. Rather crude non-bonded potential functions were constructed using the method of Scott and Scheraga [16]. The attractive portion was estimated from atomic polarizability data, and the functions were constructed so as to have a minimum at the sum of the Van der Waals radii reported by Bondi [17]. All calculations were performed using the program EMIN which has been written in this laboratory [18].

The force field used for the calculations is shown in Table 4. This force field is undoubtedly a very crude approximation compared with the more sophisticated consistent force fields or modified Urey—Bradley force fields which have been reported for the alkanes [19]. We have chosen to include valence force constants rather than Urey—Bradley force constants, and have

Silacyclopentane			Silacyclohexane		
·····	Obs.	Calc.	<u> </u>	Obs.	Calc.
∠CSiC	96.3(0.3)	96.9	4 CSiC	104.2(1.4)	104.8
∠ SiCC	103.6(0.3)	103.5	∠ SiCC	110.6(0.6)	108.9
∠CCC	108.4(0.7)	107.9	$LC_1C_2C_3$	113.7(1.1)	111.4
TSI-C	13.3(0.4)	13.3	LC,C,C	111.4(1.9)	112.1
$\tau_{\rm C}$ – C.	36.1(1.0)	36.7	τ_{Si-C}	44.0(4.2)	48.1
TC - C	49.7(1.4)	49.9	$\tau_{C} - C$	57.3(2.0)	59.3
02 03	. ,		$\tau_{\mathbf{C}} - \mathbf{C}$	67.5(2.0)	70.4

Comparison of observed conformations with those obtained from molecular mechanics model^a

Dihedral angles for silacyclopentane as a function of the pseudorotational angle, ϕ

 $\begin{aligned} {}^{\tau}\mathrm{Si-C_1} &= 34.6\,\cos{(\phi + 67.3^\circ)} \\ {}^{\tau}\mathrm{C_1-C_2} &= 44.0\,\cos{(\phi + 146.4^\circ)} \\ {}^{\tau}\mathrm{C_2-C_3} &= 50.0\,\cos{(\phi)} \\ {}^{\tau}\mathrm{C_3-C_4} &= 44.0\,\cos{(\phi - 146.4^\circ)} \\ {}^{\tau}\mathrm{Si-C_4} &= 34.6\,\cos{(\phi - 67.3^\circ)} \\ V(\phi) &= \frac{4.48}{2}\,[1-\cos{(2\phi)}] \end{aligned}$

^aAngles in degrees.

ignored the geminal interaction terms which have been shown to be important in reproducing structural trends and precise vibrational frequencies. Our primary objective in performing these simplified molecular mechanics calculations was to see if the conformations could be rationalized in terms of simple ring strain considerations.

The results of the calculations are compared with the observed conformations in Table 5. The agreement between the calculated and observed conformations is perhaps better than we had a right to expect. In fact, all of the calculated valence and dihedral angles for silacyclopentane are within the experimental error limits. The agreement for silacyclohexane is only slightly worse; however the conformational features are well reproduced even in this case.

The pseudorotational barrier height for silacyclopentane and the conformational changes which accompany the pseudorotation were also calculated. The estimated barrier height, 4.48 kcal mole⁻¹, is somewhat larger than the observed value for silacyclopentane [5, 6], 4.04 kcal mole⁻¹, and is probably indicative of certain inadequacies in the model force field. The lower half of Table 5 gives a parameterization of the silacyclopentane ring dihedral angles along the pseudorotational pathway. Each of the dihedral angles varies cosinusoidally with the pseudorotational phase angle ϕ with twist confor-

	MSU ^a	NDSU ^b	
Si-C	1.891(4)	1.892(2)	
C-Cav	1.551(7)	1.550(2)	
C,Ĉ,	1.564(9)	1.535(5)	
C,C,	1.525(17)	1.580(5)	
C-H _{av}	1.09(1)	1.112(5)	
∠CSiČ	96.4(0.6)	96.3(0.3)	
φ	24(2.5)	25.7(0.8)	

Comparison of the MSU and NDSU structure determinations for silacyclopentane^c

^aStructure determined in Laboratory of Electron Diffraction, Department of Chemistry, Moscow State University. Ref. 20. ^bStructure determined in Department of Chemistry, North Dakota State University. This paper. ^cDistances in A, angles in degrees.

mations occurring at $\phi = m\pi$ and envelope conformations occurring at $\phi = \pi/2 + m\pi$. The energy along the pseudorotational coordinate conforms rather precisely to the simple 2-fold rotational potential function expression.

DISCUSSION

Since the structure of silacyclopentane has also recently been determined at Moscow State University [20], we have a unique opportunity to compare two completely independent electron diffraction investigations of the same structure. The two independent structural studies of silacyclopentane are compared in Table 6. The major structural parameters are all within experimental error of each other except for the average C-H bond length. The two structural determinations differ slightly in the resolution of the two C-C ring distances. Mastryukov et al. [2] have reported distances of 1.564(9) Å and 1.525(17) Å for the C_1 - C_2 and C_2 - C_3 bond lengths respectively. Our combined analysis indicates a reversal of these distances with values of 1.535(5) Å and 1.580(5) Å for the same distances. The latter splitting was tested several times using the combined ED and SP data sets by reversing the distances; however, the parameters always quickly converged to the values reported in Table 2. Molecular mechanics calculations further reinforce this ordering in that they predict the C_2 - C_3 bond to be longer than C_1 - C_2 by about 0.01 Å. In any case the average C-C bond lengths reported in these two determinations, 1.551(7) Å and 1.549(3) Å, agree very well.

The Si—C and average C—C bond lengths are nearly identical in silacyclohexane and silacyclopentane, and since the two sets of data were taken at the same time under identical conditions, the reported differences should be relatively free from systematic experimental errors. The Si—C bond lengths in both compounds are slightly longer than observed bond lengths in such acyclic systems as Si₂(CH₃)₆ (ref. 21) (Si—C = 1.879(3) Å), Si(CH₃)₄ (ref. 22) (Si—C = 1.876(2) Å) and (SiH₃)₂CH₂ (ref. 23) (Si—C = 1.874(2) Å). The Si—C bond lengths in these two.compounds are, however, comparable to the observed bond lengths in 1-methyl-1-silabicyclo(2.2.1)heptane [1] (Si—C = 1.883(2) Å) and 1-methyl-1-silaadamantane [2] (Si—C = 1.879(3) Å).

It appears that the conformations of both silacyclopentane and silacyclohexane are quite easily rationalized in terms of simple strain energy considerations. Even the rather crude molecular mechanics model used in our calculations is capable of reproducing the conformations of both molecules rather well. The small $\angle CSiC$ angles in these cyclic organosilanes appear to arise from the ring strain introduced by the long Si-C bond length (relative to C-C) which is relieved by distributing the strain over the various valence and dihedral angles of the ring. The distribution of Bayer strain in the ring is governed by the relative magnitudes of the bending force constants $(H_{CSiC} = 109.2 \text{ kcal rad}^{-2}, H_{CCC} = 112.8 \text{ kcal rad}^{-2} \text{ and } H_{SiCC} = 131.1 \text{ kcal}$ rad^{-2}) with the net effect being a decrease in the $\angle CSiC$ valence angle (relative to 109.4°) and increases in the \angle CCC valence angles around the ring. The smaller dihedral angles about the Si-C bonds relative to those about the C-C bonds, on the other hand, appear to arise from the differences in the Si-C and C-C rotational barriers which are roughly 1.65 kcal mole⁻¹ and 2.90 kcal mole⁻¹ respectively.

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