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Conformations of Silicon-Containing Rings. 5.[†,‡] Conformational Properties of 1-Methyl-1-silacyclohexane: Gas Electron Diffraction, Low-Temperature NMR, and Quantum Chemical Calculations

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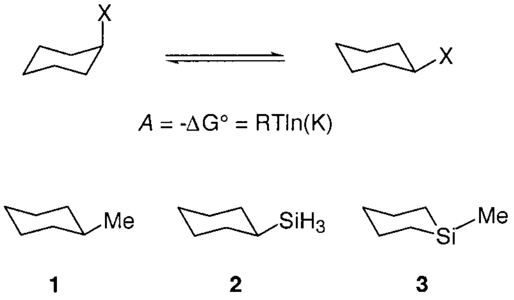
The molecular structure of 1-methyl-1-silacyclohexane **3** has been determined by gas electron diffraction (GED). The conformational preference of the methyl group was studied experimentally in the gas phase (GED) and in solution (low-temperature ^{13}C NMR) and by quantum chemical calculations (HF, MP2, and B3LYP with 6-31G* basis sets and *m*PW1PW91/6-311G(2df,p)). Both experimental methods result in a preference of the equatorial position of the methyl group, 68(7)% in the gas phase at 298 K and 74(1)% in solution at 110 K. The calulations predict 68−73% equatorial conformer at room temperature. From coalescence temperatures, Gibbs free energies of activation for ring inversion $\Delta G^{\ddagger}$ (eq → ax) = 5.81(18) and $\Delta G^{\ddagger}$ (ax → eq) = 5.56(18) kcal mol^{-1} were derived. The calculated values for $\Delta G^{\ddagger}$ (eq → ax) are 5.92 (B3LYP) and 5.84 kcal mol^{-1} (*m*PW1PW91).

Introduction

The conformational behavior of six-membered ring systems continues to be an active field of research. Cyclohexane and its derivatives play an important role in organic stereochemistry. The Gibbs free energy difference between axial and equatorial conformations in a monosubstituted cyclohexane has been used as a measure of the inherent conformational parameters of the substituent. With the rare exceptions of substituents having mercury bonded to the cyclohexane ring, a general preference for the equatorial conformer is found.[2] Consequently a positive *A* value (see Scheme 1 for definition of *A*) corresponds to a preference of the equatorial conformer. The equatorial preference of Me, Et, and i-Pr as substituents on cyclohexane has been reinvestigated very recently. The *A* value of the methyl group was found to be 1.80(2) kcal mol^{-1} by low-temperature ^{13}C NMR spectroscopy and 1.98 kcal mol^{-1} by high level ab initio calculations.[3]

Scheme 1



Silylcyclohexane **2** and 1-methyl-1-silacyclohexane **3** are the two simplest Si-analogues of methylcyclohexane **1**. Several recent studies on **2** have been published. The *A* value of the silyl group was found by ^{1}H and ^{13}C NMR to be 1.45 and 1.44 kcal mol^{-1}, respectively, at 188 K.[4] From a gas-phase electron diffraction experiment, Shen et al. reported a conformational mixture of equatorial (90 ± 10%) and axial forms at 75 °C.[5] Cho et al. have compared calculated *A* values for the methyl and silyl groups.[6] They report *A* values of 2.14 kcal mol^{-1} (CH$_3$) and 1.90 kcal mol^{-1} (SiH$_3$) from ab initio calculations, whereas MM3 calculations resulted in 1.78 kcal mol^{-1} (CH$_3$) and 1.16 kcal mol^{-1} (SiH$_3$). The authors explained the lower *A* value of the silyl group compared with the methyl group by the longer Si−C bond (1.904 Å) compared to the C−C bond (1.534 Å), which makes the axial SiH$_3$ sterically less unfavorable than the axial methyl group.

The conformational equilibrium of **3** has been studied with room temperature ^{1}H NMR spectroscopy[7] and MM calculations.[8,9] Both experimental and theoretical methods result in negative *A* values, i.e., in preference of the axial form. This is in contrast to chemical intuition.

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We have recently observed that the MM3 force field is inadequate to predict *A* values for simple alkyl groups as substituents on the 1,3,5-trisilacyclohexane ring system.[10] Therefore, force field calculations for **3** may have been in error. Furthermore, the use of the Winstein−Holness equation[11] to calculate the equilibrium constant for a dynamic system from NMR data which was applied by Carleer and Anteunis[7] suffers from serious limitations as has been pointed out by Booth in an early review.[12] Thus, the unusual conformational properties of **3** were derived with two methods whose reliability has turned out to be questionable. Therefore, we performed additional investigations, using gas electron diffraction (GED), low-temperature ^{13}C NMR spectroscopy, and quantum chemical calculations. GED has been shown to be an adequate method to determine the conformational composition of gaseous samples if the amounts of two conformers are comparable.[13] For solutions, reliable results are expected from NMR measurements at temperatures low enough to efficiently slow the conformational exchange and thus allow detection of individual conformers. This technique has been applied successfully to cyclohexane derivatives.[2] The energy barrier for the ring inversion of silicon-containing ring systems, however, is much lower than that for the corresponding cyclohexane derivatives (typically 5−6 kcal mol^{-1} vs 10−12 kcal mol^{-1}). This has prevented the detection of separate NMR signals of silacyclohexanes using traditional low-temperature solvents. However, the use of Freons as low-temperature NMR solvents has enabled the detection of separate signals for 1,1-dimethyl-1-silacyclohexane,[14] dodecamethylcyclohexasilane,[15] and 1,1,4,4-tetramethyl-1,4-disilacyclohexane[16] at very low temperatures (down to −170 °C). Nowadays molecules such as **3** can routinely be treated with standard quantum chemical methods, which are expected to predict relative energies of different conformers more reliably than MM techniques.

Experimental Section

Compound **3** was prepared according to a standard literature method,[17] and the sample was purified by preparative GLC prior to use.

Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[18] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The sample reservoir was kept at 0 °C; the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual procedures,[19] and averaged intensities in the *s*-ranges 2−18 and 8−35 Å^{-1} in intervals of $\Delta s = 0.2$ Å^{-1} are shown in Figure 1 ($s = (4\pi/\lambda) \sin \theta/2$, where λ is the electron wavelength, θ is the scattering angle).

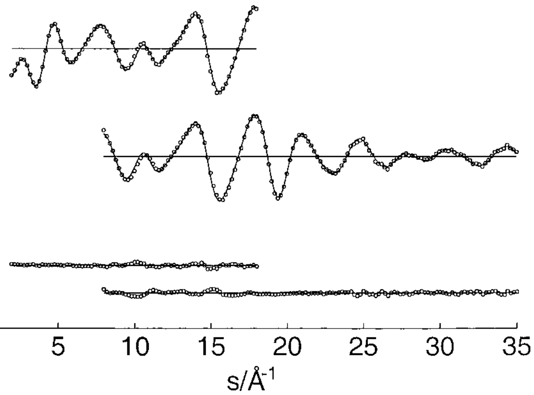

Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences for long (upper curves) and short (lower curves) nozzle-to-plate distances.

Low-temperature ^{13}C NMR spectra were recorded with a Bruker AC 250 instrument. The sample tube was charged with a solvent mixture of CD_2Cl_2, $CHFCl_2$, and CHF_2Cl in ratio of 1:1:3 on the vacuum line and sealed off. The temperatures of the probe were calibrated by means of a Type K (Chromel/Alumel) thermocouple inserted into a dummy tube after the spectral measurements. The low-temperature measurements are estimated to be accurate to ±2 K. Spectra were loaded into the data-handling program IGOR (WaveMetrics) for analysis, manipulations, and graphic display.

Quantum Chemical Calculations

The geometries of equatorial and axial conformation of **3** were optimized with HF, MP2, and B3LYP methods and 6-31G* basis sets (Table 1). All three approximations predict a lower energy for the equatorial form, with $\Delta E = E(\text{ax}) - E(\text{eq}) = 0.42$, 0.28, and 0.42 kcal mol^{-1}, respectively. The geometry of the six-membered ring is very similar in both conformers. Bond lengths and endocyclic angles differ by less than 0.002 Å and 0.4°. The largest difference between the two conformers occurs for the exocyclic C2−Si−C7 angle (Figure 2). Contrary to chemical intuition this angle is predicted to be smaller in the axial form by 1.2° (HF), 1.3° (B3LYP), or 2.0° (MP2). Vibrational frequencies were derived with the B3LYP method, and Cartesian force constants were used to calculate vibrational amplitudes. All quantum chemical calculations on structure and energy of **3** were performed with the GAUSSIAN98 program suite,[20] and vibrational amplitudes were derived with the program ASYM40.[21] ^{13}C NMR chemical shifts for the equatorial and axial conformers of **3** were calculated using the program system TURBOMOLE at the DFT level of

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Table 1. Experimental and Calculated Geometric Parameters for the Equatorial Conformer of 3.[a] For Atom Numbering, See Figure 2

	GED[b]	HF/ 6-31G*	MP2/ 6-31G*	B3LYP/ 6-31G*
(Si−C)mean	1.865(2) (p_1)	1.892	1.887	1.895
ΔSiC[c]	0.005(5)	0.003	0.002	0.005
Si−C2	1.867(4)	1.893	1.887	1.897
Si−C7	1.862(4)	1.890	1.885	1.892
(C−C)mean	1.531(2) (p_2)	1.539	1.536	1.543
ΔCC[d]	0.006(5)	0.006	0.006	0.006
C2−C3	1.534(3)	1.542	1.539	1.546
C3−C4	1.528(3)	1.536	1.533	1.540
C−H	1.104(3) (p_3)	1.088	1.098	1.099
Si−H	1.510[e]	1.485	1.497	1.497
C2−Si−C6	102.8(20) (p_4)	104.1	103.8	104.2
C3−C4−C5	116.7(34) (p_5)	114.5	114.2	114.5
Si−C2−C3	110.5(16)	111.1	110.3	111.1
C2−C3−C4	112.4(27)	113.8	113.5	113.9
C2−Si−C7	112.5(24) (p_6)	112.9	113.0	113.0
C2−Si−H1	108.8[e]	109.0	108.8	108.8
(H−C−H)ring	106.0[e]	106.1	106.2	106.0
(H−C−H)methyl	107.7[e]	107.6	107.8	107.7
Flap(Si)[f]	46.0(31) (p_7)	40.5	42.8	40.6
Flap(C4)[f]	55.9(20) (p_8)	56.7	57.4	56.6
ϕ(Si−C2−C3−C4)	56.6(10)	55.0	56.5	55.0
ϕ(C2−C3−C4−C5)	62.9(9)	−65.0	−65.6	−64.9
ϕ(C2−Si−C6−C5)	49.8(28)	43.7	46.0	43.8

[a] Values in angstroms and degrees. [b] Uncertainties are 3σ values. [c] ΔSiC = (Si−C2) − (Si−C7), uncertainty is estimated. [d] ΔCC = (C2−C3) − (C3−C4), uncertainty is estimated. [e] Not refined. [f] Flap angle from the plane of C2, C3, C5, and C6.

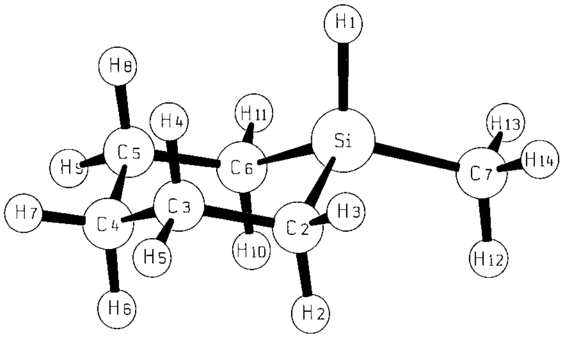

Figure 2. Molecular structure of **3** (equatorial conformer) and atom numbering used.

theory within the resolution of the identity (RI) approximation and split valence plus polarization (SV(P)) basis set.[22−28] The BP-86 functional was used for the RI-DFT calculations.[29−31]

Gas Electron Diffraction

The experimental radial distribution function (RDF) which was derived by Fourier transformation of the molecular intensities, applying an artificial damping function $\exp(-\gamma s^2)$ with $\gamma = 0.0019$ Å^2 is shown in Figure 3, together with the RDF's for the equatorial and axial conformation. The two calculated curves differ in the range $r > 3.3$ Å, which corresponds mainly to the long nonbonded distances between the methyl group and the ring atoms. Comparison between experimental and calculated curves demonstrates that both forms are present with the equatorial conformer being predominant. In the least-squares fitting of the molecular intensities the geometric parameters of equatorial and axial forms were tied together using the calculated (B3LYP) differences. The following assumptions were made in this refinement. (1) C_S overall symmetry. (2) Local C_{3v} symmetry for the methyl group. (3) The CH_2 groups were assumed to be symmetric to the bisector of the adjacent endocyclic angle. (4) The difference between the endocyclic and exocyclic Si−C bond lengths and the difference between the C−C bond lengths in the ring were set to the calculated (B3LYP) values. (5) The Si−H bond length was set equal to that in 1,3,5-trisilacyclohexane.[1] (6) All angles, which describe the positions of hydrogen atoms, were constrained to the calculated angles. (7) Vibrational amplitudes of the prevailing equatorial form, which cause large correlations or which are poorly determined in the experiment, were set to theoretical values (see Table 2). With these assumptions eight independent geometric parameters (p_1 to p_8) and seven vibrational amplitudes (l_1 to l_7) were refined simultaneously. The following correlation coefficients had values larger than $|0.7|$: $p_4/p_7 = -0.73$, $p_4/l_5 = -0.81$, $p_5/l_4 = -0.85$, $l_4/l_5 = 0.83$. Least squares refinements were performed for various fixed ratios of axial and equatorial conformers. The minimum of the R factor for the long nozzle-to-plate distance (R50), which is most sensitive to changes in the conformational composition, occurs for a ratio of 32(7) % axial and 68(7)% equatorial. The uncertainty was obtained by Hamilton's test at 1% significance. This ratio corresponds to an A value of 0.45(14) kcal mol^{-1}. The results for the geometric parameters and vibrational amplitudes are listed in Tables 1 and 2 together with the calculated values. Most geometric parameters of the axial form differ very little from those of the equatorial conformer. The largest differences are predicted (B3LYP) for the exocyclic C2−Si−C7 and C2−Si−H1 angles which

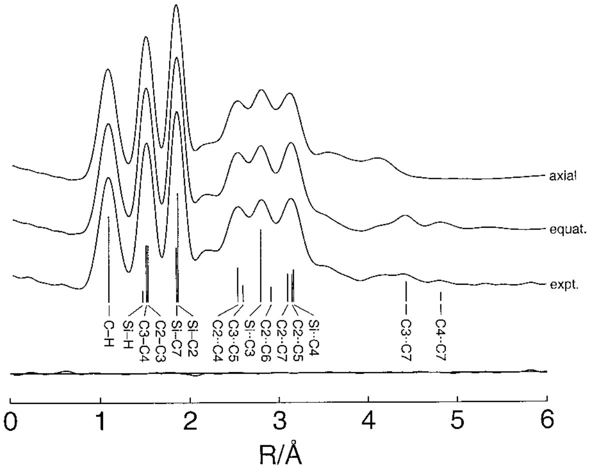

Figure 3. Experimental radial distribution function (RDF) and difference curve for **3**. Calculated RDF for equatorial and axial chair conformers of **3**. Vertical bars indicate the positions of important interatomic distances.

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Table 2. Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for 3 (without nonbonding distances involving H)[a]. For Atom Numbering See Figure 2

		amplitude		
	distance	GED		B3LYP
C−H	1.10	0.075(3)	l_1	0.077
Si−H	1.51	0.089[b]		0.089
C−C	1.53	0.053(2)	l_2	0.052
Si−C	1.86−1.87	0.051(2)	l_3	0.053
C2···C4	2.54	0.078(14)	l_4	0.071
C3···C5	2.60	0.078(14)	l_4	0.099
Si···C3	2.80	0.074(11)	l_5	0.078
C2···C7	3.10	0.107[b]		0.107
C2···C5	3.15	0.085(7)	l_6	0.083
Si···C4	3.16	0.085(7)	l_6	0.077
C3···C7	4.43	0.089(16)	l_7	0.092
C4···C7	4.81	0.121[b]		0.121

[a] Values in angstroms. Uncertainties are 3σ values. [b] Not refined.

Table 3. ^{13}C NMR Chemical Shifts for 3 in $CDCl_3$ Solution at 293 K and in 1:1:3 Solution of CD_2Cl_2, $CHFCl_2$, and CHF_2Cl at 110 K. Calculated Values Are Given in Parentheses

		δ/ppm			
	T/K	C2(6)	C3(5)	C4	C7
3	293	11.73	24.82	29.93	−5.62
3 (eq)	110	11.92 (*13.02*)	25.79 (*26.17*)	29.81 (*29.68*)	−4.32 (*−2.99*)
3 (ax)	110	10.71 (*11.99*)	24.04 (*24.84*)	29.81 (*29.56*)	−7.31 (*−5.45*)

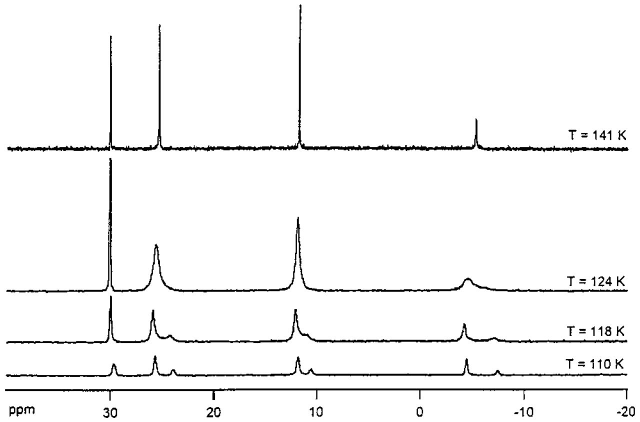

Figure 4. Low-temperature ^{13}C NMR spectra of **3**.

in the axial form are 1.3° smaller and 1.8° larger, respectively.

NMR Spectroscopy

The ^{13}C NMR spectra at room temperature and down to 141 K show rapid interconversion of the two conformers. The assignment of the signals to the different endo- and exocyclic carbon atoms is based on (i) comparison with methylcyclohexane,[32] (ii) the expected influence of Si on ^{13}C chemical shifts and (iii) on calculated values (Table 3). On cooling to 124 K, the spectrum (Figure 4) shows line broadening and at 118 K splitting occurs for all signals, except the one corresponding to the C4 atom. In each case the line splitting results in a main signal and a smaller one which is shifted to higher field, indicating a mixture of a major and a minor conformer. From methylcyclohexane it is known that the ^{13}C NMR signals of the axial chair conformer are shifted to higher field than the corresponding resonance signals of the equatorial conformer.[32] Therefore it is reasonable to assign the low-field signals in Figure 4 to the equatorial conformer of **3**. This assignment is confirmed by the calculated ^{13}C chemical shift values for both conformers. Line shape analyses were performed for the experimental spectra. From the signals for C7, C2/C6, and C3/C5 atoms in the 110 K spectrum an average ratio ax:eq of 26(1):74(1) was obtained. This ratio corresponds to an A value of 0.23(2) kcal mol^{-1}.

The coalescence temperatures T_c for the C2/C6 and C3/C5 signals were used to determine the Gibbs free energy of activation $\Delta G^{\ddagger}$ for the inversion process. Since these signals show different splittings $\Delta\delta$, they also possess slightly different T_c values. T_c for the C2/C6 signal occurs at 118 K or slightly above. 124 K was used as an upper limit for T_c of the C3/C5 signal. T_c for C7 could not be well determined. The inversion path in **3** is slightly unsymmetrical, since axial and equatorial conformers differ in energy. The activation energies $\Delta G^{\ddagger}$ (eq → ax) and $\Delta G^{\ddagger}$ (ax → eq) were derived with a method described elsewhere.[33] Furthermore, chair to chair inversion in cyclohexane-like rings occurs via a stable twist conformation and the inversion path possesses two maxima.[34] In this case a transmission coefficient $\kappa = 0.5$ has to be used in the Eyring equation.[35] In practice the use of the value 0.5 instead of 1.0 for κ decreases $\Delta G^{\ddagger}$ by 3%. This procedure resulted in mean activation energies $\Delta G^{\ddagger}$ (eq → ax) = 5.68(18) and $\Delta G^{\ddagger}$ (ax → eq) = 5.43(18) kcal mol^{-1}. The error limit for $\Delta G^{\ddagger}$ includes the uncertainty of ± 2 K for T_c.

Discussion

The gas-phase structure of the equatorial conformer of **3** (Table 1) agrees within experimental error limits with that of the unsubstituted ring,[36] except for the ring bond lengths Si−C and C−C, which are about 0.02 Å longer in the latter compound. The experimental parameters of **3** are well reproduced by quantum chemical calculations. Only the Si−C bonds are predicted too long by about 0.02 to 0.03 Å with all three methods. The same observation has been made in the case of 1,3,5-trisilacyclohexane.[1]

The main interest in the present study was the conformational equilibrium in **3**. The results are summarized in Table 4. According to the GED experiment, the equatorial conformer of **3** prevails in the gas phase ($A = 0.45(14)$ kcal mol^{-1}). Similarly, low-temperature ^{13}C NMR spectroscopy results in the preference of the equatorial form in solution at 110 K (A = 0.23(2) kcal mol^{-1}). Our quantum chemical calculations which predict A values between 0.46 (MP2) and 0.60 kcal mol^{-1} (B3LYP) reproduce the experimental GED result very well. The appropriate corrections between E and $G°$ were derived with the B3LYP method. Our experimental and theoretical results are in contrast to the previously

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Table 4. Conformational Properties for 1, 2, and 3

ring system	method	% equatorial	A (kcal mol^{-1})	ref
1	NMR (157 K)	95	1.80(2)	3
	ab initio (298 K)	97	2.05	3
2	NMR (188 K)	92	1.45(1)	4
	ab initio (298 K)	96	1.90	6
3	NMR (298 K)	36	−0.34	7
	MM2 (298 K)	45	−0.13	9
	NMR (110 K)	74(1)	0.23(2)	this work
	GED (298 K)	68(7)	0.45(14)	this work
	HF (298 K)	71	0.52	this work
	MP2 (298 K)	68	0.46	this work
	B3LYP (298 K)	73	0.60	this work
	*m*PW1PW91 (298 K)	72	0.56	this work

reported interpretation of room-temperature NMR spectra[7] and to molecular mechanics calculations[8,9] which resulted in a preference of the axial form (negative A values). Our results manifest normal conformational behavior of **3** in agreement with that of **1** and **2**. However, the A value of **3** is considerably smaller than those of **1** and **2**. In the series of the monosubstituted six-membered rings **1**, **2** and **3** A decreases steadily, which implies that sterical hindrance of the axial form decreases. This is readily explained by the longer Si−C exocyclic bond in **2** and by the longer Si−C endo- and exocyclic bonds in **3**, compared to the C−C bonds in **1**.

The dynamic process of ring inversion is described by the Gibbs free energy of activation $\Delta G^{\ddagger}$. Our experimental result for $\Delta G^{\ddagger}$ (eq → ax) = 5.68(18) kcal mol^{-1} is very similar to those for 1,1-dimethyl-1-silacyclohexane (5.5(1) kcal mol^{-1}),[14] 1,1,4,4-tetramethyl-1,4-disilacyclohexane (6.00(15) kcal mol^{-1})[16] and dodecamethylcyclohexasilane (4.8(2) kcal mol^{-1}).[15] Our quantum chemical calculations (B3LYP) predict a value of 5.92 kcal mol^{-1} for $\Delta G^{\ddagger}$ (eq → ax). More expensive calculations using the *m*PW1PW91 functional and the 6-311G(2df,p) basis set predict a lower $\Delta G^{\ddagger}$ (eq → ax) value of 5.84 kcal mol^{-1} and a similar A value of 0.56 kcal mol^{-1}. The MM3 method predicts a slightly larger enthalpy of activation for ring inversion of the unsubstituted silacyclohexane (6.6 kcal mol^{-1}).[34] These activation barriers are about half of those reported for cyclohexane (10.2(4) kcal mol^{-1}),[37] methylcyclohexane (13.4 kcal mol^{-1}),[32] or 1,1-dimethylcyclohexane (10.2 kcal mol^{-1}).[35] The strongly decreased activation barrier in silacyclohexane as compared to that in the parent ring is again readily explained by the longer endocyclic Si−C bonds.

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Supporting Information Available: Computer input and output files for all quantum chemical calculations performed. This material is available free of charge via the Internet at http://pubs.acs.org.

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