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Citation: The Journal of Chemical Physics **50**, 1946 (1969); doi: 10.1063/1.1671312
View online: http://dx.doi.org/10.1063/1.1671312
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/50/5?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 50, NUMBER 5 1 MARCH 1969

Far-Infrared Spectrum and the Barrier to Pseudorotation of Silacyclopentane

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(Received 4 November 1968)

The far-infrared spectrum arising from the transitions between the pseudorotational levels in silacyclopentane has been observed. Thirteen absorption maxima were found for the $v=0$ (radial ground) state and eight for the $v=1$ state. For each series a potential of the form $V=(V_2/2)(1+\cos 2\phi)$ predicts frequencies which agree very closely with the observed values. The values of V_2, which represent the barriers to pseudorotation, were found to be 1362 ± 25 cm^{-1} for the radial ground state and 1301 ± 50 cm^{-1} for the first excited state. The pseudorotation constants for the two radial states were found to be $B_0=1.966$ and $B_1=2.033$ cm^{-1}. The observed pseudorotation barrier of 3.89 kcal/mole represents the energy required to go from the more stable C_2 half-chair conformation to the C_s envelope form and is higher than expected from previously derived formulas.

INTRODUCTION

It is generally accepted that a saturated five-membered ring exists in a nonplanar configuration as a result of the torsional forces associated with the carbon–carbon bonds. This was first demonstrated for cyclopentane in 1941 by Aston and co-workers.[1] Somewhat later Kilpatrick, Pitzer, and Spitzer[2] postulated that the cyclopentane ring undergoes pseudorotation, that is, that the puckering of the ring is not of a definite type, but that the angle of maximum puckering rotates around the ring. For this sort of motion the pseudorotational energy levels were derived to be

$$E=n^2\hbar^2/2mq_0^2, \quad n=0, \pm 1, \pm 2, \cdots, \tag{1}$$

where mq_0^2 is essentially a moment of inertia. The separations between the different energy levels correspond to frequencies that are expected in the far-infrared region, but no such bands have been observed[3–5] due to the high symmetry of the molecule. Recently, however, Durig and Wertz[5] have succeeded in observing difference bands in the mid-infrared which result from the combination of the CH_2 deformation and the pseudorotational modes. Their results indicate that Eq. (1) above is correct and that $mq_0^2=11.0 \pm 0.2 \times 10^{-40}$ g·cm^2 for the ground vibrational state.

The first actual case of pseudorotation was observed in the far infrared by Lafferty *et al.* for tetrahydrofuran.[6] The data were analyzed in terms of free pseudorotation, and the energy levels were calculated using (1). More recent work[7,8] on this compound, however, indicates that the pseudorotation is hindered by a twofold barrier of about 50 cm^{-1} and an even smaller fourfold barrier. 1,3-Dioxolane[8] was also found to pseudorotate and has a potential similar to that of tetrahydrofuran. The only compound studied in the far infrared which shows a sizable pseudorotation barrier is cyclopentanone. The data of Carreira and Lord[9] have been interpreted by Durig *et al.*[10] to indicate that this barrier is 2.7 ± 0.8 kcal/mole.

This paper reports the results for silacyclopentane as obtained from its far-infrared spectrum. This work not only adds further data on pseudorotational barriers, but also adds information regarding the conformations of small ring silicon compounds. Silacyclobutane[11] and silacyclopent-3-ene[12] have been previously studied and the far-infrared data on silacyclopent-2-ene[13] will be published shortly.

EXPERIMENTAL

1,1-Dichloro-1-silacyclopentane was prepared from the 1,4-dibromobutane Grignard as described by West.[14] This was then reduced with lithium aluminum hydride in *n*-butyl ether to obtain silacyclopentane, $(CH_2)_4SiH_2$. After fractional distillation the sample was maintained over extra $LiAlH_4$ to assure its dryness. Far-infrared spectra were recorded in the region 28–250 cm^{-1} on a Jarrell–Ash 78–900[15] double-beam spectrometer equipped with a liquid-helium-cooled germanium detector made by Texas Instruments. The sample of silacyclopentane was examined in a multiple

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path cell with path lengths from 4 to 40 m and vapor pressures from 5 to 40 torr. Mid-infrared spectra were obtained in 10-cm glass cells with KBr or CsI windows using a Beckmann IR 12 instrument. A Raman spectrum was recorded with a Cary 81 instrument.

RESULTS

Figure 1 shows a far-infrared survey spectrum recorded in the range 70–110 cm^{-1}. Spectra were also obtained under high resolution, and Table I lists the frequencies and relative intensities of all the absorptions observed below 250 cm^{-1}. It is apparent that there exists a stronger set of bands, decreasing in intensity toward the low-frequency side, between 70 and 102 cm^{-1}. A weaker set of bands is also observed in this region with the same trend in intensities. Studies on cyclopentane,[16] tetrahydrofuran,[6,8] and 1,3-dioxolane[8] indicate that a low-frequency (about 250–300 cm^{-1}) radial band resulting from the other ring-puckering vibration is present in these compounds in addition to the pseudorotational levels. For silacyclopentane a Raman line observed at 268 cm^{-1} corresponds to this mode. As a result absorption bands due to the pseudorotation are observed both for the radial ground state ($v=0$) and the first excited level ($v=1$). For silacyclopentane, then, the stronger series of bands is assigned to transitions arising from the $v=0$ state, and the weaker series, to the transitions from the $v=1$ state. From intensity considerations it is apparent that the lowest pseudorotational transition ($n=0\rightarrow n=1$) must be assigned to the highest frequency band at 101.7 cm^{-1}. The 1→2 band is observed at 99.6, the 2–3 band at 97.3, and so on. Thirteen different transitions for the $v=0$ state and eight for the $v=1$ level were observed. The bands expected for the radial transitions ($\Delta v=1$, $\Delta n=0, \pm1$, or ±2) are not clearly observed although the weak bands between 140 and 210 cm^{-1} are very likely due to these transitions. The overtone ($\Delta n=\pm2$) pseudorotation bands also are not observed; this is unlike the case for tetrahydrofuran,[6,8] where the overtone absorptions are considerably stronger.

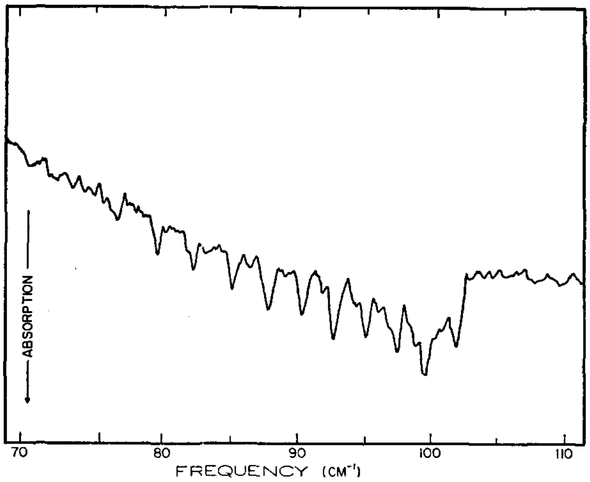

FIG. 1. Far-infrared spectrum of silacyclopentane; pressure 5 torr, path 40 m.

TABLE I. Observed far-infrared spectrum of silacyclopentane.[a]

Freq. (cm^{-1})	Relative absorbance	Freq. (cm^{-1})	Relative absorbance
70.3?	vw	95.0	0.8
72.1?	0.1	96.0 sh	0.3
73.3?	0.1	96.6 sh	~0.3
76.6	0.2	97.3	0.9
79.6	0.3	98.7 sh	~0.3
82.2	0.4	99.6	1.1
83.7?	vw	100.7	~0.2
85.2	0.4	101.7_5	(1.0)
86.6	0.1	147.7	vw
87.7_5	0.5	163.7	vw
89.2	0.1	164.9	vw
90.3	0.6	184.7	w
91.8	0.2	199.6	vw
92.6_5	0.8	200.4	vw
94.3	0.3		

[a] w, weak; v, very; sh, shoulder.

Although the mid-infrared spectrum of this molecule was not completely analyzed, it must be mentioned that the combination bands arising from the interaction of the pseudorotational vibration with the SiH$_2$ stretching modes are very prominent. This is quite different from the case of silacyclobutane,[11,17] where no combination bands arising from the ring puckering were observed, but is quite similar to that found for cyclopentane.[5] Figure 2 shows the spectrum of silacyclopentane vapor recorded between 2030 and 2270 cm^{-1}. Two strong Q branches are observed at 2148.5 and 2151.5 cm^{-1}, the former being more intense. Both of the SiH$_2$ stretching frequencies are expected in this region, but the symmetric SiH$_2$ stretch normally is about an order of magnitude weaker than the antisymmetric stretch and has a frequency a few cm^{-1} lower. Because of this, the 2148.5 band is assigned to the antisymmetric mode and the other band to a hot band of the same vibration resulting when either the radial or the pseudorotational vibration is in its first excited state. It is unlikely that the 2151.5-cm^{-1} band is the symmetric stretching one since it is

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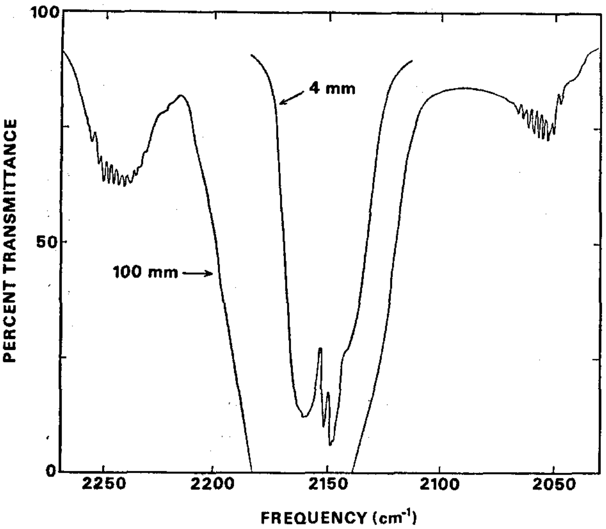

FIG. 2. Combination bands of silacyclopentane.

much too intense and also occurs at a higher frequency than the antisymmetric mode. On either side of the main bands are observed a series of weaker Q branches resulting from the combination of the SiH_2 antisymmetric stretch with the pseudorotational mode. Table II lists the frequencies of these weaker bands and compares $\nu_{\text{sum}}-2148.5$ and $2148.5-\nu_{\text{diff}}$ to the observed far-infrared absorptions. The highest frequency sum band apparently does not fit into this sequence. It can best be accounted for by assigning it to the first sum band of the $v=1$ (radial excited) state. Note that if the 2151.5-cm^{-1} band is the SiH_2 stretching in the $v=1$ state, this gives $2253.5-2151.5=102.0$ cm^{-1}, within reasonable agreement with the far-infrared frequency. It is seen that the frequencies derived from the combination bands are in fairly good agreement with the observed far-infrared frequencies. Slight deviations are expected due to both anharmonicity and perturbation effects, such as Fermi resonance.

Quite a few other combination and overtone bands are observed in the mid-infrared spectrum of silacyclopentane. A weak band at ~2400 cm^{-1} might be a combination band of the SiH_2 antisymmetric stretch and the radial band. This would suggest that $\nu_R=\sim 250$ cm^{-1} in the gas phase. The mid-infrared spectrum of this molecule has been studied more thoroughly elsewhere.[18]

CALCULATION OF ENERGY LEVELS

As Pitzer and Donath[19] have pointed out, cyclopentane derivatives are expected to have a barrier to pseudorotation since torsional strain energies do not cancel out as they do for the parent compound. Because of this, Eq. (1) is not expected to predict the energy levels of hindered pseudorotation for silacyclopentane. We can no longer define the motion by the q and ϕ as used for cyclopentane by Kilpatrick *et al.*[2] since a substituted molecule no longer has five equivalent bond lengths, atomic masses, or torsional energies. Instead, as suggested by Harris *et al.*[20] and by Greenhouse and Strauss,[8] we redefine the two out-of-plane vibrations, Q_1 and Q_2, in a complicated way so that the effective mass can be absorbed into the potential function and so that q and ϕ can still be used in simple form. We can then express the angular wave equation for hindered pseudorotation for each radial state by

$$-B(\partial^2\Psi/\partial\phi^2)+(V_{\text{psr}}-E_\phi)\Psi=0, \qquad (2)$$

where

$$B=(\hbar^2/2)\langle 1/mq_0^2\rangle \qquad (3)$$

and where the term in angle brackets represents an averaged value equal to its expectation value. For the form on the pseudorotational potential function we choose

$$V_{\text{psr}}=(V_2/2)(1+\cos 2\phi) \qquad (4)$$

and take higher-order terms (with $\cos 4\phi$, etc.) to be negligible. This can be justified on the basis of the spectra which do not show the perturbation that would be expected from a $\cos 4\phi$ term. V_2 represents the twofold barrier to pseudorotation and ϕ is the phase angle of pseudorotation. $\phi=0$ and π represent molecular conformations for the C_s structure whereas

TABLE II. Combination bands[a] of silacyclopentane.

Far-ir frequency	ν_{diff}	$2148.5-\nu_{\text{diff}}$	ν_{sum}	$\nu_{\text{sum}}-2148.5$
...	...	...	2253.5	b
101.7_5	2046.8	101.7	2250.0	101.5
99.6	2049.2	99.3	2247.7	99.2
97.3	2051.8	96.7	2245.7	97.2
95.0	2054.1	94.4	2243.3	94.8
92.6_5	2056.2	92.3	2241.0	92.5
90.3	2058.3	90.2	2238.8	90.3
87.7_5	2060.6	87.9	2236.8	88.3
85.2	2063.0	85.5	2234.0	85.5
82.2	2065.5	83.0	~2231.6	~83.1
79.6	~2068.2	~80.3	~2228.7	~80.2

[a] In cm^{-1}, ±0.3 cm^{-1}; far-infrared bands are ±0.1 cm^{-1}.

[b] This is believed to arise in the radial excited state $v=1$ for which $\nu_{SiH_2}=2151.5$ cm^{-1}; $\nu_{\text{sum}}-\nu_{SiH_2}$ $(v=1)=102.0$ cm^{-1}.

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[19] K. S. Pitzer and W. E. Donath, J. Am. Chem. Soc. **81**, 3213 (1959).

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TABLE III. Calculated[a] frequencies for the pseudorotation of silacyclopentane.

	$v=0$			$v=1$		
Transition	Obs. (cm^{-1})	Calc. (cm^{-1})	Δ	Obs. (cm^{-1})	Calc. (cm^{-1})	Δ
0–1	101.7$_5$	101.5	−0.2$_5$	100.7	100.8	+0.1
1–2	99.6	99.4	−0.2	98.7	98.7	···
2–3	97.3	97.3	···	96.6	96.5	−0.1
3–4	95.0	95.1	+0.1	94.3	94.2	−0.1
4–5	92.6$_5$	92.8	+0.1$_5$	91.8	91.8	···
5–6	90.3	90.4	+0.1	89.2	89.3	+0.1
6–7	87.7$_5$	87.9	+0.1$_5$	86.6	86.6	···
7–8	85.2	85.2	···	83.7?	83.9	(+0.2)
8–9	82.2	82.4	+0.2	···	80.9	···
9–10	79.6	79.5	−0.1	···	77.7	···
10–11	76.6	76.2	−0.4	···	74.2	···
11–12	73.3 ? 72.1	72.6	(−0.1)	···	70.3	···
12–13	70.3?	68.5	(−1.8)	···	65.5	···

[a] Using $V^v=(V_2^v/2)(1+\cos 2\phi)$; $V_2^0=1362$ cm^{-1} and $B_0=1.966$ cm^{-1} for $v=0$; $V_2^1=1301$ cm^{-1} and $B_1=2.033$ cm^{-1} for $v=1$.

TABLE IV. Calculated pseudorotational energy levels for silacyclopentane.

	$v=0$		$v=1$	
n	Energy[a]	Doublet[b] splitting	Energy	Doublet splitting
0	51.24	···	50.92	···
1	152.71	···	151.72	···
2	252.12	···	250.38	···
3	349.41	···	346.84	···
4	444.49	···	441.01	···
5	537.28	···	532.78	10^{-9}
6	627.68	10^{-9}	622.06	3×10^{-8}
7	715.57	4×10^{-8}	708.71	5×10^{-7}
8	800.81	8×10^{-7}	792.58	8×10^{-6}
9	883.25	1.2×10^{-5}	873.49	6.0×10^{-5}
10	962.70	1.7×10^{-4}	951.19	8.1×10^{-4}
11	1038.88	0.0019	1025.39	0.0080
12	1111.47	0.019	1095.65	0.073
13	1179.94	0.16	1161.17	0.53
14	1243.25	1.25	1220.01	3.12
15	1298.70	5.4	1268.21	
Barrier	1361.52	···	1301.25	···

[a] Of even level, in cm^{-1}.

[b] Between odd and even levels, in cm^{-1}.

$\frac{1}{2}\pi$ and $\frac{3}{2}\pi$ are equated to the more stable C_2 half-chair form. In no case does the molecule assume a planar configuration during the vibration.

The energy levels of (4) are calculated by using a set of Mathieu tables of large s values.[21] These can be used in the manner previously described,[22] except that for a twofold barrier we use

$$E_{\phi n}=Bb_n,\quad V_2=Bs, \tag{5}$$

where b_n and s are numbers from the tables and n refers to a particular energy level. For silacyclopentane, the best fit for the main band series corresponding to a nonexcited radial state ($v=0$) is obtained for

$$B_0=1.966\pm0.03\ \text{cm}^{-1},\quad V_2{}^0=1362\pm25\ \text{cm}^{-1}. \tag{6}$$

For the $v=1$ state these constants become

$$B_1=2.033\pm0.03\ \text{cm}^{-1},\quad V_2{}^1=1301\pm50\ \text{cm}^{-1}. \tag{7}$$

The excellent agreement between the observed values and the frequencies calculated from these constants is shown in Table III. It is evident that a $\cos 4\phi$ term would improve the fit very little since it would tend to perturb the lower energy levels the most; no such effect is apparent. It seems safe to conclude that if a fourfold barrier is present, it is less than about 30 cm^{-1}. Figure 3 shows the calculated poten-

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[22] W. G. Fateley and F. A. Miller, Spectrochim. Acta **17**, 857 (1961).

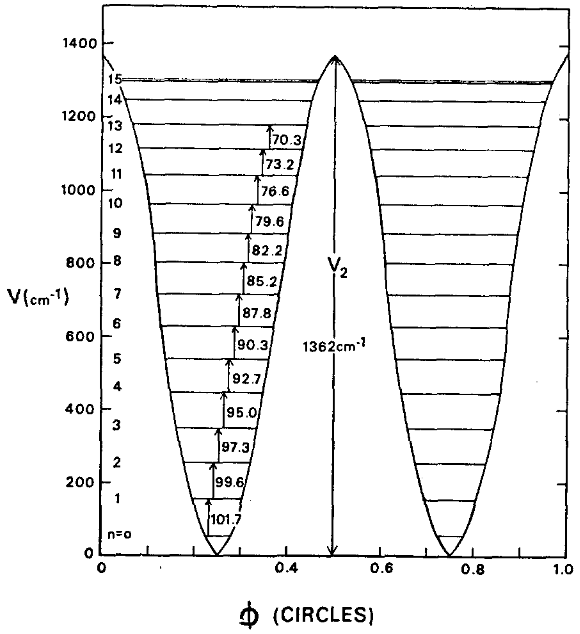

FIG. 3. Pseudorotational potential energy function of silacyclopentane for the radial ground state.

tial function for the pseudorotation of silacyclopentane in the $v=0$ state; the observed far-infrared transitions are also shown in this figure.

Note added in proof: A computer program has been written which calculates both the frequencies and intensities of the transitions. The agreement between observed and calculated intensities for the potentials (6) and (7) is excellent.

Each of the vibrational levels in Fig. 3 actually corresponds to two very nearly degenerate energy states. Table IV lists the energy calculated for each of the even states as well as the splitting between each degenerate pair of levels. The effect of the splitting on the observed far-infrared frequencies is negligible. However, since these splittings are very sensitive to the barrier height and shape of the potential, microwave information on this molecule could be used to refine the potential given by (4) and (6) although it is perfectly adequate to interpret the far-infrared data.

Although few, if any, transitions arising from the radial band in silacyclopentane were observed, the expected frequencies can be calculated from the observed bands for the $v=0$ and $v=1$ states. These are given in Table V in terms of ν_R, the frequency of the $\Delta v=1(n=0\rightarrow n=0)$ transition, which is ~ 270 cm^{-1}, as observed in the Raman spectrum of the liquid. For cyclopentane[4,5] $\nu_R=283$ cm^{-1}, for both tetrahydrofuran[8] and 1,3-dioxolane[8,23] $\nu_R=\sim 270$ cm^{-1}; cyclopentanone[5] has $\nu_R=236$ cm^{-1}.

DISCUSSION

From the far-infrared spectrum of silacyclopentane the barrier to pseudorotation for the molecule has been determined to be 3.89±0.07 kcal/mole. This value represents the energy difference between the C_2 half-chair and the C_s envelope conformations. Although it is impossible to tell from the data, it is fairly certain that the C_2 form is more stable since the $-SiH_2-CH_2-$ torsional barrier is less than the $-CH_2-CH_2-$ barrier. The analysis of Pitzer and Donath[19] for cyclopentane derivatives would predict a barrier of only about 1.6 kcal/mole if a value of 1.7 kcal/mole is assumed for the $-SiH_2-CH_2-$ torsional barrier.[24]

Table VI lists experimentally determined pseudorotational barriers for several cyclopentane derivatives. The value predicted from Pitzer and Donath's formula[19] is also given, but it appears that quantitatively this formulation is not very accurate. The reason for this is that it is difficult to estimate torsional barriers by transferring these from other molecules. Furthermore, changes in the geometry of molecules like silacyclopentane can have a significant effect. For quantitative purposes the discussion by Harris *et al.*[20] is probably more applicable.

Table VI also lists values of the pseudorotational constants B_0 and B_1. These observed values follow the expected trends. With regard to effective mass, we know that $O<CH_2<SiH_2\sim C{=}O$. As a result the value of B decreases in the order 1,3-dioxolane, tetrahydrofuran, cyclopentane, silacyclopentane, and cyclopentanone. Furthermore, in each case $B_0<B_1$.

TABLE V. Calculated frequencies[a] of the radial band ($\Delta v=1$).

n	$n\rightarrow n$	$n\rightarrow n+1$	$n\rightarrow n-1$	$n\rightarrow n+2$	$n\rightarrow n-2$
0	0.0	100.7	···	199.1	···
1	-1.0_5	97.6_5	-101.7_5	194.2_5	···
2	-1.9_5	94.6_5	-100.6_5	188.9_5	-201.3_5
3	-2.6_5	91.6_5	-99.2_5	183.4_5	-197.9_5
4	-3.3_5	88.4_5	-97.6_5	177.6_5	-194.2_5
5	-4.2	85.0	-96.0	171.6	-190.3
6	-5.3	81.3	-94.5	165.0	-186.3
7	-6.4_5	77.2_5	-93.0_5	(158.1_5)	-182.2_5
8	-7.9_5	(72.9_5)	-91.6_5	(150.6_5)	-178.2_5
9	(-9.2_5)[b]	(68.4_5)	-90.1_5	(142.6_5)	-173.8_5

[a] In cm^{-1} calculated relative to $\nu_R=\sim 270$ cm^{-1}, which is the $n=0\rightarrow n=0$ transition. The observed frequencies of pseudorotation are used for the calculation.

[b] Numbers in parentheses are derived from the calculated frequencies for $v=1$.

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[23] J. R. Durig and D. W. Wertz, J. Chem. Phys. 49, 675 (1968).

[24] R. W. Kilb and L. Pierce, J. Chem. Phys. 27, 108 (1957).

TABLE VI. Experimental pseudorotational barriers.

Molecule	Barrier (kcal/mole) Experimental	Predicted[a]	B_0	B_1	Method[b]	Reference
$CH_2CH_2CH_2CH_2CH_2$	0	0	2.54	···	M-ir	5
$CH_2CH_2CH_2CH_2O$	0.16	2.5	3.19	3.36	F-ir; MW	6, 7, 8
CH_2–O–CH_2–OCH_2	~0.15	···	3.99	4.21	F-ir	8, 23
$CH_2CH_2CH_2CH_2SiH_2$	3.89	1.6	1.966	2.033	F-ir	This work
$CH_2CH_2CH_2CH_2C{=}O$	3.5[c]	2.4	1.94	···	F-ir	9, 10
$CH_2CH_2CH_2CH_2S$	2.8	3.0	···	···	Therm.	e
$CH_2CH_2CH_2CH_2NH$	"Small"	1.3	···	···	Therm.	f
$CH_2CH_2CH\ OC{=}O$	~11[d]	···	~2[d]	···	F-ir	10
$OCH_2CH_2OC{=}O$	~18[d]	···	~2[d]	···	F-ir	10

[a] From Ref. 19.

[b] M-ir: mid-infrared spectra difference bands; F-ir: far-infrared spectra; MW: microwave spectra; Therm: thermodynamic method.

[c] From the spectra; Ref. 10 estimates 2.7±0.8 kcal/mole.

[d] Tentative estimate from solution spectra using only one frequency ($n=0\rightarrow n=1$).

[e] W. M. Hubbard, H. L. Fink, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. Waddington, J. Am. Chem. Soc. **74**, 6025 (1952).

[f] J. P. McCullough, J. Chem. Phys. **29**, 966 (1958).

This has been ascribed[8] to the lower average value of q_0^2 in (3) for the $v=1$ state.

It is interesting to note that while cyclopentane, tetrahydrofuran, and 1,3-dioxolane are essentially free to pseudorotate, silacyclopentane and cyclopentanone are constrained to the C_2 half-chair form. A negligible fraction of molecules of the last two compounds will be found in the C_s conformation at room temperature.

It must be mentioned that the spectra obtained for silacyclopentane and cyclopentanone could also have been analyzed in terms of a somewhat anharmonic vibration since no splittings of the energy levels were observed and no levels above the barrier were populated enough to be observed. However, the recorded frequencies of silacyclopentane fit so well with the cosine function that it is reasonable to conclude that the calculated function is very close to the actual one in the region where the energy transitions were observed.

It must be remembered that, as an approximation, we are really dealing with two vibrations and, therefore, have a two-dimensional problem. The potential function of Fig. 3 represents a one-dimensional cut of the actual potential. Much of the theory of this problem has been summarized by Harris *et al.*[20]

Finally, it is of interest to summarize the structures of the four- and five-membered ring silanes which have been studied. Silacyclobutane[11] is a puckered molecule with a dihedral angle of about 36°. Silacyclopent-3-ene[12] and silacyclopent-2-ene[13] are both planar molecules although the former is somewhat less rigid in this position. Both of these differ from cyclopentene,[25] a bent molecule, because of d_{Si}–π bonds. Silacyclopentane exists in the C_2 half-chair conformation which is more stable than the C_s form by 3.9 kcal/mole. It is assumed that the planar structure is even less stable. For each of the nonplanar molecules the puckering is caused by the torsional barriers between $-CH_2-CH_2-$ bonds and between $-CH_2-SiH_2-$ bonds.

ACKNOWLEDGMENTS

The author wishes to acknowledge support of the Spectroscopy Laboratory at M.I.T. in this work, part of which was carried out on the Jarrell–Ash 78–900 far-infrared instrument, constructed under NSF grant GP-4923. He thanks Professor R. C. Lord for permission to use the instrument.

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[25] J. Laane and R. C. Lord, J. Chem. Phys. **47**, 4941 (1967).