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Infrared and Raman spectra, conformational stability, normal coordinate analysis, ab initio calculations, and vibrational assignment of 1–methylsilacyclobutane

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Abstract

The infrared $(3500-40 \text{ cm}^{-1})$ spectra of gaseous and solid 1-methylsilacyclobutane, c-C₃H₆SiH(CH₃), have been recorded. In addition, the Raman spectrum $(3500-30 \text{ cm}^{-1})$ of the liquid has also been recorded and quantitative depolarization values obtained. Both the axial and equatorial conformers, with respect to methyl group, have been identified in the fluid phases. Variable temperature studies $(-55 \text{ to} - 100^{\circ}\text{C})$ of the infrared spectra of the sample dissolved in liquid xenon have been carried out. From these data, the enthalpy difference has been determined to be $122 \pm 26 \text{ cm}^{-1}$ ($1.46 \pm 0.32 \text{ kJ/mol}$), with the equatorial conformer being the more stable structure. However, with repeated annealing of the amorphous solid, it was not possible to obtain a polycrystalline solid with a single conformer. A complete vibrational assignment is proposed for the equatorial conformer based on infrared band contours, relative intensities, depolarization values and group frequencies. Most of the fundamentals for the axial conformer have also been identified. Utilizing the frequency of the silicon–hydrogen (Si–H) stretching mode, the Si–H distance has been determined to be 1.490 Å for both conformers. The vibrational assignments are supported by normal coordinate calculations utilizing ab initio force constants. Complete equilibrium geometries have been determined for both rotamers by ab initio calculations, employing the 3-21G* and 6-31G* basis sets at the levels of restricted Hartree–Fock (RHF) and/or Moller–Plesset (MP) to second order. The results are discussed and compared with those obtained for some similar molecules. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Infrared; Raman; Conformational stability; Ab initio calculations; 1-Methylsilacyclobutane

1. Introduction

In the initial far-infrared and low-frequency Raman investigations [1,2] of methylcyclobutane, the studies only referred to the methyl torsional and ring puckering modes with little attention given to the remaining portion of the vibrational spectrum. These earlier results were consistent with the equatorial conformer energetically favored over the axial form. It was inferred that a large value of the enthalpy difference, ΔH , between the two conformers should result in little or none of the high-energy axial form, being present at ambient temperature similar to what was found initially for the halocyclobutanes [3–6]. However, more recent studies [7,8] of methylcyclobutane provided clear evidence that the value of ΔH for both the liquid and vapor phases was sufficiently

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Fig. 1. Mid-infrared spectra of 1-methylsilacyclobutane in the: (A) gas; and (B) solid.

small ($<400 \text{ cm}^{-1}$) to allow direct observation of several of the vibrational modes of the high-energy axial conformation. Similarly, for the halocyclobutane molecules, the enthalpy differences between the conformers have been found in the same general range ($300-400 \text{ cm}^{-1}$) so that several fundamentals from the axial conformers have been identified [9–11].

The silacyclobutane molecule has been shown [12] to be a bent molecule with an inversion barrier of 440 cm^{-1} (5.26 kJ/mol) with the dihedral angle of the puckered ring of $35.9 \pm 2^{\circ}$. This barrier is lower than the 510 cm⁻¹ (6.10 kJ/mol) barrier for cyclobutane [13] so that the equatorial and axial conformers for the monosubstituted silacyclobutane should more easily interconvert than the corresponding monosubstituted cyclobutane molecules. For methylcyclobutane, ΔH was found to be 295 \pm 75 cm⁻¹ (3.53 \pm 0.90 kJ/mol) for the vapor with a barrier to conformer interconversion of 641 cm⁻¹ (7.67 kJ/mol). Therefore, it was expected that 1-methylsilacyclobutane should have a comparable or even smaller ΔH value for the two expected conformers. Also, the isolation of the low-energy form in the solid should be easily accomplished, as the barrier to interconversion of the conformers should be lower than that of the corresponding carbon compound. Therefore, we initiated an infrared and Raman spectroscopic study of 1-methylsilacyclobutane to determine the presence or absence of conformers at ambient temperatures, and to determine their relative stabilities if they are present. As an aid in interpreting the vibrational spectra we have carried out ab initio calculations at the RHF/3-21G*, RHF/6-31G* and MP2/6-31G* levels. The optimized geometries, conformational stabilities, harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies have been obtained to compare with the experimental results where applicable. The results of these spectroscopic and theoretical studies are reported herein.

2. Experimental

A sample of 1-chloro-1-methylsilacyclobutane was prepared by the reaction of dichloro (3-choropropyl) methylsilane with magnesium in dry diethyl ether according to the method of Damrauer [14]. This sample was then used to prepare 1-methylsilacyclobutane by reduction with LiAlH₄. This sample was



WAVENUMBER(cm⁻¹)

Fig. 2. Far-infrared spectra of 1-methylsilacyclobutane in the: (A) solid; and (B) gas. Features labelled with an asterisk are due to HCl rotational lines.



Fig. 3. Raman spectra of 1-methylsilacyclobutane in the: (A) liquid at 25° C; and (B) liquid at -120° C.

purified with a low-temperature, low-pressure fractionation column.

The mid-infrared spectra of the gas and solid (Fig. 1) were obtained from 3500 to 400 cm⁻¹ on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. The gas was contained in a 10-cm cell fitted with CsI windows. This spectrum was obtained at 0.5 cm^{-1} resolution and transformed with boxcar truncation function. The spectrum of the solid was obtained by condensing the sample onto a liquid nitrogen cooled CsI plate contained in an evacuated cell equipped with CsI windows, and 256 scans were collected for both the reference and sample interferograms at 1.0 cm^{-1} resolution and then transformed with a boxcar truncation function.

The mid-infrared spectra of the sample dissolved in liquified xenon as a function of temperature were recorded on a Bruker model IFS 66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter and a DTGS detector. In all cases, 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used which consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the cell with indium gaskets as described previously [15].

The far-infrared spectrum of the gas (Fig. 2) was recorded with a Bomen model DA3.002 Fourier transform spectrometer equipped with a vacuum bench, a 6.25 µm Mylar beamsplitter, and a liquid helium cooled Si bolometer with a wedged sapphire filter and polyethylene window. The spectra were obtained from the sample contained in a 1 m folded path cell equipped with mirrors coated with gold, and fitted with polyethylene windows with an effective resolution of 0.10 cm^{-1} . Interferograms were recorded 512 times at a resolution of 0.10 cm^{-1} and transformed with a boxcar truncation function. The spectrum of the crystalline solid was obtained with the Perkin-Elmer model 2000 spectrometer equipped with a metal grid beamsplitter and a DTGS detector.

The Raman spectra were recorded on a SPEX model 1403 spectrophotometer equipped with a SpectraPhysics model 164 argon ion laser operating on the 514.5 nm line. The laser power used was 0.5 W with a

Observed ^a infra	red and Ram	nan frequencies (cm ⁻	¹) and assign	ments for 1-methylsil	acyclobutane				
Infrared	-		-	- - -	-	Raman	-	Assignment .h	
Gas	Rel. Int.	Xenon Solution	Rel. Int	Amorphous Solid	Rel. Int.	Liquid	Rel. Int. & dp.	νī	Approximate Description
2985 Q	s							$\nu_{1}, \nu_{1'}$	CH ₃ antisymmetric stretch
2979 Q	s	2975	s	2970	s	2972	m,p	V2, V2'	(CH2)2 antisymmetric stretch
2971 max	s	2964	sh,s	2963	sh,s	2963	sh,m,dp	V 24, V 25	(CH ₂) ₂ antisymmetric stretch
								$v_{24'}, v_{25'}$	CH3 antisymmetric stretch
2948 Q	s	2939	s	2934	s	2935	sh,m,p	$\nu_{3}, \nu_{3'}$	CH2 antisymmetric stretch
2939 max	s	2928	s	2923	s	2923	s,p	ν_{4}, ν_{26}	(CH ₂) ₂ symmetric stretch
								$\nu_{4'}, \nu_{26'}$	
2921	sh,m	2917	sh,s	2915	sh,s	2908	s,p	ν_{5}, ν_{6}	CH ₂ symmetric stretch
0000						7000		$\nu_{5'}, \nu_{6'}$	CH ₃ symmetric stretch
2888 max 2879 R	Н	C/87	м	78/1	×	78/4	w,p		$\delta t + \nu \delta \delta$
2872 Q	ш	2858	ш	2855	ш	2858	vw,p		$\nu 7 + \nu 18$
2865 P		2853	ш						
2814	bd,vw					2817	vw,p		$\nu 7 + \nu 19$
2135 R									
2131 Q	VS	2122	VS	2120	vs	2122	s,p	$ u_{7} $	Si-H stretch
2128 Q	vs							$\boldsymbol{\nu}_{T'}$	Si-H stretch
2122 P									
1459	νw	1453	νw	1453	vw	1455	w,p	V8, V8'	CH ₂ deformation
1429 R									
1423 Q, C		1416	w	1416	w	1418	w,p	$\nu_{9}, \nu_{9'}$	(CH ₂) ₂ deformation
1421 Q	w							${\cal P}_{10}$	CH ₃ antisymmetric deformation
1419 Q	w	1407	w	1407	w			${\cal P}_{10'}$	CH ₃ antisymmetric deformation
1411 max	w	1401	w	1397	w			$\nu_{27}, \nu_{27'}$	CH ₃ antisymmetric deformation
				1386	vw	1389	sh,w,dp	V28, V28'	(CH ₂) ₂ deformation
1264 R									
1256 Q, A/C	ш	1251	s	1248	s	1248	vw,p	$\nu_{11}, \nu_{11'}$	CH ₃ symmetric deformation
1250 P									
1221 R									
1216 min, B	νw	1212	νw	1213	vw	1215	w,dp	V 29, V 29'	CH ₂ wag
1211 P									
1198 R									
1193 min, B	νw							$\nu_{30}, \nu_{30'}$	CH ₂ twist
1191 Q, A	vw	1186	٨w	1186	M	1188	w,p	$\nu_{12}, \nu_{12'}$	(CH ₂) ₂ twist
1183 P									
1136 R									
1133 Q, A/C	ш	1122	s	1120	s	1125	w,p	$\nu_{13}, \nu_{13'}$	(CH ₂) ₂ wag
1125 P				0101			-		
4		101	wv	1049	MN .	1054	vw,dp	$\nu_{31}, \nu_{31'}$	$(CH_2)_2$ wag
930 max	s	927	s	927	sh,s	928	m,sh,dp	$\nu_{32}, \nu_{32'}$	$(CH_2)_2$ twist

J.R. Durig et al. / Journal of Molecular Structure 477 (1999) 31-47

34

Table 1

Table 1 (contin	(pən								
Infrared						Raman		Assignment	
Gas	Rel. Int.	Xenon Solution	Rel. Int	Amorphous Solid	Rel. Int.	Liquid	Rel. Int. & dp.	$ u^{\mathrm{i}^{\mathrm{b}}}$	Approximate Description
923 max	s	920	VS	920	S	922	m,p	$\nu_{33}, \nu_{33'}$	C-C ring stretch
915	s	911	s	910	s		I	$\nu_{14}, \nu_{19'}$	Si-H bend, CH ₂ rock
904	sh,s	901	sh,s	902	sh,m	903	w,p	${m u}_{16'}$	C-C ring stretch
886 R									
881 Q, A	s	879	s	878	s	883	m,p	$ u_{15} $	CH ₃ rock
876 Q, A	s	873	s	872	s	874	m,sh,dp	${\cal V}_{16}$	C-C ring stretch
873 P									
856 Q 830 R	ш	853	ш	853	ш	857	vw,p	$\nu_{15'}$	CH ₃ rock
827 0	s					823	W.D	\mathcal{D}_{12}	$(CH_3)_3$, rock
825 min, B	s	817	s	810	s		I,	V34, V35'	Si-H bend, CH ₃ rock
822 P									
819 Q	s	811	sh,s					$\nu_{17'}$	$(CH_2)_2$ rock
815 P									
		752	sh,vw	750	νw	754	vw,dp	ν_{35}	CH ₃ rock
737	sh,s	737	sh,w	737	ш	740	vw,sh,dp	$\nu_{34'}$	Si-H bend
729 Q, C	s	723	s	722	s	725	w,p	${m u}_{18}$	Si-C stretch
725 Q	s							${m u}_{18'}$	Si-C stretch
718 P									
677 Q, C	ш	677	ш	678	ш	679	m,p	$ \nu_{19} $	$CH_2 rock$
658 R									
652 Q	w	652	sh,w	653	sh,m	652	m,p	${\cal V}_{14'}$	Si-H bend
649 min, B	w	649	ш	649	ш			$v_{36}, v_{36'}$	C-Si ring stretch
646 P 200 B									
022 K									
617 Q	WV	616	M	614	M	617	vs.p	ν_{20}	C-Si ring stretch
612 Q, A/C	ΜΛ							${\cal V}_{20'}$	C-Si ring stretch
60/P 560 D						607	معلم ماتر يبينه	;	
700 N 000						000	v w,su,up	V 37'	
562 min, B	νw	205	M	264	M	69C	w,dp	ν_{37}	$(CH_2)_2$ rock
558 P 100 D									
490 R									
481 Q, C	w	480	w	481	w	483	w,p	$\boldsymbol{\nu}_{21'}$	ring deformation
480 Q, C									
474 P									
442 R									
434 Q, A	νw	436	νw	437	W	440	vs,p	$\boldsymbol{\nu}_{21}$	ring deformation
426 P									
253 Q, C	ш			255	W	258	vw,p	ν_{22}	ring puckering
238								$\boldsymbol{\nu}_{22'}$	ring puckering

J.R. Durig et al. / Journal of Molecular Structure 477 (1999) 31-47

Infrared Gas	Rel. Int.	Xenon Solution	Rel. Int	Amorphous Solid	Rel. Int.	Raman Liquid	Rel. Int. & dp.	Assignment <i>v</i> i ^b	Approximate Description
198 R 190 min, B 188 P	×			202	ΜΛ	207	w,dp	V ₃₈ , V _{38'}	Si-C bend
140 118	wv			150	M	146	d,wv	V 39, V 39' V 23, V'23'	CH ₃ torsion Si-C bend
^a Abbreviatic	ons used: s, str	ong; m, medium; w,	weak; v, very	v; sh, shoulder; bd, bros	ad; p, polariz	ed; dp, depo	larized; Q, P and R 1	refer to vibrati	onal-rotational branches and A, B

Table 1 (continued)

and C to infrared band contours. ^b v and v' refer to the assignments made for the equatorial and axial conformers, respectively.

Table 2	
Structural parameters ^a , rotational constants, dipole moments, and energy for 1-methylsilacyclobutane	

	Internal	RHF/3-21G*		RHF/6-31G*		MP2/6-31G*	
Parameter	coordinates	Equatorial	Axial	Equatorial	Axial	Equatorial	Axial
$Si-C_2(C_3)$	R ₁ , R ₂	1.893	1.893	1.898	1.899	1.897	1.899
Si-C ₁₁	R_5	1.882	1.882	1.887	1.888	1.882	1.883
Si-H	\mathbf{r}_7	1.481	1.482	1.482	1.482	1.494	1.494
$C_4 - C_2(C_3)$	R_3, R_4	1.586	1.586	1.561	1.562	1.557	1.557
C-H ₇	r ₁	1.086	1.083	1.087	1.084	1.096	1.093
C-H ₈	\mathbf{r}_2	1.082	1.086	1.083	1.086	1.092	1.096
C-H ₉	r ₃	1.086	1.083	1.087	1.084	1.096	1.093
C-H ₁₀	\mathbf{r}_4	1.082	1.086	1.083	1.086	1.092	1.096
C-H ₅	r ₅	1.081	1.083	1.086	1.086	1.096	1.096
C-H ₆	r ₆	1.083	1.081	1.086	1.085	1.096	1.096
C-H ₁₃	r ₈	1.087	1.087	1.086	1.086	1.094	1.094
$C - H_{14}(H_{15})$	r_{9}, r_{10}	1.088	1.088	1.087	1.087	1.094	1.094
∠C ₂ Si ₃ C	θ_1	79.95	79.94	78.56	78.69	78.03	78.10
$\angle C_2 C_4 C_3$	ν_1	100.1	100.1	100.7	100.9	100.2	100.4
∠CCSi	α_1, β_1	87.43	87.49	87.16	87.42	86.22	86.56
$\angle H_{12}SiC_{11}$	θ_2	109.2	109.2	109.0	108.8	109.6	109.3
$\angle H_5C_4H_6$	ν_6	108.6	108.5	107.3	107.2	107.4	107.2
$\angle H_7C_2H_8$	α_4	108.8	108.7	108.1	108.0	108.5	108.4
$\angle H_9C_3H_{10}$	β_{A}	108.8	108.7	108.1	108.0	108.5	108.4
∠SiCH ₁₃	$\lambda 1$	111.1	110.9	111.4	111.4	110.9	110.8
\angle SiCH ₁₄ (H ₁₅)	λ_2, λ_3	111.1	111.2	111.1	111.1	111.0	111.2
$\angle H_{13}CH_{14}(H_{15})$	σ_3, σ_2	107.9	107.8	107.8	107.7	108.0	107.9
$\angle H_{14}CH_{15}$	σ_1	107.6	107.7	107.5	107.5	107.7	107.8
∠CCH6	ν_{2}, ν_{5}	110.0	113.9	109.9	114.4	109.6	114.9
∠CCH ₅	ν_2, ν_4	113.9	110.1	114.5	109.9	114.9	109.7
$\angle CCH_7(H_9)$	α_5, β_5	110.4	114.6	110.8	115.2	110.4	115.9
$\angle CCH_8(H_{10})$	α_6, β_6	114.6	110.4	115.4	111.1	116.1	110.7
\angle SiCH ₇ (H ₀)	α_2, β_2	112.8	120.9	112.0	121.5	111.4	122.0
/ SiCH _{(H10})	α_3, β_3	121.2	113.1	121.9	112.3	122.5	111.7
$\angle CSiC_{11}$	φ_1, φ_2	120.0	114.7	120.6	115.7	121.6	114.3
$/H_1$ SiC ₂ (C ₂)	δ_1, δ_2	112.6	118.0	112.7	117.8	111.3	119.0
Puckering angle	τ	24.5	24.2	27.5	25.6	33.2	31.3
$\tau(H_{12}SiC_{11}H_{12})$		180.0	180.0	180.0	180.0	180.0	180.0
A		7346	6270	7480	6359	7595	6208
В		2859	3054	2843	3027	2836	3084
C		2419	2719	2415	2704	2412	2796
lual		0.461	0.250	0.409	0.226	0.476	0.222
lub		0.000	0.000	0.000	0.000	0.000	0.000
luc		0.431	0.329	0.416	0 339	0.444	0.330
		0.631	0.413	0.583	0.337	0.651	0.397
-(F + 443)		0.91793	0.91778	3 19763	3 1071/	3 80122	3 80050
$\Delta E(cm^{-1})$		0.71775	32	5.17705	107	5.00122	137

^a Bond distances in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye, and energies in Hartrees.

spectral bandpass of 3 cm^{-1} . The spectra of the liquid were recorded with the sample sealed in a Pyrex glass capillary held in a Miller-Harney apparatus [16]. Depolarization measurements were obtained for the liquid sample using a standard Ednalite

35 mm camera polarizer with 38 mm of free aperture affixed to the SPEX instrument. The measurements of Raman frequencies are expected to be accurate to $\pm 2 \text{ cm}^{-1}$ and typical spectra are shown in Fig. 3. All the observed bands in both

Table 3		
Symmetry coordinates	for	1-methysilacyclobutane

Species	Description	Symmetry Coordinate ^a
A'	CH ₃ antisymmetric stretch	$S_1 = 2r_8 - r_9 - r_{10}$
	(CH ₂) ₂ antisymmetric stretch	$S_2 = r_2 - r_1 + r_4 - r_3$
	CH ₂ antisymmetric stretch	$S_3 = r_5 - r_6$
	(CH ₂) ₂ symmetric stretch	$S_4 = r_1 + r_2 + r_3 + r_4$
	CH ₂ symmetric stretch	$S_5 = r_5 + r_6$
	CH ₃ symmetric stretch	$S_6 = r_8 + r_9 + r_{10}$
	Si-H stretch	$S_7 = r_7$
	CH ₂ deformation	$S_8 = 4\nu_6 - \nu_2 - \nu_3 - \nu_4 - \nu_5$
	(CH ₂) ₂ deformation	$S_9 = 4\alpha_4 + 4\beta_4 - \alpha_2 - \alpha_3 - \alpha_5 - \alpha_6 - \beta_2 - \beta_3 - \beta_5 - \beta_6$
	CH ₃ antisymmetric deformation	$\mathbf{S}_{10} = 2\sigma_1 - \sigma_2 - \sigma_3$
	CH ₃ symmetric deformation	$\mathbf{S}_{11} = \mathbf{\sigma}_1 + \mathbf{\sigma}_2 + \mathbf{\sigma}_3 - \mathbf{\lambda}_1 - \mathbf{\lambda}_2 - \mathbf{\lambda}_3$
	$(CH_2)_2$ twist	$S_{12} = \alpha_2 - \alpha_3 - \alpha_5 + \alpha_6 + \beta_2 - \beta_3 - \beta_5 + \beta_6$
	$(CH_2)_2$ wag	$S_{13} = \alpha_2 + \alpha_3 - \alpha_5 - \alpha_6 + \beta_2 + \beta_3 - \beta_5 - \beta_6$
	Si-H bend	$\mathbf{S}_{14} = 4\theta_2 - \delta_1 - \delta_2 - \varphi_1 - \varphi_2$
	CH ₃ rock	$\mathbf{S}_{15} = 2\lambda_1 - \lambda_2 - \lambda_3$
	C-C ring stretch	$S_{16} = R_3 + R_4$
	$(CH_2)_2$ rock	$S_{17} = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6 + \beta_2 - \beta_3 + \beta_5 - \beta_6$
	Si-C stretch	$S_{18} = R_5$
	CH ₂ rock	$S_{19} = \nu_3 - \nu_2 + \nu_5 - \nu_4$
	C-Si ring stretch	$\mathbf{S}_{20} = \mathbf{R}_1 + \mathbf{R}_2$
	ring deformation	$\mathbf{S}_{21} = \boldsymbol{\alpha}_1 + \boldsymbol{\beta}_1 - \boldsymbol{\nu}_1 - \boldsymbol{\theta}_1$
	ring puckering	$\mathbf{S}_{22} = \boldsymbol{\alpha}_1 + \boldsymbol{\beta}_1 + \boldsymbol{\nu}_1 + \boldsymbol{\theta}_1$
	Si-C bend	$\mathbf{S}_{23} = \boldsymbol{\varphi}_1 + \boldsymbol{\varphi}_2 {-} \boldsymbol{\delta}_1 {-} \boldsymbol{\delta}_2$
Α″	(CH ₂) ₂ antisymmetric stretch	$S_{24} = r_2 - r_1 + r_3 - r_4$
	CH ₃ antisymmetric stretch	$S_{25} = r_9 - r_{10}$
	$(CH_2)_2$ symmetric stretch	$S_{26} = r_1 + r_2 - r_3 - r_4$
	CH ₃ antisymmetric deformation	$S_{27} = \sigma_3 - \sigma_2$
	(CH ₂) ₂ deformation	$S_{28} = 4\alpha_4 - \alpha_2 - \alpha_3 - \alpha_5 - \alpha_6 - 4\beta_4 + \beta_2 + \beta_3 + \beta_5 + \beta_6$
	CH ₂ wag	$S_{29} = \nu_4 + \nu_5 - \nu_2 - \nu_3$
	CH ₂ twist	$S_{30} = \nu_2 - \nu_3 - \nu_4 + \nu_5$
	$(CH_2)_2$ wag	$S_{31} = \alpha_5 + \alpha_6 - \alpha_2 - \alpha_3 + \beta_2 + \beta_3 - \beta_5 - \beta_6$
	$(CH_2)_2$ twist	$S_{32} = \alpha_3 - \alpha_2 + \alpha_5 - \alpha_6 + \beta_2 - \beta_3 - \beta_5 + \beta_6$
	C-C ring stretch	$S_{33} = R_3 - R_4$
	Si-H bend	$\mathbf{S}_{34} = arphi_1 - arphi_2 + \delta_1 - \delta_2$
	CH ₃ rock	$S_{35} = \lambda_2 - \lambda_3$
	C-Si ring stretch	$S_{36} = R_1 - R_2$
	(CH ₂) ₂ rock	$S_{37} = \alpha_3 - \alpha_2 - \alpha_5 + \alpha_6 + \beta_2 - \beta_3 + \beta_5 - \beta_6$
	Si-C bend	$\mathrm{S}_{38}=arphi_2-arphi_1+\delta_1\!-\!\delta_2$
	CH ₃ torsion	$\mathrm{S}_{39}= au$

^a Not normalized; for definitions of internal coordinates see Table 2.

the infrared and Raman spectra, along with the proposed assignments, are listed in Table 1.

3. Ab initio calculations

The LCAO-MO-SCF restricted Hartree–Fock (RHF) calculations were performed with the GAUS-

SIAN-94 program [17] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters consistent with the symmetry restrictions using the gradient method of Pulay [18]. The structural optimization for both the equatorial and the axial conformers were carried out with initial parameters taken from those of

Table 4 Observe	ed and c	alculated frequencies	s (cm ⁻¹) :	for 1-me	thylsilacy	yclobuta	ne									
Species	Vib No.	Fundamental	Equatorial Ab Initio ^a	Fixed Scaled ^b	IR Int.°	Raman Act. ^d	dp Ratio ^d	Obs. ^e	PED ^í	Axial Ab Initio ^a	Fixed Scaled ^b	IR Int.°	Raman Act. ^d	dp Ratio ^d	¹ Obs ^e	PED ^í
A'	ν ₁	CH ₃ antisymmetric stretch	3200	3036	6.6	8.66	0.44	2985	1866	3198	3034	9.4	78.7	0.62	2985	1866
	ν_2	(CH ₂) ₂ antisymmetric stretch	3198	3034	17.4	77.4	0.75	2979	86S ₂	3194	3030	20.3	78.6	0.73	2979	89S ₂
	ν_3	CH ₂ antisymmetric stretch	3159	2997	22.8	104.7	0.30	2948	92S ₃	3156	2995	23.5	106.6	0.21	2948	90S ₃
	$ u_4 $	(CH ₂) ₂ symmetric stretch	3119	2959	5.6	201.6	0.09	2939	86S ₄ , 10S ₂	3123	2962	3.5	210.4	0.14	2939	$89S_4$
	ν_5	CH2 symmetric stretch	3103	2944	34.4	77.4	0.74	2921	$91S_5$	3102	2943	28.4	110.7	0.01	2921	$69S_5, 31S_6$
	ν_6	CH ₃ symmetric stretch	3102	2943	10.4	111.6	0.01	2921	92S ₆	3103	2944	12.7	70.2	0.54	2921	69S ₆ ,31S ₅
	<i>Γ</i> α ::	Si-H stretch	2765	2149	181.0	111.8	0.20	2131	$100S_7$	89721	2143	223.2	12/.8	0.21	2128	100S7 07E
	V8 V0	CH ₂ deformation (CH ₂), deformation	1528	1485	0.7 10.5	7.0 28.7	0.75	1423 1423	9238 76Se. 17Sio	1526	1485 1448	5.4	0.8 12.3	0.75	1423 1423	9258 698a. 25810
	ν_{10}	CH ₃ antisymmetric	1521	1443	0.8	8.6	0.74	1421	79S ₁₀ , 16S ₉	1523	1445	4.0	25.9	0.75	1419	$70S_{10}, 23S_{9}$
		deformation														
	ν_{11}	CH ₃ symmetric deformation	1365	1295	26.0	0.6	0.54	1256	98S ₁₁	1366	1296	27.6	0.7	0.58	1256	98S ₁₁
	ν_{12}	(CH ₂) ₂ twist	1262	1197	2.3	5.0	0.67	1191	46S ₁₂ , 24S ₁₉ , 15S ₁₇ ,	1260	1195	2.8	5.4	0.67	1191	
		$47S_{12}, 23S_{19}, 15S_{17}, 11S_{13}$							81cc1							
	ν_{13}	(CH ₂) ₂ wag	1211	1149	28.4	2.6	0.71	1133	67S ₁₃ , 11S ₁₂ , 11S ₁₆	1211	1149	26.2	2.3	0.68	1133	$69S_{13}$, $10S_{16}$, $10S_{12}$
	ν_{14}	Si-H bend	977	927	92.8	12.7	0.20	915	$\frac{16S_{14}}{12S_{12}}, \frac{21S_{16}}{11S_{17}}, \frac{15S_{19}}{1}, \\$	681	647	9.3	5.8	0.30	652	
		$26S_{14}, 26S_{15}, 15S_{18}, 13S_{23}$														
	V15	CH3 rock 36S.e. 29S.e. 14S.e. 10S.o	945	896	48.1	14.0	0.15	881	$34S_{15}$, $16S_{12}$, $14S_{14}$, $11S_{19}$	917	870	36.9	6.8	0.55	856	
	<i>1</i>	C_C ring stratch	030	887	30.7	4.0	0.62	876	535 105 115	958	000	37.8	19.0	0.15	904	536 148
	v17	(CH ₂) ₂ rock	877	832	7.6	2.7	0.34	827	$20S_{17}$, $22S_{19}$, $19S_{20}$,	867	823	14.2	4.6	0.13	819	$22S_{17}$, $22S_{19}$, $19S_{20}$
						1			$21S_{21}, 10S_{13}$							
	V ₁₈	Si-C stretch CH ₂ rock	711	716 675	8.1c 17.0	6.7 5.7	0.38 0.11	677	$60S_{18}, 11S_{20}, 10S_{17}$ $21S_{19}, 17S_{20}, 14S_{15},$	973	716 923	39.2 112.3	4.6 6.0	0.22 0.22	615 915	$47S_{18}$, $15S_{19}$, $15S_{20}$ $18S_{19}$, $23S_{14}$, $19S_{12}$,
									$12S_{14}, 11S_{21}, 11S_{23}$							$14S_{23}, 10S_{17}$
	$\boldsymbol{\nu}_{20}$	C-Si ring stretch	643	610	2.9	8.6	0.11	617	$15S_{20}, 22S_{15}, 22S_{18}, 16S_{14}, 14S_{17}$	636	603	1.9	12.1	0.14	612	$27S_{20}, 30S_{18}, 23S_{17}$
	ν_{21}	ring deformation	452	429	3.4	10.3	0.29	434	$55S_{21}, 22S_{20}, 10S_{18}$	504	478	14.2	7.1	0.25	481	$58S_{21}, 19S_{20}$
	ν_{22}	ring puckering/Si-C	267	254	1.8	0.4	0.69	253	$46S_{22}, 25S_{23}, 11S_{14}, 11S_{15}$	250	237	1.1	1.4	0.41	238	$45S_{22}, 25S_{23}, 12S_{17}$
	ν_{23}	Si-C bend/ring	137	130	0.3	0.4	0.44	118	$46S_{23}, 44S_{22}$	139	132	0.4	0.2	0.74	118	$45S_{23},44S_{22}$
;		puckering														
ž	ν_{24}	(CH ₂) ₂ antisymmetric stretch	3197	3033	15.9	90.6	0.75	2971	$90S_{24}$	3193	3029	12.5	95.7	0.75	2971	$94S_{24}$
	ν_{25}	CH ₃ antisymmetric	3196	3032	5.7	99.3	0.75	2971	$100S_{25}$	3198	3034	7.2	99.1	0.75	2971	$100S_{25}$
		stretch	0110	0200	0 1	c t	100	0000	501 500	0010	0,00	001	0.01	L L C	0000	570
	V 26	CH ₂ ₂ symmetric surficence CH ₂ antisymmetric	5119 1523	9662 1444	0.c1 2.6	c./1 2.11	c/.0	(1397)	95S27 95S27	5122 1523	2902 1445	10.2	16.0	c/.0	(1397)	94.5_{26} 93.8_{27}
	17.	deformation			ì		2	(17		2	;		2		17.000
	ν_{28}	(CH ₂) ₂ deformation	1509	1431	5.4	8.2	0.75	(1386)	99528	1508	1431	7.8	3.3	0.75	(1386)	96S ₂₈
	V ₂₉ V ₃₀	CH ₂ wag CH, twist	1282 1282	1216	c.u 1.2	9.1 9.0	c/.0 0.75	1193	783_{29} 57 8_{30} ,20 8_{31}	ccc1 1282	120/	0.8	0.9 10.6	c/.0 0.75	0121 1193	795_{29} $595_{30},195_{31}$

Species	Vib No.	Fundamental	Equatorial Ab Initio ^a	Fixed Scaled ^b	IR Int. [°]	Raman Act. ^d	dp Ratio ^d	Obs.°	PED ^f	Axial Ab Initio ^a	Fixed Scaled ^b	IR Int.°	Raman Act. ^d	dp Ratio ^d	¹ Obs ^e	PED ^r
Α'	<i>ν</i> 1	CH ₃ antisymmetric stretch	3200	3036	9.9	8.66	0.44	2985	99S ₁	3198	3034	9.4	78.7	0.62	2985	99S ₁
	ν_{31}	(CH ₂) ₂ wag	1126	1069	1.6	2.0	0.75	1049	72S ₃₁	1131	1073	1.8	1.7	0.75	1049	73S ₃₁
	ν_{32}	(CH ₂) ₂ twist	1009	957	2.3	4.7	0.75	930	$67S_{32}, 18S_{30}$	1006	954	4.2	8.5	0.75	930	$49S_{32}, 25S_{33}, 10S_{30}$
	ν_{33}	C-C ring stretch	994	943	15.5	6.8	0.75	923	$82S_{33}$	994	943	8.7	3.2	0.75	923	$59S_{33}, 19S_{32}, 12S_{30}$
	ν_{34}	Si-H bend	878	833	111.5	1.3	0.75	825	$34S_{34}, 37S_{37}$	774	734	21.6	5.8	0.75	737	$22S_{34}, 34S_{38}, 32S_{37}$
	ν_{35}	CH ₃ rock	804	763	0.9	3.7	0.75	(750)	$39S_{35}, 31S_{37}, 21S_{38}$	879	834	94.3	0.1	0.75	825	$59S_{35}, 29S_{34}$
	ν_{36}	C-Si ring stretch	667	633	8.3	9.1	0.75	649	$85S_{36}$	687	652	16.4	7.4	0.75		$52S_{36}, 19S_{37}, 19S_{35}$
	ν_{37}	(CH ₂) ₂ rock	600	570	6.9	2.0	0.75	562	$48S_{37}, 23S_{34}, 10S_{32}$	608	578	1.1	3.2	0.75	(583)	$29S_{37}, 34S_{36}, 19S_{34}$
	ν_{38}	Si-C bend	191	181	0.3	0.9	0.75	190	$57S_{38}, 31S_{34}$	192	182	0.2	1.0	0.75	190	$58S_{38}, 31S_{34}$
	ν_{39}	Si-CH ₃ torsion	152	152	0.0	0.0	0.75	140	$96S_{39}$	163	163	0.0	0.0	0.75	140	$98S_{39}$
a Ca	lenlated	with the MP2/6-31	G* hasis se	+												

^b Scaling factors of 0.9 for stretching and bending coordinates and 1.0 for torsional coordinates. ^c Calculated infrared intensities in km/mol, using the MP2/6-31G* basis set.

 d Calculated Raman activities in Å⁴/amu, using RHF/6-31G* basis set.

^e Frequencies are taken from the infrared spectrum of the gas, except the ones in parentheses, which are taken from the infrared spectrum of the solid. ^f For a description of the symmetry coordinates see Table 3.

Table 4 (continued)



Fig. 4. Temperature-dependent Raman spectrum $(380-520 \text{ cm}^{-1})$ of liquid 1-methylsilacyclobutane.

1,1-diethylsilacyclobutane [19]. The 3-21G* and 6-31G* basis sets were employed at the level of RHF and Moller–Plesset (MP2) to second order. The determined structural parameters are listed in Table 2.

In order to obtain a complete description of the molecular motions involved in the normal modes of 1-methylsilacyclobutane, we have carried out a

Table 5

Temperature and intensity ratio for the conformational stability determination of 1-methylsilacyclobutane dissolved in liquid xenon^a

T(° C)	$1000/T(K^{-1})$	I481(ax)/I437(eq)	-lnk
-55	4.58	2.06	-0.724
-60	4.65	2.06	-0.724
-65	4.80	1.88	-0.633
-70	4.92	1.74	-0.552
-80	5.18	1.88	-0.629
-85	5.31	1.77	-0.573
-90	5.46	1.76	-0.566
-95	5.61	1.62	-0.480
-100	5.78	1.67	-0.515

 a $\Delta H = 122 \pm 26$ cm $^{-1}$ (1.46 \pm 0.32 kJ/mol) with the equatorial form the more stable conformer.

normal co-ordinate analysis. The force fields in Cartesian co-ordinates were calculated by the GAUSSIAN-94 program [16] with the MP2/6-31G* basis set. Internal co-ordinates (Table 2) were used to calculate the G and B matrices using the structural parameters given in Table 2. Using the B matrix [20], the force field in Cartesian coordinates was then converted to a force field in internal co-ordinates, and the pure ab initio vibrational frequencies were reproduced. The force constants for both the equatorial and axial conformers can be obtained from the authors. Subsequently, scaling factors of 0.9 for stretching and bending and 1.0 for the torsional co-ordinates, and the geometric average of scaling factors for interaction force constants were used to obtain the fixed scaled force field and resultant wavenumbers. A set of symmetry co-ordinates was used (Table 3) to determine the corresponding potential energy distributions (PED). A comparison between the observed and calculated frequencies of 1-methylsilacyclobutane along with the calculated infrared intensities, Raman activities, depolarization ratios, and PED are given in Table 4.

4. Conformational stability

The determination of the conformational stability is not straightforward as most of the fundamentals of the two conformers are predicted to be near coincident. Nevertheless, it is clear from the spectral data that conformers are present in the fluid phases. For

Table 6

Temperature and intensity ratio for the conformational stability determination of 1-methylsilacyclobutane in the liquid state^a

T(°C)	1000/T	I439(eq)/I483(ax)	-lnK
+ 6	3.58	4.8262	-1.5741
-11	3.81	4.9364	-1.5699
-30	4.11	4.8076	-1.5702
-44	4.36	4.7386	-1.5557
-56	4.60	5.6686	-1.7349
-68	4.87	5.3136	-1.6703
-78	5.12	5.9895	-1.7900
-91	5.49	6.5464	-1.8789
-101	5.81	6.8157	-1.9192
-121	6.58	8.0251	-2.0826

 $^{a}\,\Delta H = 127\,\pm\,14~cm^{-1}$ (1.52 \pm 0.17 kJ/mol) with the equatorial form the more stable conformer.



WAVENUMBER (cm⁻¹)

Fig. 5. Temperature-dependent infrared spectrum (420-500⁻¹) of 1-methylsilacyclobutane dissolved in liquid xenon.

example, a comparison of the Raman spectrum of the liquid as a function of temperature indicates that the band at 481 cm⁻¹ decreases in intensity relative to the band at 437 cm^{-1} with decreasing temperature (Fig. 4). The ab initio calculations indicate that the band at 481 cm^{-1} is due to the axial conformer where the ring deformation, ν_{21} , is predicted at 478 cm⁻¹. Similarly, the 437 cm^{-1} band is assigned as the corresponding ring deformation for the equatorial conformer with a predicted frequency of 429 cm⁻¹. No other fundamentals for either conformer are predicted between 550 and 260 cm^{-1} , so the assignment for these two bands to the individual conformers can be made with confidence. Finally, it should be noted that this conformer pair has the largest predicted frequency separation, which further supports the assignment as given.

There is other evidence for conformers in the fluid phases but it is not as definitive. For example, the $(CH_2)_2$ rock and C–Si ring stretch are predicted as the next higher frequency fundamentals after the ν_{21} conformer doublets and both of these fundamentals have identifiable doublets at 569/583 and 617/612 cm⁻¹ with the first listed frequencies due to the equatorial conformer. Also, the ring puckering/Si–C bend, ν_{22} , is well-defined for both conformers with bands at 253 and 238 cm⁻¹ for the equatorial and

axial conformers, respectively. Other conformer doublets are listed in Table 4 but none are as clear as the conformer doublet in the 400 cm^{-1} region.

The conformer pair at 481/437 cm⁻¹ was used to determine the enthalpy difference between the conformers by the temperature-dependent infrared spectra of xenon solutions. The spectral changes are shown in Fig. 5 and from these data, the increase in the intensity of the infrared band assigned to the equatorial conformer as the temperature decreases, confirms the stability of the equatorial form over the axial conformer in the xenon solution. In order to obtain the enthalpy difference, ten sets of spectral data were obtained for these bands over the temperature range -55° C to -100° C (Table 5). The intensity data for the conformer pair were fit to the van't Hoff equation, $\ln K = (\Delta H/RT) - (\Delta S/R)$, where K is the intensity ratio (I_{ax}/I_{ea}) , and it was assumed that ΔH is not a function of temperature. Using the least-squares fit and the slope of the van't Hoff plot, a ΔH value of $122 \pm 26 \text{ cm}^{-1}$ (1.46 $\pm 0.32 \text{ kJ/mol}$) was obtained. This value should be near the value for the gas [21,22] as both conformers have similar sizes. We also determined the enthalpy difference in the liquid state by the temperature-dependent Raman spectra (Fig. 4). Utilizing the same conformer doublet as used in the



Fig. 6. Raman spectra of 1-methylsilacyclobutane: (A) experimental spectrum of the liquid; (B) calculated spectrum of the mixture of both conformers; (C) calculated spectrum of the axial conformer; and (D) calculated spectrum of the equatorial conformer.

infrared study, a ΔH value of 127 \pm 14 cm⁻¹ (1.52 \pm 0.17 kJ/mol) was obtained from the data listed in Table 6.

5. Vibrational assignment

Both the axial and equatorial conformers of 1methylsilacyclobutane have a plane of symmetry and their 39 normal modes are classified by the symmetry species of the C_s symmetry group, A' and A". There are 23 A' vibrations which are expected to produce polarized Raman bands and A/C-type hybrid infrared band contours. The remaining 16 A" modes should give rise to depolarized lines in the Raman spectrum and yield B-type infrared band envelopes. Thus, to identify the A' and A" vibrations, we utilized the measured depolarization ratios and observed infrared band contours, whereas to distinguish the equivalent modes of the two conformers we relied



Fig. 7. Mid-infrared spectra of 1-methylsilacyclobutane: (A) xenon solution at -65° C; (B) calculated spectrum of the mixture of both conformers; (C) calculated spectrum of the axial conformer; and (D) calculated spectrum of the equatorial conformer.

on the predicted frequency order, infrared intensities, and Raman activities from the ab initio calculations.

In the CH stretching region $(3000-2900 \text{ cm}^{-1})$, there are nine expected fundamentals. The three sharp Q-branches in the infrared spectrum of the gas at 2985, 2979, and 2948 cm⁻¹, respectively, must be attributed to the CH₃ (A'), (CH₂)₂ (A'), and CH₂ antisymmetric stretches of both conformers. The three corresponding symmetric stretches are associated with the two strong polarized Raman bands at 2923 cm⁻¹ for the A' (CH₂)₂ vibration and at 2908 cm⁻¹ for the CH₂ and CH₃ modes. The A'' (CH₂)₂ and CH₃ antisymmetric stretches are overlapped in the shoulder at 2964 cm⁻¹ in the infrared spectrum of the xenon solution, whereas the A'' (CH₂)₂ symmetric stretch is coincident with the



Fig. 8. Equatorial conformation of 1-methylsilacyclobutane.

respective A' vibration. The Si–H stretches of the equatorial and axial conformers give rise to the very strong Q-branches located at 2131 and 2128 cm⁻¹, respectively.

The intensities of the bands in the C–H deformation region are quite low, in both the infrared and Raman spectra. Nevertheless, the CH₂ deformations from the A' symmetry block are observed in the Raman spectrum of the liquid at 1455 and 1418 cm⁻¹, respectively. Three of the remaining four C–H deformational modes, ν_{10} , ν_{27} , and ν_{28} , are masked on the low-frequency side of the latter band, but in the infrared spectrum of the solid they appear to be separated. The remaining CH₃ symmetric deformation produces the Q-branch at 1256 cm⁻¹.

The CH₂ wagging and twisting fundamentals are both in the A["] block and, therefore, give rise to the B-type bands at 1216 and 1193 cm⁻¹, respectively, in the infrared spectrum of the gas. In the same spectrum, A/C-type bands are observed for the A' (CH₂)₂ wag and twist at 1133 and 1191 cm⁻¹, respectively. The corresponding A["] wag and twist, ν_{31} and ν_{32} , yield the depolarized Raman bands at 1050 and 928 cm⁻¹.

The strongest band in the infrared spectrum of the sample dissolved in liquid xenon is due to the A" C–C ring stretch at 920 cm⁻¹. The A' C–C ring stretches of the axial and equatorial conformers are separated in the Raman spectrum of the liquid and appear at 903 and 874 cm⁻¹, respectively. Due to apparent differences in the PEDs (Table 4) of the two conformers, the Si–H "in-plane" band of the axial form is assigned at a much lower frequency of 652 cm⁻¹ than the corresponding vibration of the equatorial

conformer which overlaps with the CH₂ rock of the axial form of the strong infrared band at 911 cm⁻¹ in the spectrum of the xenon solution. Thus, the sharp C-type Q-branch at 677 cm⁻¹ is assigned to the CH₂ rock of the equatorial conformer. The "out-of-plane" Si–H band of the equatorial form is associated with the B-type band with a minimum at 825 cm⁻¹ in the infrared spectrum of the gas, where it is overlapped with the CH₃ rock of the axial conformer.

The A' CH₃ and (CH₂)₂ rocks are assigned to the four Q-branches located at 881/827 cm⁻¹ for the equatorial conformer and 856/819 cm⁻¹ for the axial form, respectively. The corresponding A'' modes are depolarized in the Raman spectrum of the liquid and appear at 754/569 cm⁻¹ for the equatorial rotamer. The Si–C stretch of the methyl group is observed at 723 cm⁻¹ in the infrared spectrum of the xenon solution, whereas the C–Si ring stretch is found as a very strong, polarized band at 617 cm⁻¹ in the Raman spectrum of the liquid. For both C–Si stretching modes, double Q-branches are observed in the infrared spectrum of the gas due to the two different conformers. The weak B-type band at 649 cm⁻¹ is then assigned to the A'' C–Si ring stretch.

The ring deformation conformer doublet at 480/ 436 cm⁻¹ is well separated and has been discussed earlier. A C-type band at 253 cm⁻¹ and a maximum at 238 cm⁻¹ in the far-infrared spectrum of the gas are observed for the ring puckering/Si-C bend motions of the two conformers. The Si-C bend/ring puckering mode is observed at 118 cm^{-1} for both conformers. These vibrational modes are strongly coupled with nearly equal contribution from the Si-C bend and ring puckering vibrations for the lower wavenumber band. Surprisingly, these two fundamentals in the 200 cm⁻¹ region are not separated in the Raman spectrum of the liquid. Finally, the "out-of-plane" Si-C bend is assigned to the B-type band located at 190 cm^{-1} in the far-infrared spectrum of the gas. whereas the CH₃ torsion is associated with the weak absorption at 150 cm⁻¹ in the far-infrared spectrum of the solid.

6. Results and discussion

To aid in the vibrational assignment, we predicted the Raman and infrared spectra (Figs.

6 and 7) for 1-methylsilacyclobutane using the calculated frequencies, scattering activities and intensities determined from the ab initio calculations. The GAUS-SIAN-94 program [17] with the option of calculating the polarizability derivatives (RHF/6-31G*) was used. The Raman scattering cross sections, $\partial \sigma_j / \partial \Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activities and the predicted frequencies for each normal mode using the following relation [23]:

$$\frac{\partial \sigma_j}{\partial \Omega} = \left(\frac{2^4 \pi^4}{45}\right) \left(\frac{\left(\nu_0 - \nu_j\right)^4}{1 - \exp\left[-hc \nu_j/kT\right]}\right) \left(\frac{h}{8\pi^2 c \nu_j}\right) S_j$$

where ν_0 is the exciting frequency, ν_i the vibrational frequency of the *j*th normal mode, h, c and k are universal constants, and S_i the corresponding Raman scattering activity. To obtain the polarized Raman scattering cross section, the polarizabilities are incorporated into S_i by $S_i [(1-\rho_i)/(1+\rho_i)]$ where ρ_i is the depolarization ratio of the *j*th normal mode. The Raman scattering cross sections and calculated frequencies are used together with a Lorentzian line shape function to obtain the calculated spectrum. Since the calculated frequencies are $\approx 10\%$ higher than those observed, the frequency axis of the theoretical spectrum was compressed by a factor of 0.9. The predicted Raman spectra of the pure equatorial and axial conformers are shown in Fig. 6C and D, respectively. The predicted Raman spectrum of the mixture of the two conformers with an assumed ΔH of 127 cm⁻¹ is shown in Fig. 6B which should be compared to the experimental spectrum of the liquid (Fig. 6A). The calculated Raman spectrum is quite similar to the experimental spectrum particularly in the $500-1500 \text{ cm}^{-1}$ region which makes it very useful for making the vibrational assignment.

Infrared intensities were also calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculations at the MP2/6-31G* level and transformed to normal coordinates by

$$\left(\frac{\partial \mu_{\mu}}{\partial Q_{i}}\right) = \sum_{j} \left(\frac{\partial \mu_{\mu}}{\partial X_{j}}\right) L_{ji}$$

where Q_i is the *i*th normal coordinate, X_j the *j*th Cartesian displacement coordinate, and L_{ji} the

transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by

$$I_i = \frac{N\pi}{3c^2} \left[\left(\frac{\partial \mu_x}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i} \right)^2 \right]$$

In Fig. 7D and E, the predicted infrared spectra of the axial and equatorial conformers Fig. 8, respectively, are shown. The combination of the spectra of the two conformers with a ΔH of 122 cm⁻¹ is shown in Fig. 7C and the experimental spectrum of the sample dissolved in liquid xenon is shown in Fig. 7B along with that for the gas (Fig. 7A). Again, these spectra were very valuable for making the vibrational assignment particularly in the region from 400 to 1500 cm⁻¹.

The assignment of the C–H stretching modes depends almost entirely on the ab initio predictions and it is necessary to assign several degeneracies. Also, we have rather arbitrarily assigned the same frequencies for the corresponding bands for the two conformers. We similarly relied on the ab initio calculations for the assignment of the CH₂ and CH₃ deformations. It should be noted that for both the CH₃ symmetric deformation and the (CH₂)₂ deformation the predicted values are about 40 cm⁻¹ too high. Beginning with the Si–H bend, ν_{14} in the A' symmetry block, there is so much mixing that the descriptions are rather arbitrary except for the ring modes. The mixing is considerably less for the corresponding modes in the A'' symmetry block.

In the low-frequency region, there is extensive mixing of the ring puckering mode with the siliconmethyl bending mode where the band at 118 cm⁻¹ has about equal amounts of each motion. The band at 253 cm⁻¹ has 46% ring puckering and 25% Si– C(H₃) bend with 11% contributions from the Si–H bend and the (CH₂)₂ rock. Thus, it would not be possible to use excited state transitions from either of these bands to obtain information on the potential function governing interconversion of the conformers.

The vibrational assignments for both conformers are summarized in Table 4. There were only a limited number of bands which could be identified with a single conformer. Nevertheless, the ab initio predicted spectra made it possible to assign a few of the bands to one or the other conformer so the presence of both conformers in the fluid states was definitively shown from the data.

Utilizing the Si-H stretching frequencies, it is possible to calculate the Si-H distances (r_0) for both conformers [24]. Utilizing the frequencies of 2131 and 2128 cm⁻¹ for the Si-H vibrations for the equatorial and axial conformers, respectively, the Si-H bond distances are calculated to be 1.490Å. This value compares very well with the 1.494 Å predicted for this bond distance for both conformers from the MP2/6-31G* calculations. The predicted Si-H bond distances from the RHF/3-21G* and RHF/6-31G* calculations are shorter with values of 1.481 and 1.482Å, which makes them smaller by 0.008 Å than the r_0 values obtained from the infrared spectrum. Therefore, the agreement from the MP2/6-31G* calculation is quite good and indicates that the structural parameters obtained from the relatively small 6-31G* basis set with electron correlation at the MP2 level provides good predictions of the structural parameters for the Si-H bonds of these types of molecules.

The barrier to conformer interconversion of 1methylsilacyclobutane was obtained through the ab initio energies of the axial and equatorial conformers and the energy of the transition state along the puckering coordinate calculated with the MP2/6-31G* basis set. A value of 686 cm⁻¹ (8.21 kJ/mol) was obtained for the equatorial-to-axial puckering barrier. This value compares well with the barrier to inversion of 641 \pm 20 cm⁻¹ (7.67 \pm 0.24 kJ/mol) for methylcyclobutane [7], which was determined from the ring puckering transitions in the low-frequency Raman spectrum. However, the axial-to-equatorial barrier of methylcyclobutane [7] is about 150 cm^{-1} (1.80 kJ/ mol) lower than the one obtained in this study for 1methylsilacyclobutane (549 cm^{-1}). The reason for this difference is mainly due to the different ΔH values of the two compounds. It should also be noted that the barrier heights evaluated through the ab initio method may be different from the actual experimental quantities which are not available at this time for c- $C_3H_6SiH(CH_3)$.

The enthalpy difference of $122 \pm 26 \text{ cm}^{-1}$ between the axial and equatorial conformers of 1-methylsilacyclobutane is less than one-half the respective value for the carbon analog, $295 \pm 75 \text{ cm}^{-1}$. Evidently, the larger size of the Si atom reduces the spatial restrictions for the conformation with the methyl group in the axial position. This conclusion is supported by the much larger puckering angles of $\sim 32^{\circ}$ calculated for 1-methylsilacyclobutane (Table 2) compared to the values of 20.7° and 16.4° for the equatorial and axial conformers of methylcyclobutane [7], respectively.

It is clear from the structural parameters listed in Table 2 that the main differences in the geometry of the conformers arise from the conversion of the equatorial hydrogen atoms in the axial position and vice versa during the inversion of the molecule. The equatorial hydrogens in both rotamers have slightly shorter (by about 0.004Å) C-H distances and much larger CCH and SiCH angles. For example, the CCH bond angles are about 5° larger and the SiCH bond angles are about 10° larger for the equatorial hydrogen atoms. Similarly, the $CSiC(H_3)$ bond angle of the equatorial conformer is about 7° larger than that in the axial form. As it was expected, the puckering angle in the axial form is approximately 2° smaller than the angle in the equatorial form and this is consistent with the results for the carbon analog of 1-methylsilacyclobutane.

The apparent resemblance in the geometric parameters of the two conformers reflects in very similar values for the diagonal elements of the two force constant matrices. The only significant difference is found in the values of the CCSi and CCC ring bending force constants, which are about 5% larger for the axial form. This fact results in a lower frequency of the ring deformation fundamental (see Table 4) for the equatorial compared to the axial rotamer. Thus, the only well separated conformer doublet appears to be the ring deformation located at 434/481 cm⁻¹.

As no experimental structural parameters have been reported for 1-methylsilacyclobutane it is not possible to assess how well the other parameters are predicted from the MP2/6-31G* calculation. Nevertheless, based on some of our earlier studies [25,26] of the four-membered rings, we believe the C–H and C–C bond distances should be well predicted, i.e. the C–H distances within 0.005 Å and C–C distances within 0.008Å. The angles are usually predicted within about one degree from the MP2/6-31G* calculations so we expect the listed parameters given in Table 2 are about as accurate as one could obtain from an electron diffraction or microwave investigation of this molecule. It is not clear why it was not possible to obtain one conformer in the polycrystalline state. However, the molecule remained as a liquid at very low temperatures where it became very viscous but it did not appear to be a solid. Since the barrier to inversion is comparable with that for methylcyclobutane and the enthalpy difference is smaller than that of the carbon compound it should be possible to obtain a single conformer as was found for methylcyclobutane.

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