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Infrared and Raman spectra, conformations, *ab initio* calculations and spectral assignments of 1-fluoro-1-silacyclohexane

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ABSTRACT

Raman spectra of 1-fluoro-1-silacyclohexane as a liquid were recorded at 293 K and polarization data obtained. Additional Raman spectra were recorded at various temperatures between 293 and 143 K, and intensity changes of certain bands with temperature were investigated. An apparently plastic phase was observed around 170 K, but no definite crystallization was ever obtained on cooling. The infrared spectra have been studied of the vapor, of an amorphous solid at 78 K and of the liquid in the range 600–100 cm⁻¹. No infrared bands present in the vapor or liquid vanished upon cooling.

The compound exists a priori in two conformers, equatorial (e) and axial (a), and the experimental results suggest an equilibrium in which the *a*-conformer has $1.2 \text{ kJ} \text{ mol}^{-1}$ lower enthalpy than the e-conformer in the liquid, leading to 60% a-conformer at ambient temperature.

B3LYP calculations with various basis sets and the G3 model chemistry gave conformational enthalpy difference $\Delta H(e-a)$ in the range 0.6 and 1.8 kJ mol⁻¹. Infrared and Raman intensities, polarization ratios and vibrational frequencies for the *e* and *a* conformers were calculated. The wavenumbers of the vibrational modes were derived in the anharmonic approximation in B3LYP/cc-pVTZ calculations. An average relative deviation of ca. 1% between the observed and calculated wavenumbers for the 48 modes of the eand *a* conformers was found.

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1. Introduction

The stereochemistry of cyclohexane has been studied for more than 70 years, and substituted cyclohexanes were among the first examples of molecules exhibiting conformational equilibria. Thus, it has been established from numerous studies that the low energy form for the cyclohexane ring is the chair, while the craddle and twisted forms have much higher energies and are not observed under ordinary conditions. Moreover, in monosubstituted cyclohexanes the *e*-conformer has generally lower energy than the *a*-conformer, leading to a larger abundance of the *e*-conformer in the vapor and in the liquid states. In the crystalline state, however, obtained by cooling or by high pressure, the monosubstituted cyclohexanes generally exist only in the *e*-conformation since the a-conformer is not accommodated in the crystal lattice. Traditionally, the preference for the *e*-conformer has been explained as a 1,3-diaxial repulsion between the parallel C-X and C-H bonds increasing the energy of this conformer, although additional effects might be involved.

Much less information is available on the steric effect when a carbon atom in cyclohexane is substituted with a neighboring atom in the periodic system - silicon. Silicon differs from carbon in various respects, it has lower electronegativity and larger covalent radius than carbon, leading to increased conformational flexibility. It was suggested [1] from force field calculations that silacyclohexane and various substituted silacyclohexanes exist in a modified chair form in which the ring is more flattened than cyclohexane in the region of silicon and is more puckered in the opposite part of the ring. The parent molecule, silacyclohexane and a few molecules with a substituted atom on the silicon have been investigated. The preparation of silacyclohexanes and their derivatives is difficult, and these compounds are much more unstable than the corresponding cyclohexanes, and therefore few experimental studies have been made.

Many quantum chemical calculations of silacyclohexane [1–4] revealed the chair form to be the dominant conformer. 1-Methyl-1-silacyclohexane was studied by gaseous electron diffraction and by NMR spectroscopy, giving the *e*-conformer to be the more stable form [4–6]. Quantum chemical calculations indicated [7–9]

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that most of the substituted silacyclohexanes have the *a*-form as the preferred conformer (Fig. 1).

In the present study, we present an infrared and Raman spectroscopic investigation of 1-fluoro-1-silacyclohexane (later to be abbreviated FSC). Special emphasis is put on the conformational equilibrium between the e and a conformers, and a comparison with the results of fluorocyclohexane. The stereochemistry of FSC has previously been investigated by microwave spectroscopy [10], and by gaseous electron diffraction, low temperature NMR and Raman spectroscopy, and by quantum chemical calculations [11].

2. Experimental

2.1. Preparation

First, a sample of 1-chloro-1-silacyclohexane was prepared by the formation of a double Grignard of 1,4-dibromopentane in dry ethyl ether. The Grignard was then coupled with freshly distilled trichlorosilane in dry ethyl ether overnight with refluxing. The magnesium salt was separated from the ethereal solution by filtration under dry nitrogen. The ether was distilled off at reduced pressure and the final purification was obtained by a trap to trap distillation. The sample of 1-fluoro-1-silacyclohexane was prepared from the chloro derivative using freshly sublimed antimony trifluoride. The sample purity was checked by infrared spectroscopy giving distinct bands for the Si–H and Si–F stretches. ¹³C NMR spectra in CDCl₃ solution gave three signals for the carbons with the positions at 13.333 ppm, 23.469 ppm and 29.395 ppm.

2.2. Raman measurements

The Raman spectra were recorded with a multichannel spectrometer from Horiba (Jobin Yvon) model T 64000 employing both single and triple monochromator detection. The spectrometer was fitted with a CCD detector, cooled to ca. 130 K. The spectra were excited by a Milennia Pro diode-pumped (Nd:YVO₄ crystal) laser from Spectra-Physics (Model J 40), using 90° scattering geometry, adjusted to give approximately 50 mW of the 532 nm line on the sample. The spectrometer was applied with: (1) a single monochromator using a notch filter, or a triple monochromator with (2) additive or (3) subtractive collection. A higher signal to noise ratio was achieved with the single monochromator, the triple additive collection gave slightly higher resolution, while the triple subtractive set-up allowed the spectra to be recorded at wavenumbers closer to the exciting line. In the liquid sample the low wavenumber modes were recorded to $60 \, \mathrm{cm}^{-1}$ with the triple subtractive mode, compared to 120 cm⁻¹ with the single monochromator and the notch filter.

The high sensitivity of the CCD detector gave spectra with large signal/noise ratio, and the spectra were recorded at ca. 2 cm^{-1}

resolution. Depolarization measurements were carried out in the 90° illumination mode, employing a polarizer and a scrambler between the sample and the monochromator. The polarizer unit was calibrated with carbon tetrachloride filled into a cylindrical tube identical to the one used for FSC. Except for very weak and/ or overlapping bands, fairly comprehensive depolarization data were obtained.

Raman spectra of the liquid, including depolarization measurements were recorded at room temperature. Additional spectra were obtained for every 10° between 293 and 143 K in a capillary tube of 2 mm inner diameter. The tube was surrounded by a Dewar, cooled by gaseous nitrogen evaporated from a liquid reservoir [12]. From these spectra, the enthalpy difference $\Delta_{conf}H$ between the conformers were calculated. Various (*a*)/(*e*) band pairs were attempted for determining the enthalpy difference. The vapor of FSC was condensed on a copper finger at 78 K. An amorphous phase was formed, and the bands were quite similar to those of the liquid. Many annealing experiments were tried, but the sample never crystallized in any of the temperature ranges employed.

2.3. Infrared measurements

The middle infrared spectra (MIR) were recorded on two Fourier transform spectrometers: a Bruker spectrometer, Vertex 80 and a Perkin–Elmer model 2000 (4000–400 cm⁻¹). Additional far infrared (FIR) spectra were obtained using the Vertex 80 spectrometer ($600-100 \text{ cm}^{-1}$) in the FIR set-up. Both spectrometers had DTGS detectors. Beamsplitters of Ge coating on KBr substrate were employed in the MIR region, and a multilayer coating on Mylar was used in the FIR region.

The vapor was studied in cells with CsI windows (10 cm path) in the MIR region and polyethylene widows (18 cm path) in FIR. The spectrometer was flushed with dry nitrogen gas to diminish the absorption of water vapor in the FIR region. FIR spectra were recorded with the sample confined in a liquid cell of polyethylene (throw away cells) of ca. 0.2 mm path. The vapor was deposited on a CsI window in a glass cryostat, cooled with liquid nitrogen, and an amorphous solid was observed on the window. The sample was annealed to various temperatures between 120 and 150 K and recooled to 78 K before recording of the spectra. When heated above 180 K the sample melted.

3. Results

3.1. Raman spectral results

Raman spectra of FSC as a liquid at ambient temperature are presented in Figs. 2 and 3, respectively, whereas depolarization spectra are given in Fig. 4. A Raman spectrum of the amorphous sample deposited on a Cu finger at 78 K is presented in Fig. 5, quite similar to that recorded of the liquid at ambient temperature. The





Fig. 2. Raman spectra of FSC as a liquid at 293 K in the range $3200-600 \text{ cm}^{-1}$ in a capillary with 2 mm inner diameter.



Fig. 3. Raman spectra of FSC as a liquid at 293 K in the range 700–100 $\rm cm^{-1}$ in a capillary with 2 mm inner diameter.



Fig. 4. Raman spectra of FSC in the range 3200–200 $\rm cm^{-1}$ recorded at 293 K, giving the parallel and perpendicular polarization directions.

sample was subsequently annealed to 90, 110, 130, 150 and 180 K and recooled to 78 K before recording. Visual observation suggested that the sample formed a solid at 170 K, maintained after



Fig. 5. Raman spectra of FSC in the range 1550-80 cm⁻¹, recorded of a sample deposited on a cold finger at 78 K.

cooling to 78 K, but negligible spectral changes were observed. The experimental data for the Raman and infrared spectra are collected in Table 1.

Raman spectra of the liquid were recorded at 15 temperatures (every 10°) in two series of experiments between 293 and 143 K. Minor intensity variations with temperature of some Raman bands were observed relative to neighboring bands, interpreted as a displacement of the conformational equilibrium. The theoretical calculations give an enthalpy difference between the conformers amounting to 0.6-1.8 kJ mol⁻¹ (see below), with *a* being the more stable conformer. The Raman bands which are enhanced at lower temperatures belong to the *a*, and those which diminish upon cooling should belong to the *e*-conformer. However, most of the Raman (and infrared) bands observed do not belong to a single conformer, but to both the *e* and *a*-conformers Thus, only a few Raman bands are suitable for calculations of the enthalpy differences.

The intensities of each band pair were fitted to the van't Hoff equation: $\ln\{I_a(T)/I_e(T)\} = -\Delta_{conf}/RT + constant$; where I_a/I_e is the ratio in peak heights or integrated areas, and it is assumed that $-\Delta_{conf}H$ is constant with temperature. Both peak heights and integrated band areas were employed for determining band intensities. The following two pairs of bands were employed in the van't Hoff plots: 630/659 and 395/311 cm⁻¹ (liquid) employing peak heights (Fig. 6), giving the values 0.94 and 1.62 kJ mol⁻¹, respectively, (293–143 K). The band pair $630/659 \text{ cm}^{-1}$ was also treated in integrated areas, giving the value 0.98 kJ mol⁻¹. An average value of 1.2 kJ mol⁻¹ was obtained for the Δ_{conf} H, in reasonable agreement with our quantum chemical results 0.7-1.8 kJ mol⁻¹. Earlier determinations of Δ_{conf} H from variable temperature Raman spectroscopy [11], all based upon the 630/659 cm⁻¹ band pair, gave the values: 1.04, 0.92 and 1.17 kJ mol⁻¹ in neat liquid, pentane and dichloromethane, respectively.

3.2. Infrared spectral results

A MIR spectrum of FSC is presented in Fig. 7. Some rotational vapor contours with resolved P, Q and R peaks were observed in the spectra both for the assumed *e* and *a* conformers, but in other cases apparent fine structure is attributed to close-lying conformer peaks. A FIR spectrum of the sample is given in Fig. 8 while MIR spectra of FSC deposited on a CsI window at 78 K are shown in Fig. 9. A complete list of the infrared and Raman bands for FSC including assignments are listed in Table 1, based upon the results of the calculations and on experimental Raman depolarization data and infrared vapor contours.

Table 1

Infrared and Raman spectral data^a for 1-fluoro-1-silacyclohexane, C₅H₁₁SiHF.

Infrared			Raman		Assignments		
Vapor 298 K ^b	Liquid 298 K ^b	Solid 78 K ^b	Liquid 298 K ^b	Solid 78 K ^b	Equatorial	Axial	
2944 s, Q ^c 2940 s P			2939 vvs		$v_1 A'$		
2940 S, F 2938 vs			2937 vvs. P		v ₂ A'		
2934 vs		2931 s, sh	,		v ₂₈ A″		
2931 m		2929 s	2932 sh		v ₃ A′		
2927 vs		2927 vs	2925 vvs, D	2922 vvs		$v_1 A'$	
2924 s		2923 s, sh	2010		v ₄ A'	v ₂ A'	
2921 s		2921 vs	2919 m, sh	2000	v ₅ A' v ₂₉ A''	v ₃ A' v ₂₈ A'	
2890 W 2871 m sh		2890 W, DF 2871 VW	2889 VS P	2890 VS 2872 VUW	V6A V30A	$v_4 A' v_{29} A''$ $v_7 A' v_{29} A''$	
2865 m		2857 vs	2859 vvs. P	2853 vs	v21A"	v ₆ A'v ₂₁ A"	
2175 s, R		2007 10	2000 110,1	2000 10	,31.1	,0.1,31.1	
2170 vvs, Q		2166 s	2162 vsP	2163 s, br		v ₇ A′	
2165 s, P							
2162 vs R							
2158 vs Q					v ₇ A′		
2150 III, P 1498 your		1/0/ 1/14	1/06 104	$\nu = \Delta' \nu = = \Delta''$			
1468 w		1464 vw	1450 VW	v8/1 v32/1		v _° A′	
1461 w		1462 vw	1462 w. P	1458 w	voA'	v32A"	
1456 w		1455 vw	,			v ₉ A'	
1454 w, R							
1450 s, Q		1446 m	1451 m, D	1447 s	v ₃₃ A″	v ₁₀ A′	
1446 w, P							
1418 w			1400 m D		v ₁₀ A′	A.//	
1409 S			1406 M, D		ν Δ /	V ₃₃ A″	
1348 w			1344 m	1347 w D	v11A v24A"	v ₁₁ A v ₂₄ A″	
1341 vw			1334 w. D	1341 w	v344 V35A″	v341 v35A″	
1299 w		1303 vw	1305 vw,	1306 vw	v ₁₂ A'		
1288 w		1291 m	1293 m, P	1289 m		v ₁₂ A′	
1277 w		1275 m	1271 w, D			v ₃₆ A″	
1269 w		1269 w	1267 w, br		v ₃₆ A″		
1101 D		1251 m	1254 m	1249 m	v ₃₇ A"	v ₃₇ A″	
1194 m, R		1107 c	1109 m D	110E m			
1192 S, Q 1189 vs P		1197 5	1 196 III, P	1195111	v ₁₃ A	v ₁₃ A	
1185 vs r 1186 m. R							
1184 vs Q		1182 vs	1184 m, D	1180 m	v ₁₄ A′	v ₁₄ A′	
1179 s, P							
1105 vw		1106 w	1106 w, D	1103 m	v ₃₈ A″	v ₃₈ A″	
1098 vw		1099 m	1097 vw	1094 w, sh			
1040 ···· D		1074 w	1077 w, D	1074 m	v ₃₉ A″	v ₃₉ A″	
1048 W, K 1042 w O		1022 1047	1029 w br		ν Δ //	ν Δ ″	
1042, w, Q 1039 w P		1052 VW	1038 W, DI		V ₄₀ A	v ₄₀ n	
1009 s		1008 m	1006 m, P	1004 m	v ₁₅ A′	v ₁₅ A'	
1001 vs, R							
996 vs Q		996 s	995 w, sh, br	997 m, sh	v ₁₆ A′	v ₁₆ A′	
991 s, P							
920 s		012	914 w	005	v ₁₇ A'	v ₁₇ A′	
910 VS 910 s		912 VS 891 m. sh	909 m, D	905 111	V ₄₁ A	v A″	
885 s sh		887 m	887 w D	885 w sh	v. A''	v41/1	
881 vs R		007 111	007 11, 5	000 11, 511	, 42.1		
878 vvs, Q		877 s	875 m			v ₁₈ A′	
873 vs P							
869 m			866 m	873 w, D		v ₄₂ A"	
845 s		855 vs	863 w	863 w	v ₁₈ A′		
840 VS K		022	925 mar ch	920 w hr	ν Δ ″	N A//	
808 vw		000 VVS 814 c	000 vw, sii, 818 m P	ου w, μr 811 m	v43A	V ₄₃ A'	
796 vw		794 m	796 s. P	793 s	v20A'	v 19/ v	
780 m R				. 55 5	· 20* *		
776 s, Q		771 s	768 vw		v ₂₁ A′	v ₂₀ A′	
771 m, P						-	
742 w		743 m	741 m, P	741 m		v ₂₁ A′	
721 w		719 m	720 w, D	717 w	v ₄₄ A″		
670 vw		CC0	671 vw, sh	671 w, sh		v ₄₄ A″	
628 W		621 w	630 vs P	620 Marc	V ₂₂ A'		
020 vw 615 m Ω		614 m	611 vw ch	020 448	v ₂₂ A v ₄₅ A'	V or A'	
515 m, Q		017111	011 999, 511		v45 ¹	*45/1	

(continued on next page)

Table 1 (continued)

Infrared			Raman		Assignments	
Vapor 298 K ^b	Liquid 298 K ^b	Solid 78 K ^b	Liquid 298 K ^b	Solid 78 K ^b	Equatorial	Axial
610 m, P						
511 w, R 506 s, Q 499 w,P	508 s	506 s	506 w, br, P			v ₂₃ A′
480 vw	482 m	482 w	482 m, P	477 w	v ₂₃ A'	
396 m	395 s	397 s	395 m, P	394 m		v ₂₄ A′
389 w	391 m	385 m	385 vw, sh		Comb	
	363 s, br	365 m	366 w, D	364 w	v ₄₆ A″	v ₄₆ A″
353 w	347 w		346 m, P	344 w	v ₂₄ A′	v ₂₅ A'
312 vvw	313 w	314 vw	311 m, P	311 w	v ₂₅ A′	
281 w	280 w	283 w	279 w, D	282 w		v ₄₇ A"
260 w	263 w	262 vw	262 w, P	260 vw	v ₂₆ A′	
235 w	235 m	237 vw	233 w, br,D	233 vw	v ₄₇ A″	
	220 vw	217 vw	219 w, P	217 w		v ₂₆ A'
171 vw		170 w	166 vw	166 vw	Comb	
	155 m		155 w	158 vw	v ₄₈ A″	
140 vw			137 w	141 vw		v ₄₈ A″
105 vw	104 w, sh	102 w	102 w	106 w ?	v ₂₇ A′	
101 w			98 w			v ₂₇ A′

^a Wavenumbers.

^b Recording temperature.

^c Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; P, polarized; D, depolarized in the Raman spectra; P, Q and R signify rotational band contours in the infrared vapor spectra.



Fig. 6. Van't Hoff plots of the *axial/equatorial* band pairs 630/659 (open circles) and 395/311 (black squares) cm⁻¹ of FSC in the temperature range 293–143 K, employing peak heights as measures of the scattering intensities.

3.3. Quantum chemical calculations

MP2 and DFT calculations were performed using Gaussian 09 [13]. The minima on the potential surface were found by relaxing the geometry. The Cartesian coordinates and the structural parameters for the *e*- and *a*-conformers from B3LYP/cc-pVTZ calculations are given in Tables S1 and S2, respectively (Supporting information). The conformational energy difference, $\Delta_{conf}H(e - a)$, obtained from the MP2/6-31G calculations was 0.7, while B3LYP calculations gave 1.8, 0.7 and 0.6 kJ mol⁻¹ employing the cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets, respectively. A value of 1.0 kJ mol⁻¹ was obtained in our G3 calculations [14], giving an average value of $\Delta_{conf}H(e - a)$ =0.96 kJ mol⁻¹. Earlier density functional calculations $\Delta_{conf}H$ equal to: 0.5 (B3LYP), 1.1 (B3LYP-D), 0.6 (B2PLYP), 1.0 (B2PLYP-D) and 0.7 kJ mol⁻¹ (MO6-2X) were reported with widely different basis sets [7]. MP2 calculations gave: 0.6



Fig. 7. Mid infrared spectra (MIR) of FSC as a vapor at room temperature in the range 3200–2000 and 1350–480 cm⁻¹ in a 10 cm cell with KBr windows, pressures 20 (solid curve) and 4 Torr (broken curve), resolution 0.5 cm⁻¹.

(6-31G(d)), 0.9 (6-31++G(d)), 1.0 (6-311++G(d)) and -0.4 kJ mol⁻¹ (6-311G(2df,2pd)) [9], suggesting an average [7,9] value of Δ_{conf} H(e - a)=0.85 kJ mol⁻¹.

The vibrational wavenumbers of the *e*- and *a*-conformers of FSC, resulting from three B3LYP/cc-pVXZ (X = D, T, Q) calculations are compared in Tables S3 and S4, respectively. Only minor differences were obtained between the results with triple and quadruple zeta basis sets, suggesting that the B3LYP electron density is described with sufficient accuracy employing the triple zeta basis set. Provided an adequate basis set is used in calculations of the normal modes of vibration, the calculated wavenumbers are invariably too high. A common procedure to remedy this discrepancy is to scale the calculated wavenumbers to compensate for, among others, mechanical anharmonicity. In the present study the cubic and quartic force constants were obtained in the B3LYP/cc-pVTZ calculations allowing a prediction of the anharmonic vibrational wavenumbers directly.



Fig. 8. FIR spectra of FSC as a liquid in a polyethylene cell with ca. 0.2 mm path at room temperature in the range $600-100 \text{ cm}^{-1}$.



Fig. 9. MIR spectrum of FSC as a solid on a CSI window at 78 K in a cryostat in the range 3400-2000 and 1500-480 cm⁻¹.

3.4. Normal coordinate calculations

Harmonic force constants were obtained for each of the two conformers of FSC in B3LYP/cc-pVTZ calculations. The harmonic, unscaled force constants were transformed from Cartesian to symmetry coordinates, listed in Table S5, derived from a set of valence coordinates to obtain an approximate description of the normal modes. These calculations were carried out both for the e- and the *a*-conformers employing the VIBROT program [15] and the results are listed in Tables 2 and 3. The calculated infrared intensities and Raman polarization ratios, in the harmonic approximation, are included in these tables combined with the experimental wavenumbers, The theoretical Raman intensity, R, which mimics the measured Raman spectrum is related to the Raman scattering activity: $R_i = C(v_L - v_i)^4 \cdot v_i^{-1} \cdot B_i^{-1} \cdot S_i$, where v_i is the frequency and S_i the corresponding Raman scattering activity of mode *i*, v_L is the laser excitation frequency, $B_i = 1 - \exp(-h \cdot v_i \cdot c/kT)$, and C a constant [16]. Finally, the wavenumbers derived from the anharmonic calculations are included in Tables 2 and 3 to be directly compared with the experimental values as observed in the infrared and Raman spectra.

The PED (potential energy distribution) is expressed in terms of the symmetry coordinates. They are constructed from a set of valence coordinates, and the numbering of the atoms appears in Fig. 1. Only PED terms larger than 10% have been included in Tables 2 and 3 and the largest term in PED is also described in terms of valence coordinates in these tables.

3.5. Conformations

It can be seen from Tables 1–3 that all the *e* and *a*-bands have been tentatively identified. The experimental enthalpy difference $\Delta_{conf}H(e-a)=1.2$ kJ mol⁻¹ (see above) favors *a*, and the calculated entropy difference was calculated to be $\Delta_{conf}S(e-a)=0.59$ J mol⁻¹ K⁻¹. The conformational equilibrium is derived from $\Delta_{conf}G(e-a)$:

$$\Delta_{conf} G(e - a) = \Delta_{conf} H(e - a) - T\Delta_{conf} S(e - a)$$

= 1.2 - 293 \cdot 0.59 \cdot 10^{-3}
= 1.03 kI mol^{-1}, giving 60% a.

In the gaseous electron diffraction study [10,11], an equilibrium of 63 % axial and 37% equatorial conformer was observed at 298 K. Since the *e* and *a* conformers of FSC are expected to have nearly the same dipole moments, the conformational equilibrium should be nearly the same in the vapor phase and in the neat liquid and also in solvents of different polarity previously recorded [11]. In fluoro-cyclohexane the enthalpy difference $\Delta_{conf}H(a - e)$ is reported to be 5.4 [17] and 5.7 kJ mol⁻¹ [18] measured by infrared spectroscopy in liquid krypton solution. Thus, a comparison between the mono-substituted 1-silacyclohexanes with the corresponding cyclohexanes reveals the former group of molecules to have a much more stable *a*-conformer than the latter.

This trend has also been found by quantum chemical calculations [7,9]. From B3LYP/6-311+G(d,p) calculations the enthalpy difference between the twists and boat transition state to chair-chair conversion in silacyclohexane [1-3] is given as 16.3–21.6 kJ mol⁻¹. In cyclohexane the twist, boat and half chair/sofa conformers are compared with the stable chair form in various MP2 and B3LYP calculations [19]. In B3LYP/6-311+G(d,p) calculations the much higher values 26.5, 30.0 and 46.1 kJ mol⁻¹ in twist, boat and half chair compared to the chair conformation were derived [19]. From kinetic measurements in krypton, the ΔH of activation between the *a* and *e*-conformers in fluorocyclohexane were measured as 37.8 kJ mol⁻¹ [17]. With lower barrier to e - a conversion in silacyclohexane than in cyclohexane, the spectral shifts from equatorial to axial conformer should be smaller in FSC, leading to more frequent coincidences of the *e* and *a* vibrational modes in FSC than in fluorocyclohexane [18,20]. As is apparent both from Tables 2 and 3, the vibrational modes derived from the anharmonic calculations are with a few exceptions at lower wavenumbers than those from the harmonic approximation both for the *e* and *a*-conformations.

A number of monosubstituted cyclohexanes crystallize readily in the *e*-conformer at low temperature and at high pressures [21], giving experimental support for the spectral interpretation. An exception was fluorocyclohexane which formed a plastic phase, containing both conformers after cooling to 78 K [20]. Only after prolonged annealing did the compound crystallize. Bands of the amorphous solid were observed at 90 K, bands of the plastic phase at 190 K and an anisotropic crystal was observed at 160 K when the *a*-conformer vanished. It has been observed that when a plastic phase is formed by cooling, the conversion to an anisotropic phase is frequently difficult to achieve [21–23]. Because of the close similarity between FSC and fluorocyclohexane, it is possible that also FSC forms a plastic phase.

4. Spectral interpretation

With 18 atoms, each conformer of FSC has 48 modes of vibration. Both the *e*-and *a*-conformers have a plane of symmetry (C_s

Table 2	
Observed and calculated vibrational modes	of the <i>e</i> - conformer of 1-fluoro-1-silacyclohexane (FSC).

No.	Sym. spec.	Harm ^a wave.	Anharm. wave.	Obs. ^b wave.	IR ^c int.	Ra ^d int.	Dep. ratio	PED ^e	Description
1	A′	3007	2945	2944	34	130	0.16	$34S_8 + 62S_{10}$	CH ₂ symmetric stretch
28	A″	3065	2916	2934	20	141	0.75	$11S_{35} + 86S_{36}$	CH ₂ antisymmetric stretch
2	A′	3066	2915	2938	27	254	0.36	88S13	CH ₂ antisymmetric stretch
3	A′	2997	2914	2931	9	476	0.15	$45S_8 + 19S_9 + 20S_{10} + 15S_{11}$	CH ₂ symmetric stretch
4	A'	3049	2910	2924	57	225	0.35	$13S_{\circ} + 79S_{\circ}$	CH_2 antisymmetric stretch
5	A'	3045	2904	2921	55	458	0.13	765	CH_2 antisymmetric stretch
29	A″	3040	2899	2921	47	132	0.75	$11S_{22} + 79S_{24}$	CH_2 antisymmetric stretch
30	A″	3015	2891	2890	0	91	0.75	77S ₂₅	CH_2 symmetric stretch
6	A'	3017	2882	2890	26	238	0.15	80512	CH_2 symmetric stretch
31	A″	3001	2853	2865	14	230	0.75	$77S_{22} + 16S_{24}$	CH_2 symmetric stretch
7	A'	2204	2142	2158	146	447	0.18	1005.	Si_H stretch
8	Α/	1493	1544	1498	8	35	0.73	905	CH _a scissor
32	Α"	1495	1500	1498	3	53	0.75	90516	CH ₂ scissor
0	Δ'	1507	1464	1450	1	20	0.58	945	CH ₂ scissor
10	Α'	1457	1404	1401	4	36	0.38	935	CH ₂ scissor
22	Δ"	1453	1410	1410	2 Q	57	0.74	925	CH ₂ scissor
11	Δ/	1380	1351	1354	3	27	0.75	77S	CH ₂ seissor
24	A	1201	12/2	12/9	0	2	0.75	$125 \pm 625 \pm 125$	CH twist
25	л л//	1361	1342	1240	0	10	0.75	$133_{28} + 033_{37} + 123_{42}$	CII ₂ twist
10	A'	1224	1341	1341	5	12	0.75	$123_{29} + 103_{38} + 303_{41}$	CH ₂ twist
12	A	1324	1290	1299	2	41	0.09	155 + 425 + 265	CH_2 twist
20	A"	1301	1209	1209 1254	0	10	0.75	$105_{31} + 425_{42} + 205_{45}$	CH ₂ twist
3/	A''	1282	1200	1234	0	19	0.75	$195_{38} + 195_{44} + 185_{46} + 195_{48}$	CH ₂ twist
13	A'	1227	1202	1192	8	14	0.10	$213_{19} + 133_{21} + 333_{24}$	CH ₂ FOCK
14	A'	1209	11//	1184	26	29	0.75	$12S_2 + 21S_{24} + 35S_{25}$	CH ₂ twist
38	A''	1125	1105	1105	1	8	0.75	$115_{41} + 145_{42} + 315_{45}$	CH ₂ rock
39	A''	1084	1062	10/7	2	15	0.75	$28S_{28} + 35S_{29} + 10S_{42}$	C-C stretch
40	A''	1061	1036	1042	6	3	0.75	$11S_{29} + 26S_{46} + 36S_{48}$	CH ₂ twist
15	A'	1017	999	1009	27	22	0.45	$11S_{17} + 22S_{19} + 33S_{25}$	CH ₂ wag
16	A'	1014	995	996	0	58	0.69	$19S_1 + 3/S_2 + 13S_{24}$	C-C stretch
17	A'	930	911	920	64	8	0.75	$12S_2 + 13S_5 + 18S_{17} + 12S_{19}$	CH ₂ wag
41	A''	919	899	916	50	24	0.75	$2/S_{29} + 32S_{31} + 29S_{44}$	CH ₂ twist
42	A″	900	886	885	25	34	0.75	$15S_{29} + 24S_{40} + 45S_{44}$	CH ₂ wag
18	A'	870	859	845	148	20	0.70	$55S_{15} + 22S_{26}$	Si–F stretch
43	A''	843	828	835	69	22	0.75	$18S_{29} + 18S_{32} + 15S_{40} + 20S_{44}$	C–C stretch
19	A'	821	812	808	4	48	0.75	$29S_{15} + 15S_{23} + 41S_{26}$	FSiH bend
20	A'	796	780	796	0	85	0.07	$54S_1 + 21S_2$	CC stretch
21	A'	784	778	776	47	17	0.72	$16S_{17} + 42S_{23} + 20S_{26}$	CH ₂ wag
44	Α″	709	696	721	14	65	0.75	$53S_{30} + 28S_{32}$	C–Si antisymmetric stretch
22	A'	650	641	659	13	314	0.04	73S ₃	C–Si symmetric stretch
45	A″	622	619	615	15	21	0.75	$57S_{44} + 37S_{48}$	CH ₂ wag
23	A'	481	488	480	2	25	0.12	$24S_4 + 28S_5 + 10S_{17} + 14S_{19}$	C–C–C bend
46	A″	374	367	366 ^r	0	60	0.75	$56S_{31} + 14S_{32} + 24S_{48}$	C–C–C bend
24	A'	339	353	353	2	36	0.20	$26S_4 + 30S_5 + 18S_7 + 10S_{23}$	CCC bend
25	A'	309	309	312	1	116	0.41	$16S_4 + 18S_6 + 23S_7 + 26S_{27}$	C–Si–F bend
26	A'	258	264	260	5	38	0.61	$14S_6 + 33S_7 + 10S_{23} + 10S_{25} + 17S_{27}$	C–Si–C bend
47	Α″	227	217	235	7	20	0.75	$18S_{31} + 11S_{47} + 69S_{48}$	Ring deformation
48	A″	159	152	155 ^f	1	17	0.75	$50S_{32} + 33S_{48}$	C-C-Si bend
27	Α′	94	99	105	1	99	0.74	$38S_6 + 16S_7 + 35S_{27}$	C–C–C bend

^a Calculated with B3LYP/cc-pVTZ basis set.

^b The observed wavenumbers are derived from IR vapor spectra. except when noted.

^c Calculated infrared intensities in km/mole.

^d Calculated Raman scattering intensities in arbitrary units. see text and Ref. [16].

^e For definition of symmetry coordinates. see Table S5.

^f From the Raman spectra of the liquid.

symmetry). The fundamentals will divide into 27 modes of species A' and 21 A", and give rise to polarized and depolarized Raman bands, respectively. They are numbered v_1-v_{27} for species A' and $v_{28}-v_{48}$ for A". Since the order of the fundamentals sometimes change between the harmonic and the anharmonic calculations (Tables 2 and 3), the latter are made the basis for the numbering. The assignments agree well with the results of the B3LYP/cc-pVTZ anharmonic calculations, and are supported by the Raman depolarization measurements and the infrared vapor contours. As is apparent from Table 1 practically all the A' modes appearing at a separate wavenumber are described as P or the polarization ratio is uncertain and left out. Similarly, the A" modes appear as D or are left out. An exception is v_{14} of both *e* and *a* conformers coinciding at 1184 cm⁻¹ and observed as D. However, from Tables 2 and 3 the depolarization ratios for both these modes were calculated to

be 0.75 (contrary to the theory), justifying the observed value D for these A' modes. The smallest and intermediate axes of inertia lie in the symmetry plane and the largest axis is perpendicular to this plane, leading to AB hybrid contour for the A' modes and C type contour for the A" modes for both conformers. As apparent from Table 1, only the vapor bands at 2170, 2158, 878 and 506 cm⁻¹ with PQR contours are attributed to a single conformer, while those at 1450, 1192, 1184, 1042, 996 and 776 cm⁻¹ are coinciding *e* and *a* conformer bands with very uncertain overlapping contours. A careful investigation of the vapor spectra suggests no definite cases in which the AB hybride contour or the C-type contours give a definite clue to the attributions.

From the experimental results it was concluded that a majority of the *e*-conformer bands overlapped those of the *a*-bands in agreement with the results of the calculations. Sometimes the A' and A"

 Table 3

 Observed and calculated vibrational modes of the *a*- conformer of 1-fluoro-1-silacyclohexane (FSC).

No	Sym	Harm ^a wave.	Anharm. wave.	Obs. ^b wave.	IR ^c Int.	Ra ^d Int.	Dep. ratio	PED ^e	Description
1	A′	3061	2912	2927	38	242	0.23	$11S_{12} + 79S_{13}$	CH ₂ antisymmetric stretch
28	Α″	3061	2912	2921	18	156	0.75	$14S_{35} + 81S_{36}$	CH ₂ antisymmetric stretch
2	A′	3049	2908	2924	54	153	0.64	$64S_9 + 16S_{11}$	CH ₂ antisymmetric stretch
3	A′	3046	2906	2921	55	502	0.18	$15S_8 + 67S_{11}$	CH ₂ antisymmetric stretch
29	Α″	3041	2897	2890	39	107	0.75	91S ₃₄	CH_2 antisymmetric stretch
4	A'	3011	2894	2890	37	136	0.06	84510	CH_2 symmetric stretch
30	Α″	3005	2878	2871	6	21	0.75	69535	CH_2 symmetric stretch
5	A'	3008	2874	2871	12	442	0.13	$74S_{12} + 17S_{13}$	CH_2 symmetric stretch
31	Α″	3011	2860	2865	19	115	0.75	895	CH_2 symmetric stretch
6	A′	2995	2845	2865	17	299	0.18	$68S_{2} + 22S_{0}$	CH_2 symmetric stretch
7	A'	2213	2148	2170	185	610	0.21	100514	Si–H stretch
32	A″	1498	1498	1461	3	54	0.75	89520	CH ₂ scissor
8	Α'	1508	1468	1468	3	19	0.59	94518	CH ₂ scissor
g	Α′	1493	1457	1456	7	38	0.73	92516	CH ₂ scissor
10	A'	1448	1413	1450	6	31	0.75	94522	CH_2 scissor
33	A″	1445	1403	1409	9	53	0.75	91542	CH ₂ scissor
11	A'	1381	1351	1354	5	1	0.68	775	CH ₂ rock
34	A″	1381	1343	1348	0	6	0.00	$125_{20} + 635_{27} + 125_{42}$	CH ₂ rock
35	A″	1370	1340	1341	0	13	0.75	$125_{28} + 165_{29} + 545_{44}$	CH ₂ rock
12	Δ'	1325	1295	1288	2	46	0.68	$69S_{22} + 19S_{23}$	CH ₂ twist
36	A″	1303	1235	1277	4	10	0.00	$155_{21} + 195_{22} + 275_{45}$	CH ₂ twist
37	Δ″	1284	1251	1254 ^f	0	10	0.75	$11S_{24} + 20S_{25} + 18S_{44} + 21S_{45} + 17S_{45}$	CH ₂ twist
13	Δ'	1204	1199	1192	3	19	0.15	$195_{40} + 135_{04} + 335_{04} + 105_{46} + 175_{48}$	CH ₂ took
14	Δ/	1225	1180	1192	25	28	0.75	$135_{19} + 225_{10} + 355_{20}$	CH ₂ twist
28	Δ"	1214	1110	1104	25	17	0.75	$135_2 + 225_{24} + 335_{25}$ $135_{} + 155_{} + 335_{}$	CH ₂ rock
30	Δ"	1086	1062	1077 ^f	0	15	0.75	$30S_{} + 36S_{}$	C_C stratch
40	Λ"	1057	1002	10/7	2	15	0.75	225 + 205	CH twist
40	Δ/	1037	1032	1042	24	11	0.75	$11S_{+} + 12S_{+} + 10S_{+} + 30S_{+}$	CH ₂ twist
16	Δ/	1024	996	996	24	61	0.15	205 + 345 + 155	C_C stratch
17	Δ/	078	900	920	/1	1	0.71	$13S_{1} + 14S_{2} + 18S_{24} + 17S_{14}$	CH- wag
17	Λ"	012	802	010	-11	20	0.75	1352 · 1455 · 18517 · 17519	C C stratch
41	л л″	915	850	910	9 10	20	0.75	$433_{29} + 373_{31}$	CH rock
42	л л/	007 975	864	809	164	21	0.75	$153_{32} + 265_{40} + 105_{44} + 105_{46} + 155_{48}$	E Si H bond
10	л л″	07J 04D	804	070	104	27	0.75	$333_{15} + 323_{26}$	C Si E bond
10	л л/	042 917	805	808	12	55	0.75	40044 + 20048 505 + 265	Si E strotch
20	л л/	705	770	776	15	22	0.50	$505_{15} + 505_{26}$	G C stratch
20	л л/	750	775	770	6	50	0.17	$323_1 + 133_2$ 125 + 445 + 155	
21	л л″	672	670	670	1	J6	0.30	155 ₁₇ + 445 ₂₃ + 155 ₂₆	
44	л л//	624	621	615	1	40	0.75	125 425 225	
45	A'	620	621	610	1	200	0.75	155 ₃₀ + 425 ₄₄ + 555 ₄₈	C_{12} wag
22	A'	508	609 512	506	16	15	0.00	125 + 105 + 175 + 105 + 175	C-SI Sylli Stretch
25	A	207	207	200	10	15	0.24	$1554 \pm 1955 \pm 1756 \pm 10517 \pm 17519$	C-C-C Della
24 46	л л//	250	264	266	6	16	0.40	2334 + 1035 + 1136 + 1437 + 11327 575 + 105 + 215	C = C = C bond
40	л //	208	251	252	0	10	0.75	$373_{31} + 133_{2} + 213_{48}$	C = C = C bend
20 47	A"	520 270	221	222	5	19	0.50	$233_4 + 103_5 + 113_6 + 143_7 + 113_{27}$	C-C-C Dellu Ding deformation
4/	A''	270 210	∠00 212	281 210 ^f	5	30	0.75	265 + 205	
20 49	A' A//	∠10 142	213 120	219	U 1	42	0.09	145 + 275 + 105 + 205	C = Si = r bend
48	A''	145	139	140	1	31 20	0.75	14331 + 3732 + 10547 + 29548	C C C Si hand
27	A'	81	98	101	2	38	0.72	5256 + 26527	C-C-SI bend

^a Calculated with B3LYP/cc-pVTZ basis set.

^b The observed wavenumbers are derived from IR vapor spectra. except when noted.

^c Calculated infrared intensities in km/mole.

^d Calculated Raman scattering intensities in arbitrary units, see text and Ref. [16].

^e For definition of symmetry coordinates. see Table S5.

^f From the Raman spectra of the liquid.

modes of the same conformer coincided as a result of accidental degeneracy. Ca. 15 separate e and a pairs were tentatively assigned (Tables 1–3). As expected, the observed wavenumbers in FSC are in many cases very similar to those of fluorocyclohexane [18,20].

The 6 A' and 4 A" modes of the *e* and *a* conformers, attributed to CH₂ antisymmetric and symmetric stretch are observed as overlapping IR and Raman bands between 3000 and 2850 cm⁻¹ in which the *e*-modes were calculated at slightly higher wavenumbers than the *a*-modes. They were quite similar to the CH₂ stretching vibrations in fluorocyclohexane [18,20] and in 1-chloro-1-silacyclohexane [24]. The Si–H stretch v_7 was attributed to the very intense IR vapor bands with Q-branches at 2170 (*a*) and 2158 cm⁻¹ (*e*), separated 12 cm⁻¹ while the calculations suggested 6 cm⁻¹ distance. They have one strong, overlapping Raman peak at 2162 cm⁻¹ in the liquid, common for both conformers. In 1-chloro-1-silacyclo-

hexane the Si–H stretches were observed at 2174 (*a*) and 2163 cm⁻¹ (*e*) as Q-branches in the IR vapor spectra [24] very close to the present results in FSC.

With 10 hydrogens in FSC attached to carbon, we expect 20 fundamentals involving CH₂ scissor, wag, twist and rock. These vibrational modes are expected in the range below 1500 and as far as 700 cm⁻¹, although a few modes mainly involving C–C stretch v_{39} , v_{16} , v_{43}), Si–F stretch (v_{18}), F–Si–H bend (v_{19}) and C–Si–C stretch (v_{44} , v_{22}) are also anticipated in this range (Tables 2 and 3). Prominent vapor bands with possible A/B hybride or C-type band contours and R and/or P branches separated ca. 10 cm⁻¹ were observed with Q-branches at 1450, 1192, 1184, 1042, 996, 878, 776 and 506 cm⁻¹. The agreement between the observed and calculated fundamentals in the anharmonic approximation is generally very good (with average relative deviations around 1%, see below.

Very strong IR bands with a Q-branch at 996 cm⁻¹ are attributed to v_{16} of both conformers, involving predominantly C-C stretch. The vapor bands at 881, 878 and 873 $\rm cm^{-1}$ form R, O and P branches with possible AB hybride contour, and they are, in addition to Si–H stretch (v_7) , the most intense in the IR spectra in agreement with the calculations (Tables 2 and 3). They are assigned to v_{18} (FSiH bending) of the *a*-conformer, whereas the corresponding *e*-conformer band is found at 845 cm^{-1} in the vapor. Strong vapor bands at 835 cm^{-1} are attributed to Q-branches for the *e* and *a*conformers of the mixed stretching and bending modes, v_{43} .

The IR vapor bands at 845 (v_{18}) and 808 (v_{19}) cm⁻¹ and the corresponding Raman bands have 55 and 50 % contribution from Si-F stretch, for the *e*- and *a*-conformers, respectively, but they are weaker and less characteristic than the Si-Cl stretching bands in 1-chloro-1-silacyclohexane [24]. Both of these modes are mixed with F-Si-H bend. In fluorocyclohexane the C-F stretches of the e and a conformers are also mixed with various bending modes. but they appear widely separated at 1065 and 954 cm⁻¹ in the vapor [18,20] (at 1054 and 940 cm⁻¹ in the Raman spectra). It is well known that in chloro- and bromocyclohexanes the C-X stretch is at a higher wavenumber in the *e* than in the *a* conformer [22,23].

Two Raman bands are observed at 659 and 630 cm^{-1} , and according to PED they are more than 70% localized to the symmetric C–Si–C stretches of the *e* and *a*-conformers, respectively. Both of these bands are highly polarized, they are among the most intense in the Raman spectra (Tables 2 and 3 and Fig. 3), they are very weak in IR, but well suited for the determination of $\Delta_{conf}H(e-a)$. They were employed in Fig. 6 and in the earlier studies [11].

Below 630 cm⁻¹ three overlapping *e* and *a*-modes 615 (v_{45}), 366 (v_{46}) and 353 cm⁻¹ $(v_{24}$ and $v_{25})$ were observed. The remaining IR and Raman bands interpreted as fundamentals have been assigned as separate *e* or *a*-fundamentals. Exceptions are the bands around 170 cm⁻¹, tentatively interpreted as combination bands. The Raman band at 395 cm^{-1} attributed to $v_{24} \text{ A}'$ of the *a* conformer was combined with the *e* mode v_{25} at 311 cm⁻¹ to give $\Delta_{conf}H$ (e-a).

The average relative deviations between the observed and calculated (anharmonic), unscaled modes give 1.16% for the e-conformer and 0.92% for the *a*-conformer. The largest contributions to the deviations for both conformers are given by the four modes situated below 800 cm⁻¹: v_{22} , v_{27} , v_{44} and v_{47} as is apparent from Tables 2 and 3.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2012.02.016.

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