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Raman and infrared studies supported by ab initio calculations for the determination of conformational stability, silyl rotational barrier and structural parameters of cyclohexyl silane

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Abstract

The Raman spectra $(4000-100 \text{ cm}^{-1})$ of liquid and solid and infrared spectra $(4000-400 \text{ cm}^{-1})$ of gaseous, liquid and solid cyclohexyl silane, c-C₆H₁₁SiH₃, have been recorded and assigned. These spectral data indicate the presence of two conformers in the fluid states. Variable temperature (21 to -71 °C) Raman spectra of the liquid were also recorded and by utilizing three conformer pairs, an enthalpy difference of 520 ± 70 cm⁻¹ (6.22 ± 0.84 kJ/mol) was obtained with the *chair-equatorial* form the more stable conformer. It is calculated that at ambient temperature there is only $7.5 \pm 2.4\%$ of the *chair-axial* form present in the liquid phase. Comparison with the spectra of the polycrystalline solid phase shows that the *chair-equatorial* conformer is the only form remaining in the solid. MP2 and DFT calculated conformational energy differences are slightly larger but in reasonable agreement with the experimental value. In addition, force constants, infrared intensities, Raman activities, depolarization ratios, scaled vibrational frequencies and potential energy distributions have been calculated from the MP2(full)/6-31G(d) results for both chair forms. These data support the complete vibrational assignment for the chair-equatorial form as well as the assignments for several of the fundamentals of the chair-axial form. By utilizing a series of sum and difference bands on the SiH stretching modes, the barrier to SiH₃ internal rotation has been determined to be 684 ± 10 cm⁻¹ (8.18 ± 0.12 kJ/mol) for the *chair-equatorial* form. Estimated r_0 structural parameters have been obtained for both conformers by adjusting MP2(full)/6–311+G(d,p) structural predictions. Three additional twist forms (equatorial, axial and form III) were also predicted to be local minima since all calculated vibrational frequencies are real. However, all three twist forms are much higher in energy $(2000-3000 \text{ cm}^{-1})$ than the *chair* forms. Effects of electronegativity and steric effect on the conformational stability are compared among a series of mono-substituted cyclohexanes by NBO analyses of the donoracceptor delocalization interactions.

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1. Introduction

Studies on the conformational preferences of monosubstituted cyclohexanes have been reported in the past. The fluoro- [1–8], chloro- [4,9–13], bromo- [4,11,12,14,15] and methyl-cyclohexane [15–19] were found to exist as *chairequatorial* and *chair-axial* conformers in the gaseous and liquid states. Extensive results have been reported in the past two decades on the determination of the conformational enthalpy (Table 1) of all these compounds using different techniques [20]. Vibrational analyses for these molecules were also carried out, and the assignments for the ring modes, the ring methylene groups, and the substituent on the cyclohexyl ring have been documented in the literature.

There have been extensive studies on mono-substituted silanes over the past five decades and more recently with the silyl group attached to three- [21], four- [22] and fivemembered [23] rings. Rotational constants, possible conformers and vibrational analyses of these molecules have been discussed in detail [23–26]. However, only a few studies have been carried out in the past to determine the molecular structure [27] or conformational equilibrium [27–30] of cyclohexyl silane (silyl cyclohexane) (Fig. 1). Initial predictions were given by Ouellette et al. [29] who calculated the conformational energies by utilizing force constants for

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Table 1

Comparison of experimentally determined conformational energies of several mono-substituted cyclohexanes

Molecule	Conformational energy difference		Method ^a	Reference
	cm^{-1}	Kcal/mol		
Cyclohexyl fluoride	59	0.17	ED	[1]
	140 ± 105	0.4 ± 0.3	MW	[2]
	104 ± 10	0.30 ± 0.03	MW	[3]
	52	0.15	NMR (soln)	[4]
	74	0.21	NMR (liq)	[5]
	88 ± 5	0.25 ± 0.01	NMR (gas)	[6]
	67	0.19	MM	[7]
	109 ± 33	0.31 ± 0.09	Liq Kr	[8]
	33	0.09	MP2	b
Cyclohexyl	150	0.43	NMR (soln)	[4]
chloride	178 ± 52	0.51 ± 0.15	MW	[9]
	92 ± 11	0.26 ± 0.03	Raman	[10]
	226 ± 58	0.65 ± 0.17	ED	[11]
	133	0.38	MM2	[12]
	140	0.40	IR	[13]
	150	0.43	MP2	b
Cyclohexyl	129	0.37	NMR (soln)	[4]
bromide	252 ± 105	0.72 ± 0.30	MW	[14]
	176 ± 18	0.50 ± 0.05	ED	[11]
	164	0.47	MM2	[12]
	213 ± 7	0.61 ± 0.02	IR	[15]
	202	0.58	MP2	b
Cyclohexyl	690 ± 21	1.97 ± 0.06	IR	[15]
methane	1014 ± 175	2.9 ± 0.5	U. Relax	[16]
	603 ± 20	1.74 ± 0.06	¹³ C NMR	[17]
	615 ± 34	1.76 ± 0.10	¹³ C NMR	[18]
	671	1.92	¹³ C NMR	[19]
	588	1.68	MP2	Ь
Cyclohexyl	507 ± 10	1.45 ± 0.03	NMR	[28]
silane	511 ± 70	1.46 ± 0.20	Force con- stants	[29]
	402 ± 17	1.15 ± 0.05	MM2	[30]
	482 ± 203	1.38 ± 0.58	ED	[27]
	520 ± 70	1.48 ± 0.20	Raman	b
	538	1.54	MP2	b

^a ED, electron diffraction; MW, microwave; MM, molecular mechanics; LKr, liquid krypton; U Relax, ultrasonic relaxation; MP2, MP2(full)/6–311+G(d,p) level of calculation; soln (solution); liq (liquid).

^b Present study.

the axial and equatorial conformers of cyclohexyl silane. They predicted that the conformational energy difference between the two forms of cyclohexyl silane should be twice that between the gauche and anti conformers of 1-silabutane. Their calculations also indicated that the equatorial/axial ratio in methyl cyclohexane (cyclohexyl methane) would be larger than the one in cyclohexyl silane. This anomaly was attributed to the long Si-H and Si-C bonds which increase the distances between substituent protons and the ring protons. In methylcyclohexane, Van der Waals force terms favor the equatorial conformation, and the (H₃)CCH bending force constant is larger than the corresponding one in cyclohexyl silane, contributing to the observed conformational energetics of methylcyclohexane. An experimental determination of the enthalpy difference between the two stable conformers of cyclohexyl silane is of interest since it can lend



Fig. 1. The *chair-equatorial* and *chair-axial* conformers of cyclohexyl silane with atom numbering.

further understanding into the conformational stabilities of mono-substituted cyclohexanes and silanes. Owing to the fact that the chlorine atom compares favorably with the SiH₃ group in terms of mass and size, a comparison of the conformational energies of these two molecules should indicate the effect of differences in electronegativities, bond distances to the substituent and spatial arrangement of substituents on conformational energetics.

Studies of combination bands arising from the sum and difference bands between the silyl torsion and the Si–H stretching mode for several silane derivatives [23–26,31] have been useful in the past for determining torsional barriers. Similar data for cyclohexyl silane should be a useful contribution to the existing knowledge on the torsional barriers of mono-substituted silanes. To the best of our knowledge, there is no previously published study concerning the assignments of the other vibrational frequencies of cyclohexyl silane, it is appropriate to complete the vibrational assignment, particularly for the purpose of conformation analysis.

With these goals in mind, a vibrational study of cyclohexyl silane was undertaken. Infrared data for all three phases were collected and these data combined with the Raman spectra of the liquid and crystalline solid led to the vibrational assignment of most fundamentals. By monitoring the relative Raman intensities of several conformational peaks as a function of temperature, the conformational enthalpy difference was determined for the liquid phase. To support the spectroscopic studies, ab initio calculations have been carried out with a variety of basis sets at the level of the restricted Hartree-Fock (RHF) and with electron correlation by the perturbation method [32] to the second order (MP2) to obtain the geometric parameters, harmonic force constants, infrared intensities, Raman activities, depolarization ratios and vibrational frequencies. Additionally conformational stabilities have been predicted along with barriers to inter-conversion of the conformers and internal rotation of the SiH₃ group for comparison to the experimentally determined values. Density functional theory (DFT) calculations have also been carried out by the B3LYP method. The results of these spectroscopic and theoretical studies are reported herein.

2. Experimental and theoretical section

The sample of c-C₆H₁₁SiH₃ was prepared from cyclohexyltrichloro silane (trichlorosilyl cyclohexane, c-C₆H₁₁SiCl₃, obtained from Petrarch Systems, Bristol, PA) by reduction with lithium aluminum hydride in diglyme with both chemicals obtained from Aldrich Chem. Co. (St. Louis, MO). The reaction was carried out in a three-necked flask which was kept under dry nitrogen purge with the LiAlH₄ placed in the flask. The dry diglyme was added to the LiAlH₄ with stirring and the flask temperature was maintained at 0 °C. After adding c-C₆H₁₁SiCl₃, the icy mixture was removed and warmed to room temperature. Stirring was continued for 24 h in hot water bath. The reduction product obtained was purified by trap-to-trap distillation with acetonitrile slushes (-32 °C) for the first two traps and liquid nitrogen for the third trap. The purity of cyclohexyl silane was confirmed by the infrared spectrum of the vapor phase.

The Raman spectrum of the liquid was recorded with a Ramanlog DUV spectrophotometer equipped with a Spectra-Physics 171 argon ion laser operating on the 4880 Å line. Laser power at the sample ranged from 0.4 to 1.0 W and a bandpass of 3 cm⁻¹ was utilized. The spectrum of the liquid was obtained with the sample sealed in a glass capillary whereas that of the solid was obtained with a low-temperature Raman cell [33]. The measured Raman frequencies are expected to be accurate to ± 2 cm⁻¹ and a typical spectrum of the liquid is shown in Fig. 2. The frequencies of all observed bands for both the liquid and solid are listed in Table 1S. The predicted and observed frequencies of fundamental modes are listed in Tables 2 and 3, respectively, for the *chair-equatorial* and *chair-axial* forms.

The mid-infrared spectra of the gas, liquid and solid were recorded on a Nicolet model 7199 Fourier transform spectrometer equipped with a water-cooled Globar source, Ge/KBr beamsplitter and MCT detector. The spectrum of the gas (Fig. 3A) was obtained by using a 12 cm cell fitted with KBr windows. The spectrum of the liquid (Fig. 3(B)) was obtained at room temperature with 32 scans at 4 cm^{-1} resolution and that of the gas with 128 scans at 0.5 cm^{-1} resolution. The frequencies of the observed bands in the gas,

Fig. 2. Raman spectra of liquid cyclohexyl silane.

liquid and solid phases are also listed in Table 1S and the assignments for the fundamentals in Tables 2 and 3.

The LCAO-MO-SCF restricted Hartree-Fock calculations were carried out initially, followed by the Møller-Plesset perturbation method [32] to the second order as well as with hybrid density functional theory by the B3LYP method, utilizing a variety of basis sets from 6-31G(d) to 6-311+G(2df,2pd). All calculations were performed with the Gaussian-03 program [34]. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [35]. The predicted energy differences among the various conformations are listed in Table 4 and the structural parameters from the MP2(full)/6-311+G(d,p) calculations for the two identified *chair* forms are listed in Table 5.

In order to obtain a complete description of the molecular motions involved in the normal modes, we carried out a normal coordinate analysis. The force field in Cartesian coordinates was obtained with the Gaussian 03 program [34] at the MP2(full)/6-31G(d) level. The internal coordinates listed in Table 5 were used to form the symmetry coordinates listed in Table 2S. These data are provided since the choice of symmetry coordinates is not unique. The B-matrix elements [36] were used to convert the ab initio force field from Cartesian coordinates into the force field in desired internal coordinates. The force constants were applied to massweighted Cartesian coordinates to reproduce the ab initio vibrational frequencies and to determine the potential energy distributions (PEDs) which are given in Tables 2 and 3. The diagonal elements of the force field in internal coordinates were then modified with scaling factors of 0.88 for the CH and SiH stretches, 1.0 for the heavy atom bends, and 0.90 for all other coordinates, along with the geometric average for offdiagonal elements. The calculation was repeated to obtain the fixed scaled force field and scaled vibrational frequencies. The values of the scaled diagonal force constants are listed in Table 3S.



Table 2 Observed and calculated frequencies (cm^{-1}) for cyclohexyl silane (*chair-equatorial*)

Block	Vib. No.	Fundamental	Ab initio	Fixed scaled ^a	IR int.	Raman act.	dp Ratio	IR obs ^b	Raman obs ^c	PED ^d	A ^e	B ^e	C ^e
A'	ν_1	(CH ₂) ₄ antisymmetric stretch	3146	2952	67.2	34.9	0.75	2945	2940	43S ₁ , 47S ₂	2	-	98
A'	ν_2	CH ₂ antisymmetric stretch	3136	2942	48.8	101.8	0.36	2945	2940	46S ₂ , 38S ₁	84	_	16
A'	ν_3	(CH ₂) ₄ antisymmetric	3131	2937	8.7	146.3	0.37	2925	2916	75S ₃ , 15S ₁	2	_	98
		stretch											
A'	ν_4	CH ₂ symmetric stretch	3084	2893	24.2	24.5	0.63	2880	2873	72S ₄ , 17S ₅	5	-	95
A'	ν_5	(CH ₂) ₄ symmetric stretch	3083	2892	23.0	196.2	0.07	2880	2873	35S ₅ , 33S ₆ ,	89	-	11
										$20S_4$			
A'_{\cdot}	ν_6	(CH ₂) ₄ symmetric stretch	3076	2886	26.4	59.0	0.07	2880	2873	$44S_6, 42S_5$	27	-	73
A'	ν_7	CH stretch	3057	2868	3.9	86.9	0.27	2858	2857	89S ₇	18	-	82
A'	ν_8	SiH ₃ antisymmetric	2998	2156	161.9	62.3	0.65	2156	2147	99S ₈	14	-	86
		stretch	2200	21.40	06.7	144.2	0.01	0150	21.47	000	00		0
A'	ν_9	SiH ₃ symmetric stretch	2289	2148	96.7	166.3	0.01	2152	2147	99S ₉	92	-	8
A'	ν_{10}	$(CH_2)_4$ deformation	1566	1486	1.0	1.6	0.34	1462	1450	$65S_{10}, 34S_{12}$	2	-	98
A'	ν_{11}	$(CH_2)_4$ deformation	1554	14/5	14.6	4.1	0.65	1453	1450	86S ₁₁	12	-	88
A'	v_{12}	CH_2 deformation	1546	1467	3.6	17.3	0.74	1449	1442	$5/S_{12}, 29S_{10}, 13S_{11}$	98	_	2
A'	v_{13}	(CH ₂) ₄ wag	1430	1358	3.1	0.9	0.69	1357	1357	$62S_{13}, 11S_{14}$	89	-	11
A'	v_{14}	(CH ₂) ₄ wag	1427	1355	0.8	5.9	0.44	1357	1357	55S ₁₄ , 15S ₁₃	97	-	3
A'	v_{15}	(CH ₂) ₄ twist	1342	1277	1.1	19.5	0.69	1276	1277	79S ₁₅	2	-	98
A'	v_{16}	(CH ₂) ₄ twist	1334	1269	3.0	0.9	0.32	1268	1265	59S ₁₆ , 15S ₁₇	96	-	4
A'	v_{17}	CH in-plane bend	1258	1198	3.3	10.4	0.38	1193	1188	$39S_{17}, 28S_{18}$	30	-	70
A'	v_{18}	$(CH_2)_4$ rock	1165	1114	9.2	6.6	0.73	1106	1100	25S ₁₈ , 16S ₁₇ , 13S ₂₄	74	-	26
A'	v_{19}	Ring stretch	1081	1027	0.2	16.0	0.73	1029	1027	$41S_{19}, 26S_{14}, 21S_{25}$	0	-	100
A'	ν_{20}	(CH ₂) ₄ rock	1047	1009	15.3	2.4	0.22	1001	1003	31S ₂₀ , 24S ₂₈ , 15S ₁₇	0	-	100
A'	ν_{21}	SiH ₃ antisymmetric defor- mation	986	936	48.0	23.5	0.75	944	942	97S ₂₁	6	-	94
A'	ν_{22}	SiH ₃ symmetric defor- mation	965	916	313.1	10.3	0.74	916	910	97S ₂₂	97	-	3
A'	ν_{23}	Ring stretch	937	890	8.1	0.3	0.71	890	-	59S ₂₃ , 13S ₁₆	71	-	29
A'	v_{24}	CH ₂ rock	889	845	5.0	3.6	0.27	851	852	35S ₂₄ , 18S ₂₀ , 14S ₂₃	45	-	55
A'	ν_{25}	Ring stretch	858	815	0.8	7.5	0.19	824	822	44S ₂₅ , 24S ₁₉ , 11S ₂₆	15	-	85
A'	ν_{26}	SiC stretch	781	747	12.2	8.7	0.22	753	753	$18S_{26}, 17S_{27}, 17S_{18}, 12S_{32}, 11S_{25}$	10	-	90
A'	ν_{27}	SiH ₃ rock	610	581	20.8	10.5	0.45	603	603	61S ₂₇	4	_	96
A'	ν_{28}	Ring puckering	519	503	1.1	2.0	0.15	495	492	$22S_{28}, 23S_{20}, 15S_{31}, 12S_{24}, 10S_{26}$	65	_	35
A'	ν_{29}	Ring bending	411	403	0.5	0.9	0.51	_	401	71S ₂₉	25	_	75
A'	ν_{30}	Ring puckering	343	336	1.3	4.2	0.25	_	342	55S ₃₀ , 23S ₂₆	100	_	0
A'	ν_{31}	Ring bending	296	288	0.7	0.9	0.26	-	302	$32S_{31}, 33S_{32}$	44	-	56

A'	v_{32}	Ring-Si in-plane bend	123	122	0.3	0.008	0.58	122	_	$44S_{32}, 24S_{28}, 21S_{31}$	10	-	90
A''	ν_{33}	(CH ₂) ₄ antisymmetric stretch	3139	2944	11.1	89.4	0.75	2945	2940	82S ₃₃ , 16S ₃₄	-	100	-
A''	v_{34}	(CH ₂) ₄ antisymmetric stretch	3129	2935	50.9	8.2	0.75	2925	2916	73S ₃₄ , 17S ₃₃	-	100	-
A''	v_{35}	(CH ₂) ₄ symmetric stretch	3083	2892	17.7	35.0	0.75	2880	2873	60S ₃₅ , 36S ₃₆	-	100	-
A''	ν_{36}	(CH ₂) ₄ symmetric stretch	3072	2882	19.6	9.2	0.75	2880	2873	53S ₃₆ , 40S ₃₅	-	100	-
A''	ν_{37}	SiH ₃ antisymmetric stretch	2300	2158	167.3	72.0	0.75	2156	2147	100S ₃₇	-	100	-
A''	v_{38}	(CH ₂) ₄ deformation	1548	1469	3.1	1.5	0.75	1453	1450	96S ₃₈	-	100	-
A''	v_{39}	(CH ₂) ₄ deformation	1542	1464	0.1	27.1	0.75	1449	1442	95S ₃₉	-	100	-
A''	ν_{40}	CH ₂ wag	1430	1358	0.03	2.7	0.75	1357	1357	47S ₄₀ , 15S ₄₂ , 11S ₄₅	-	100	-
A''	v_{41}	(CH ₂) ₄ wag	1417	1345	0.4	0.3	0.75	1352	1347	44S ₄₁ , 20S ₄₅ , 14S ₄₃	-	100	-
A''	v_{42}	(CH ₂) ₄ wag	1399	1328	0.5	3.5	0.75	1331	1331	44S ₄₂ , 19S ₄₀ , 11S ₄₃	-	100	-
A''	ν_{43}	CH out-of-plane bend	1361	1292	1.0	14.7	0.75	1299	1297	$22S_{43}, 33S_{47}, 22S_{42}, 11S_{44}$	-	100	-
A''	v_{44}	CH ₂ twist	1326	1260	0.8	1.2	0.75	1268	1265	31S ₄₄ , 23S ₄₃ , 19S ₅₁ , 13S ₄₅	-	100	-
A''	v_{45}	$(CH_2)_4$ twist	1234	1174	4.7	4.8	0.75	1178	1172	30S ₄₅ , 21S ₄₁ , 15S ₄₈	-	100	-
A''	v_{46}	Ring stretch	1153	1094	1.6	0.4	0.75	1101	-	60S ₄₆ , 26S ₅₀	-	100	-
A''	v_{47}	$(CH_2)_4$ twist	1121	1065	1.0	2.2	0.75	1078	1076	27S ₄₇ , 18S ₄₄ , 13S ₄₂ , 13S ₄₈	-	100	-
A''	ν_{48}	Ring stretch	1093	1038	1.6	4.2	0.75	1048	1042	$36S_{48}, 28S_{47}, 14S_{40}, 12S_{43}$	-	100	-
A''	v_{49}	SiH ₃ antisymmetric defor- mation	987	937	55.7	20.2	0.75	944	942	$99S_{49}$	-	100	-
A''	v_{50}	Ring stretch	960	912	4.9	0.5	0.75	914	-	30S ₅₀ , 27S ₅₁ , 13S ₄₆	-	100	-
A''	v_{51}	(CH ₂) ₄ rock	925	879	1.1	0.5	0.75	_	870	$52S_{51}, 20S_{50}$	_	100	_
A''	v_{52}	(CH ₂) ₄ rock	819	778	0.4	0.6	0.75	784	788	82S ₅₂ , 11S ₄₈	-	100	-
A''	ν_{53}	SiH ₃ rock	647	615	31.2	12.0	0.75	635	633	86S ₅₃	-	100	-
A''	v_{54}	Ring twisting	447	440	0.0001	0.3	0.75	42	-	82S ₅₄	-	100	-
A''	ν_{55}	Ring twisting	246	243	0.005	0.006	0.75	-	-	89S ₅₅	-	100	-
A''	v_{56}	Ring-Si out-of-plane bend	183	182	0.4	0.009	0.75	175	_	85S ₅₆	-	100	-
A''	ν_{57}	SiH ₃ torsion	134	127	0.02	0.01	0.75	129	_	96S ₅₇	-	100	-

All ab initio frequencies, infrared intensities (km/mol), Raman activities (Å⁴/u), depolarization ratios and percentage potential energy distributions are calculated at MP2(full)/6–31G(d) level.

^a Scaled frequencies with scaling factors of 0.88 for CH and SiH stretches, 1.0 for heavy atom bends and 0.90 for all other modes.

^b Infrared spectrum of the gas except those with asterisks which are from condensed phase or summation band.

^c Raman spectrum of the liquid except those with asterisks which are from the solid.
 ^d Symmetry coordinates with PED contribution less than 10% are omitted.

^e Values refer to percentage A, B and C-type infrared band contour composition; entries with bars are symmetry forbidden.

Table 3 Observed and calculated frequencies (cm⁻¹) for cyclohexyl silane (*chair-axial*)

Block	Vib. No.	Fundamental	Ab initio	Fixed scaled ^a	IR int.	Raman act.	dp Ratio	Obs	PED ^b	A^{c}	B ^c	C^*
A'	ν_1	(CH ₂) ₄ antisymmetric stretch	3150	2955	68.7	33.4	0.70		$50S_1, 29S_2, 20S_3$	40	_	60
A'	ν_2	CH ₂ antisymmetric stretch	3137	2943	37.7	112.7	0.34		62S ₂ , 17S ₁ , 10S ₃	76	_	24
A'	ν_3	(CH ₂) ₄ antisymmetric stretch	3127	2933	18.3	120.4	0.49		$58S_3, 30S_1, 11S_6$	87	_	13
A'	ν_4	CH ₂ symmetric stretch	3083	2892	23.7	97.1	0.15		91S ₄	93	_	7
A'	ν_5	(CH ₂) ₄ symmetric stretch	3093	2902	13.1	126.1	0.08		$51S_5, 42S_6$	5	_	95
A'	ν_6	(CH ₂) ₄ symmetric stretch	3073	2883	48.7	160.9	0.06		34S ₆ , 36S ₅ , 23S ₇	0	_	100
A'	ν_7	CH stretch	3057	2867	13.1	62.1	0.75		77S ₇ , 11S ₆ , 11S ₅	100	_	0
A'	ν_8	SiH ₃ antisymmetric stretch	2307	2164	127.9	54.2	0.36		82S ₈ , 18S ₉	19	_	81
A'	ν_9	SiH ₃ symmetric stretch	2290	2148	115.6	158.7	0.05		82S ₉ , 18S ₈	99	_	1
A'	ν_{10}	$(CH_2)_4$ deformation	1569	1489	2.0	3.9	0.43		$73S_{10}, 25S_{12}$	81	_	19
A'	ν_{11}	$(CH_2)_4$ deformation	1558	1478	13.6	1.5	0.72		95S ₁₁	0	_	100
A'	v_{12}	CH ₂ deformation	1547	1468	3.1	22.0	0.75		$72S_{12}, 23S_{10}$	100	_	0
A'	v_{13}	$(CH_2)_4$ wag	1424	1351	4.0	1.0	0.75		73S ₁₃	97	_	3
A'	ν_{14}	$(CH_2)_4$ wag	1436	1364	0.3	2.8	0.72		$57S_{14}, 13S_{15}$	76	_	24
A'	v_{15}	(CH ₂) ₄ twist	1334	1269	0.3	27.2	0.73		$60S_{15}, 14S_{16}$	42	_	58
A'	ν_{16}	$(CH_2)_4$ twist	1352	1288	0.009	3.0	0.17		32S ₁₆ , 17S ₁₅ , 14S ₁₇	2	_	98
A'	ν_{17}	CH in-plane bend	1139	1086	4.2	1.4	0.61		33S ₁₇ , 21S ₁₈ , 13S ₂₄	96	_	4
A'	ν_{18}	(CH ₂) ₄ rock	1266	1205	6.2	5.5	0.71		29S ₁₈ , 28S ₁₇ , 13S ₁₆ ,	99	_	1
									11S ₂₄			
A'	ν_{19}	Ring stretch	1084	1029	0.8	10.0	0.74		37S ₁₉ , 26S ₁₄ , 21S ₂₅	86	-	14
A'	ν_{20}	(CH ₂) ₄ rock	1054	1018	2.9	3.0	0.54		32S ₂₀ , 26S ₂₈ , 13S ₃₁	41	-	59
A'	ν_{21}	SiH ₃ antisymmetric deformation	989	938	76.0	19.2	0.74		82S ₂₁ , 15S ₂₂	2	-	98
A'	ν_{22}	SiH ₃ symmetric deformation	968	919	259.2	11.3	0.75		83S ₂₂ , 15S ₂₁	82	-	18
A'	ν_{23}	Ring stretch	926	881	4.7	3.0	0.65		66S ₂₃	99	_	1
A'	ν_{24}	CH ₂ rock	891	848	19.7	1.3	0.75		45S ₂₄ , 17S ₂₀	84	-	16
A'	ν_{25}	Ring stretch	848	805	2.9	13.4	0.19	816	53S ₂₅ , 26S ₁₉ , 11S ₁₈	100	-	0
A'	ν_{26}	SiC stretch	593	566	4.9	11.8	0.16	576	53S ₂₆ , 11S ₂₀ , 10S ₂₅	98	_	2
A'	ν_{27}	SiH ₃ rock	753	720	24.0	7.4	0.37	724	$36S_{27}, 11S_{18}, 10S_{26}$	45	-	55
A'	ν_{28}	Ring puckering	541	520	7.6	2.7	0.67	529	$21S_{28}, 33S_{27}, 20S_{20}, 10S_{31}$	40	-	60
A'	ν_{29}	Ring bending	386	381	0.7	0.7	0.55		58S ₂₉ , 26S ₃₀	60	_	40
A'	ν_{30}	Ring puckering	458	447	1.8	1.6	0.75	426	34S ₃₀ , 28S ₂₉ , 16S ₂₇	56	-	44
A'	ν_{31}	Ring bending	135	132	0.004	0.1	0.69		41S ₃₁ , 26S ₃₂ , 23S ₂₈	27	-	73
A'	v_{32}	Ring-Si in-plane bend	273	269	0.3	0.8	0.22		49S ₃₂ , 22S ₃₁ , 13S ₃₀	57	-	43
A''	ν_{33}	(CH ₂) ₄ antisymmetric stretch	3144	2950	14.3	68.2	0.75		70S ₃₃ , 30S ₃₄	_	100	-
A''	v_{34}	(CH ₂) ₄ antisymmetric stretch	3126	2932	43.7	18.2	0.75		60S ₃₄ , 30S ₃₃ , 12S ₃₆	-	100	-
A''	v_{35}	(CH ₂) ₄ symmetric stretch	3093	2902	19.9	42.0	0.75		56S ₃₅ , 41S ₃₆	-	100	-
A''	ν_{36}	(CH ₂) ₄ symmetric stretch	3068	2878	20.3	12.6	0.75		47S ₃₆ , 44S ₃₅	-	100	-
A''	ν_{37}	SiH ₃ antisymmetric stretch	2298	2156	164.0	69.5	0.75		100S ₃₇	-	100	-
A''	ν_{38}	(CH ₂) ₄ deformation	1552	1473	7.2	0.1	0.75		98S ₃₈	-	100	-
A''	ν_{39}	(CH ₂) ₄ deformation	1547	1468	0.1	29.7	0.75		98S ₃₉	-	100	-
A''	ν_{40}	CH ₂ wag	1430	1358	0.003	2.1	0.75		48S ₄₀ , 15S ₄₅ , 12S ₄₂	-	100	-
A''	ν_{41}	(CH ₂) ₄ wag	1423	1351	0.2	0.5	0.75		53S ₄₁ , 13S ₄₃ , 11S ₄₄	-	100	-
A''	v_{42}	(CH ₂) ₄ wag	1386	1316	0.8	0.3	0.75		$70S_{42}$	-	100	-
A''	v_{43}	CH out-of-plane bend	1351	1285	8.1	0.2	0.75		33S ₄₃ , 32S ₄₅	-	100	-

A''	v_{44}	CH ₂ twist	1329	1265	0.002	18.3	0.75	$44S_{44}, 19S_{47}, 13S_{43}$	I	100	Ι
A''	V45	(CH ₂) ₄ twist	1162	1103	0.1	0.3	0.75	$35S_{45}, 22S_{41}, 16S_{43}, 11S_{44}$	I	100	I
A''	v_{46}	Ring stretch	1188	1129	1.8	3.5	0.75	$28S_{46}, 33S_{47}, 17S_{50}$	I	100	I
A''	$ u_{47} $	(CH ₂) ₄ twist	1146	1087	0.0000	0.5	0.75	$31S_{47}, 22S_{46}, 13S_{41}, 11S_{50}, 10S_{40}$	I	100	I
A''	ν_{48}	Ring stretch	1085	1030	0.9	8.5	0.75	$53S_{48}, 14S_{42}, 12S_{43}$	I	100	I
A''	ν_{49}	SiH ₃ antisymmetric defor-	266	946	54.4	18.0	0.75	$98S_{49}$	I	100	I
		mation									
A''	ν_{50}	Ring stretch	905	860	0.05	0.3	0.75	$55S_{50}, 25S_{46}$	I	100	I
A''	ν_{51}	(CH ₂) ₄ rock	976	926	0.1	1.1	0.75	69S ₅₁	I	100	I
A''	V52	$(CH_2)_4$ rock	826	785	0.03	0.8	0.75	$82S_{52}, 12S_{48}$	I	100	I
A''	ν_{53}	SiH ₃ rock	664	633	33.0	9.6	0.75	$83S_{53}$	I	100	Ι
A''	v_{54}	Ring twisting	436	429	0.3	0.6	0.75	$82S_{54}$	I	100	I
A''	v_{55}	Ring twisting	293	289	0.2	0.1	0.75	$58S_{55}, 26S_{56}$	I	100	I
A''	v_{56}	Ring-Si out-of-plane bend	181	180	0.3	0.02	0.75	$64S_{56}, 29S_{55}$	I	100	I
A''	ν_{57}	SiH ₃ torsion	103	98	0.004	0.01	0.75	97S ₅₇	I	100	I
All ab initio ^a Scaled fre	frequencies,	, infrared intensities (km/mol), Re ith scaling factors of 0.88 for CH	aman activitie I and SiH stre	s ($Å^4/u$), depolarization tches, 1.0 for heavy atc	ratios and pe om bends and	ercentage pot 0.90 for all	ential energy distributio other modes.	ns are calculated at MP2(full)/	6–31G(d) level		

Values refer to percentage A, B and C-type infrared band contour composition; entries with bars are symmetry forbidden

Symmetry coordinates with P.E.D. contribution less than 10% are omitted

c p



WAVENUMBER (cm⁻¹)

Fig. 3. Infrared spectra of (A) gaseous and (B) liquid cyclohexyl silane.

The simulated Raman spectrum is plotted with the scaled ab initio frequencies and Raman scattering activities calculated at the MP2(full)/6-31G(d) level. The Raman scattering cross sections, $\partial \sigma_i / \partial \Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activities and the predicted frequencies for each normal mode [37-40]. In order to obtain the polarized Raman cross sections, the polarizabilities are incorporated into S_i by multiplying S_i with $(1-\rho_i)/(1+\rho_i)$, where ρ_i is the depolarization ratio of the jth normal mode. The Raman scattering cross sections and the predicted scaled frequencies were utilized, together with a Lorentzian line-shape function, to obtain the simulated spectra. The predicted spectra and the experimental Raman spectrum of the polycrystalline solid are shown in Fig. 4. The predicted spectrum of the chair-equatorial form is in excellent agreement with the observed spectrum.

The infrared spectrum is also predicted at the MP2(full)/6-31G(d) level. The predicted scaled frequencies were utilized, together with a Lorentzian function, to obtain the simulated spectra. Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the

Α

Method/Basis set	Chair		Twist			Boat	
<u>-</u>	⁵ quatorial	Axial	Equatorial	Axial	Ш	Equatorial	Axial
RHF/6-31G(d)	-524.2799346	-524.2765412 (745)	- 524.2694513 (2301)	-524.2657910 (3104)	-524.2685667 (2495)	-524.2675060 (2728)	-524.2613656 (4075)
RHF/6-31+G(d)	-524.2828060	-524.2792678 (777)	- 524.2723400 (2297)	-524.2685674 (3125)	-524.2714041 (2502)	-524.2703990 (2723)	-524.2641875 (4086)
MP2/6-31G(d)	-525.1865137	-525.1837501 (607)	-525.1763089 (2240)	-525.1732006 (2922)	-525.1756058 (2394)	-525.1738010 (2790)	-525.1679533 (4074)
MP2/6-31+G(d)	-525.1997434	-525.1968393 (637)	-525.1898296 (2176)	-525.1865549 (2895)	-525.1891126 (2333)	-525.1870746 (2780)	-525.1812176 (4066)
MP2/6-311G(d,p)	-525.6081759	-525.6057725 (527)	- 525.5987059 (2078)	-525.5957140 (2735)	-525.5980112 (2231)	-525.5959547 (2682)	-525.5904366 (3893)
MP2/6-311+G(d,p)	-525.6125482	-525.6100969 (538)	-525.6030574 (2083)	-525.5999727 (2760)	-525.6023835 (2231)	-525.6002825 (2692)	-525.5947203 (3913)
MP2/6-311G(2d,2p)	-525.6986692	-525.6962901 (522)	- 525.6892039 (2077)	-525.6864100 (2691)	-525.6886721 (2194)	-525.6866535 (2637)	-525.6811106 (3854)
MP2/6-311 + G(2d,2p)	-525.7009732	-525.6986332 (514)	-525.69151930 (2075)	-525.6887602 (2680)	-525.6910017 (2188)	-525.6889296 (2643)	-525.6834790 (3840)
B3LYP/6-31G(d)	-526.5694949	-526.5662144 (720)	-526.5594275 (2210)	-526.5561613 (2926)	-526.5585219 (2408)	-526.5578920 (2747)	-526.5525326 (3723)
B3LYP/6-31+G(d)	-526.5765981	-526.5732524 (734)	-526.5667357 (2165)	-526.5632887 (2921)	-526.5657540 (2380)	-526.5651319 (2517)	-526.5597457 (3699)
B3LYP/6-311G(d,p)	-526.6596798	- 526.6566366 (668)	-526.6499983 (2125)	-526.6468337 (2819)	-526.6491591 (2309)	-526.6484315 (2469)	-526.6433658 (3581)
B3LYP/6–311+G(d,p)	-526.6605707	- 526.6575382 (666)	-526.6508933 (2124)	-526.6477229 (2820)	-526.6500679 (2305)	-526.6493014 (2473)	-526.6442826 (3575)
B3LYP/6-311G(2d,2p)	-526.6720029	- 526.6689287 (675)	-526.6623697 (2114)	-526.6592048 (2809)	-526.6615562 (2293)	-526.6608709 (2443)	-526.6558180 (3552)
B3LYP/6-311+G(2d,2p) -	-526.6726379	-526.6695531 (677)	-526.6629995 (2115)	-526.6598153 (2814)	-526.6621843 (2294)	-526.6614672 (2452)	-526.6564222 (3559)

ab initio calculations and transformed to normal coordinates by: $(\partial \mu_u / \partial Q_i) = [\Sigma(\partial \mu_u / \partial X_j)] L_{ij}$, where Q_i is the ith normal coordinate, X_j is the *j*th Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by: $I_i = [(N\pi)/(3c^2)]$ $[(\partial \mu_x / \partial Q_i)^2 + (\partial \mu_y / \partial Q_i)^2 + (\partial \mu_z / \partial Q_i)^2]$.

The predicted infrared spectrum of the conformeric mixture is shown in Fig. 5(A) which was obtained by utilizing the experientially determined Δ H value (see under Section 3.2 Results). The predicted infrared spectra of the *chair-axial* and *chair-equatorial* conformers are shown in Fig. 5(B) and (C), respectively. Again, the predicted infrared spectrum is in excellent agreement with the observed spectra (Fig. 3) with only minor differences in the intensities of a few bands. Clearly, these spectral data provide excellent support for the assignment of the observed bands to the indicated fundamentals for the chair-equatorial conformer.

3. Results

Our extensive investigation of the infrared spectra of the gas (Fig. 3(A)), liquid (Fig. 3(B)), amorphous (Fig. 6(A)) and annealed solids (Fig. 6(B)) as well as the Raman spectra of the liquid (Fig. 2) and solid (Fig. 4(A)) provides compelling evidence that a second form is present in the fluid phases at ambient temperature. It is also clear that this second form is not present in the spectra of the polycrystalline solid. Thus, the bands which disappear from the spectra of the amorphous solid with annealing (Fig. 6) can be used for the determination of the enthalpy difference between the two forms.

3.1. Vibrational assignments

Cyclohexyl silane has 21 atoms which give rise to 57 fundamental vibrations. Both the *equatorial* and *axial* conformers have C_s point group and they both span the irreducible representation of 32 A' + 25 A''. Thus, the 32 A' fundamental vibrations should be polarized in the Raman effect whereas the remaining 25 A'' modes should be depolarized.

With the structural prediction at the MP2(full)/6-311+G(d,p) level, the rotational constants for both the *chair-equatorial* and *chair-axial* forms were obtained. By using these calculated rotational constants, a band envelope program was used to calculate pure A, B and C-type band contours (Fig. 7) and P-R separations of the infrared rotational-vibrational bands for both the *axial* and *equatorial* conformers. The predicted P-R separations closely matched the observed separations in the spectra of gaseous cyclohexyl silane for both conformations.

There are 11 carbon–hydrogen stretches where the five antisymmetric stretches are predicted to range from a low value of 2935 cm⁻¹ to a high of 2952 cm⁻¹, the five symmetric modes in the range from 2882 to 2893 cm⁻¹, and the CH stretch for the carbon attached to the silicon atom predicted at 2868 cm⁻¹. In the infrared spectra of the gas these appear to be at 2945, 2925 cm⁻¹ as a shoulder and 2880 cm⁻¹ with slightly lower frequencies in the Raman spectrum of the liquid

Fable 4

Table 5

Structural parameters, rotational constants and dipole moments for chair-equatorial and chair-axial conformations of cyclohexyl silane

Structural	Internal	MP2(full)/6-311+G(d,p)))	Electron diffraction	$(r_{\rm g})^{\rm a}$
Parameters	Coordinates	chair-equatorial	chair-axial	Model 1	Model 2
$r(C_1C_{10,11})$ (Å)	R ₁ , R ₂	1.5287	1.5294	1.542(3)	1.535(3)
$r(C_{10}C_{16}, C_{11}C_{17})$	R ₃ , R ₄	1.5304	1.5305	1.542(2)	1.535(3)
$r(C_4C_{16,17})$	R ₅ , R ₆	1.5375	1.5392	1.542(2)	1.550(5)
$r(C_4Si_6)$	R_7	1.8854	1.8927	1.882(6)	1.882(6)
$r(C_1H_2)$	r_1	1.0987	1.0988	1.112(5)	1.113(5)
$r(C_1H_3)$	r_2	1.0959	1.0958	1.112(5)	1.113(5)
$r(C_{10}H_{12}, C_{11}H_{13})$	r_4, r_5	1.0985	1.0974	1.112(5)	1.113(5)
$r(C_{10}H_{14}, C_{11}H_{15})$	r_{6}, r_{7}	1.0962	1.0959	1.112(5)	1.113(5)
$r(C_{16}H_{18}, C_{17}H_{19})$	r_8, r_9	1.1001	1.0998	1.112(5)	1.113(5)
$r(C_{16}H_{20}, C_{17}H_{21})$	r_{10}, r_{11}	1.0969	1.0968	1.112(5)	1.113(5)
$r(C_4H_5)$	r ₁₂	1.1017	1.1008	1.112(5)	1.113(5)
$r(Si_6H_7)$	r ₁₃	1.4806	1.4787	1.477 ^b	1.477 ^b
$r(\mathrm{Si}_{6}\mathrm{H}_{89})$	r_{14}, r_{15}	1.4797	1.4800	1.477 ^b	1.477 ^b
$\angle C_{10}C_1C_{11}$ (°)	ϕ_2	111.01	111.21	112.2(25)	112.6(26)
$\angle C_1 C_{10} C_{16}, \angle C_1 C_{11} C_{17}$	ϕ_2, ϕ_3	111.11	111.01	111.1(13)	111.5(13)
$\angle C_4 C_{16} C_{10}, \angle C_4 C_{17} C_{11}$	ϕ_4, ϕ_5	111.61	112.08	111.1(13)	112.0(13)
$\angle C_{16}C_4C_{17}$	φ ₆	110.30	110.05	112.2(25)	110.9(25)
$\angle Si_6C_4C_{16,17}$	θ_1, θ_2	111.63	113.72	112.8(12)	112.4(12)
$\angle C_{10,11}C_1H_2$	α_1, α_2	109.17	109.07	109.5(9)	109.7(9)
$\angle C_{10,11}C_1H_3$	β_1, β_2	110.29	110.27	109.5(9)	109.7(9)
$\angle H_2C_1H_3$	γ	106.82	106.85		
$\angle C_1 C_{10} H_{12}, \angle C_1 C_{11} H_{13}$	$\varepsilon_1, \varepsilon_2$	109.21	109.18	109.5(9)	109.7(9)
$\angle C_1 C_{10} H_{14}, \angle C_1 C_{11} H_{15}$	δ_1, δ_2	110.35	110.17	109.5(9)	109.7(9)
$\angle C_{16}C_{10}H_{12}$, $\angle C_{17}C_{11}H_{13}$	n_1, n_2	108.96	109.94	109.5(9)	109.7(9)
$\angle C_{16}C_{10}H_{14}, \angle C_{17}C_{11}H_{15}$	K_1, K_2	110.11	109.74	109.5(9)	109.7(9)
$\angle H_{12}C_{10}H_{14}$, $\angle H_{13}C_{11}H_{15}$	χ_1, χ_2	107.01	106.70		
$\angle C_4 C_{16} H_{18}, \angle C_4 C_{17} H_{19}$	μ_1, μ_2	109.14	108.60	109.5(9)	109.7(9)
$\angle C_4 C_{16} H_{20}, \angle C_4 C_{17} H_{21}$	ν_1, ν_2	110.45	110.71	109.5(9)	109.7(9)
$\angle C_{10}C_{16}H_{18}, \angle C_{11}C_{17}H_{19}$	π_1, π_2	108.80	108.38	109.5(9)	109.7(9)
$\angle C_{10}C_{16}H_{20}, \angle C_{11}C_{17}H_{21}$	σ_1, σ_2	109.98	110.28	109.5(9)	109.7(9)
$\angle H_{18}C_{16}H_{20}$, $\angle H_{19}C_{17}H_{21}$	ρ_1, ρ_2	106.72	106.59		
$\angle C_{16,17}C_4H_5$	ω_1, ω_2	107.95	107.79	109.5(9)	109.7(9)
$\angle Si_6C_4H_5$	ζ	107.19	103.23		
$\angle C_4 Si_6 H_7$	01	109.38	113.58		
$\angle C_4 Si_6 H_{8.9}$	O_{2}, O_{3}	110.61	108.97		
$\angle H_8Si_6H_9$	ψ_1	108.93	109.10		
$\angle H_7Si_6H_{8.9}$	ψ_2, ψ_3	108.63	108.07		
$\tau C_1 C_{10} C_{16} C_4, -C_1 C_{11} C_{17} C_4$	12.10	55.90	55.73	54.3 ^c	53.8 ^c
A (MHz)		4101.6	3155.7		
В		1366.1	1654.8		
С		1107.1	1422.3		
$ \mu_a $ (D)		0.871	0.715		
$ \mu_{\rm b} $		_	_		
$ \mu_c $		0.199	0.439		
$ \mu_t $		0.883	0.852		
$\Delta E/\Delta G \ (\text{cm}^{-1})$			538	560 ± 209^{d}	482 ± 203^{d}
			220	200 - 207	.52 - 205

^a Ref. [27]. Model 1: all C–C bond distances are identical; model 2: the two C–C bonds adjacent to Si are assumed to be 0.015 Å longer than the other four C–C bonds.

^b Assumed parameters.

^c Dependent parameters.
 ^d Calculated from Ref. [27] results.

(Table 2). In the infrared and Raman spectra of the crystalline solid, these bands are extensively split, thus it is not possible to give individual assignments for the split bands.

Most of the CH_2 bending modes can be assigned based on their predicted frequencies and intensities, along with their group frequencies and previous assignments for several other mono-substituted cyclohexane molecules. This is particularly true for the CH_2 deformations, wags and twists. However, the CH out-of-plane bend and several of the CH₂ rocking modes are extensively mixed, some of them are mixed with the ring modes. Therefore there is some arbitrariness in describing these normal vibrations, for example, ν_{20} which has the largest contribution of 25% from S₁₈ ((CH₂)₄ rock) with 16% S₁₇ (CH in-plane bend) and 13% S₂₄ (CH₂ rock), with the remaining contributions being less than 10%. Most of the normal vibrations described as ring modes of A' symmetry have at



Fig. 4. Raman spectra of cyclohexyl silane: (A) solid at -75 °C; (B) simulated spectrum of a mixture (at -75 °C) of the two conformers with ΔH of 520 cm⁻¹ with the *chair-equatorial* form more stable; (C) simulated spectrum for pure *chair-axial* form; (D) simulated spectrum for pure *chair-equatorial* form.



Fig. 5. Infrared spectra of cyclohexyl silane: (A) simulated spectrum of a mixture (at 25 °C) of the two conformers with ΔH of 520 cm⁻¹ with the *chair*-*equatorial* form more stable; (B) simulated spectrum for pure *chair-axial* form; (C) simulated spectrum for pure *chair-equatorial* form.



Fig. 6. Infrared spectra of (A) amorphous and (B) polycrystalline solid cyclohexyl silane. Bands marked with asterisks are due to the *chair-axial* form which disappears with annealing.

least 40% contribution from the designated symmetry coordinate except for v_{28} and v_{31} . However there is more mixing of the ring modes for those of A'' symmetry but the twelve ring modes for the mono-substituted cyclohexyl moiety have been well-characterized so their assignments can be given with little doubt. Similarly, eight of the nine normal modes from the silicon-hydrogen motions can be readily assigned, based on their intensities and frequencies with only the SiH₃ torsion not initially observed. Therefore, nearly all of the fundamentals of the *chair-equatorial* form of cyclohexyl silane can be confidently assigned.

For the *chair-axial* conformer, most of the carbon-hydrogen modes are predicted to have frequencies nearly the same as the corresponding modes for the equatorial form and the same is true for the silicon-hydrogen modes. However, the predicted frequencies for several skeletal modes of this less stable conformer differ significantly from the corresponding ones of the equatorial form. If one uses the skeletal frequencies it is fairly easy to find several of the A' fundamentals of the *chair*axial conformer. For example, ν_{26} and ν_{27} are observed at 753 and 603 cm^{-1} with the predicted at 747 and 581 cm⁻¹, respectively, for the chair-equatorial form; whereas the corresponding bands for the axial form are observed at 724 and 576 cm^{-1} and predicted at 720 and 566 cm^{-1} . By the same process additional skeletal modes of the chair-axial form are assigned at 816, 529 and possibly 426 cm^{-1} and they are predicted at 805, 520 and 447 cm⁻¹, respectively. Confident assignments for all of these bands except maybe the last one can be made since these bands are not present in the spectra of the solid.

3.2. Conformational stability

In order to obtain a reliable enthalpy difference between the two stable conformers of $c-C_6H_{11}SiH_3$, it is important to choose bands that are 'isolated' and with confident assignments. To minimize the number of potential overtones and



Fig. 7. Predicted pure A-, B-, and C-type infrared contours for the chair-equatorial conformer and the chair-axial conformers of cyclohexyl silane utilizing the predicted rotational constants at MP2(full)/6-311+G(d,p) level.

combinations that can interfere, fundamentals with as low a frequency as possible should be chosen. For this purpose the Raman spectrum of the liquid provides the best data where three pronounced lines are observed at 810, 725 and 580 cm⁻¹. The intensity of these three bands decreases markedly as the temperature was lowered by 90 °C (Fig. 8). These three lines can be confidently assigned to the *chair-axial* conformer. The corresponding lines of the *chair-equatorial* form are observed at 820, 750 and 601 cm⁻¹, the intensity of these fundamentals increases with lowering temperature. The rather large change in the intensity ratios of these three pairs of lines is indicative of the relatively large enthalpy differences between the two conformers.

Seven sets of data were obtained from the three conformer pairs by using the band areas and they were fit to the Van't Hoff equation, $-\ln K = \Delta H/RT - \Delta S/R$, where the intensity ratio of the more stable conformer to the less stable one is used for K and it is assumed that ΔH is not a function of temperature in the experimental temperature range. By using a least squares fit, the ΔH values which correspond to the slope of the three Van't Hoff plots (Fig. 9) were determined for the three conformer pairs, with conformational enthalpy differences of 445 cm⁻¹ (I_{750} / I_{725}), 549 cm⁻¹ (I_{601}/I_{580}) and 563 cm⁻¹ (I_{820}/I_{810}). The average value for these three determinations is 520 cm^{-1} with a statistical uncertainty of 70 cm^{-1} . The relative spread in the values is normally what is obtained by this technique because of the interference from combination and overtone bands as well as the baseline correction and band deconvolution processes. For example, the bands in the 700–850 cm^{-1} range include as many as 16 combination bands from the chair-equatorial

conformer alone. Additionally, there is some difficulty in obtaining the intensities of relatively weak bands which appear as shoulders on much stronger bands. Clearly, the overall uncertainties in the obtained ΔH values can not be described statistically alone, since systematic errors described above can not be ignored. Thus, the realistic uncertainty may be as much as 20%, though it is beyond doubt that the ΔH value is relatively large and only a very small amount of the second form exists in the fluid phases at ambient temperature.

3.3. Barrier to SiH_3 rotation

In Fig. 10 combination bands in the SiH₃ stretching region are shown. It is evident from the high pressure spectra (Fig. 10(B)) that three sets of combination bands are observed in the region between 2350 and 1950 cm^{-1} . These are centered at approximately 60, 125, and 175 cm^{-1} on either side of the very intense SiH₃ stretch at 2156 cm^{-1} . The vibration at 60 cm^{-1} seems too low for the ring mode and was initially left unassigned. The mode at 175 cm^{-1} , which was observed in the Raman spectrum at 170 cm^{-1} , is the Ring-Si out-of-plane bend. Individual transitions for the sum bands between the SiH₃ torsion of the chair-equatorial conformer and SiH₃ stretch were observed at 2286, 2278 and 2268 cm^{-1} (Table 7). Two transitions for the corresponding difference bands at 2027 and 2034 cm^{-1} were also observed. Using this information, the $\nu = 0 \rightarrow 1$ transition for the skeletal torsion is assigned a value of 129 cm^{-1} , the $\nu =$ $1 \rightarrow 2$ transition is assigned a value of 122 cm^{-1} . The assignments for the $\nu = 2 \rightarrow 3$ and $\nu = 3 \rightarrow 4$ transitions are



Fig. 8. Raman spectrum of cyclohexyl silane at 20 and -75 °C. Bands marked with asterisks were used for ΔH determinations.

112 and 102 cm⁻¹, respectively (Table 7). The barrier to internal rotation of the silyl group for the *chair-equatorial* conformer was calculated with a potential function of the form: $V(\alpha) = \frac{1}{2} V_3$ (1 - cos 3 α), where α is the dihedral angle and V₃ is the three-fold barrier. The Hamiltonian operator used for this system is defined by: $H = H_r + F(p-P)^2 + \frac{1}{2}V_3(1 - \cos 3\alpha)$, where H_r is the rigid rotor Hamiltonian; $F = h^2/8I_r$ is the internal rotational constant and I_r is the



Fig. 9. van't Hoff plots for the Raman line intensities at $(+) I_{820}/I_{810}$; (*) I_{750}/I_{725} ; and $(\bullet) I_{601}/I_{580}$.



Fig. 10. Infrared spectra of cyclohexyl silane between 2500 and 1800 cm^{-1} which shows the combination bands arising from the coupling of the SiH₃ stretch with three low frequency modes.

reduced moment of inertia for internal rotation; and p-P is the relative angular momentum of the SiH₃ group and the frame. The silyl barrier obtained from the fit of these data (Table 8) is $684 \pm 3 \text{ cm}^{-1}$ (1.96 ±0.01 kcal/mol). The corresponding barriers for several mono-substituted silanes are listed in Table 9 for comparison.

3.4. Structural parameters

As can be seen from the data in Table 5, the ab initio MP2(full)/6-311+G(d,p) calculation predicts very small differences in the various atom distances between the equatorial and axial conformers with the exception of the Si-C distance which is predicted to be 0.007 Å longer in the axial conformer. Also it should be noted that the two C-C distances adjacent to Si are predicted to be 0.0071 and 0.0087 Å shorter in the equatorial and axial conformers than the $C_{10}C_{16}$ and $C_{11}C_{17}$ bond distances. Since there is essentially a single SiH stretch observed, it is possible to calculate the SiH bond distance from this 'isolated' frequency [41]. By using the frequency of 2156 cm⁻¹, the SiH bond distance is calculated to be 1.4853 Å from the empirical equation: SiH distance (in Å)=1.8729- $0.0001798 \nu_{SiH}$ (in cm⁻¹) [41]. This distance is about 0.005 Å longer than the calculated one which is in agreement with the systematic error in ab initio distances found for several silanes. Since we have found that the ab initio MP2(full)/6-311+G(d,p) calculations predict the Si-C distance about 0.005 Å too long, it should be possible to predict the heavy atom structural parameters to at least an accuracy of 0.005 Å. Additionally, we have found of about fifty different CH distances that the predicted CH distances at MP2(full)/6-311+G(d,p) level agree to the values obtained from 'isolated' stretching frequencies to within 0.002 Å [42]. Therefore, the estimated r_0 parameters listed in Table 5 for both the equatorial and axial conformers are expected to be as accurate as those that could be obtained from microwave spectral data.

4. Discussion

The mixing of the vibrational modes is relatively small for such a large molecule with the exception of v_{26} and v_{28} in the A' symmetry block and v_{43} and v_{47} in the A["] symmetry block. For the first two there are five symmetry coordinates contributing to each mode with the largest contribution only 23%. Therefore the description for these vibrations is rather arbitrary and is more for bookkeeping than providing accurate atom motions. In several cases it was necessary to assign a band to more than one fundamental, i.e. cases in which differences of the predicted frequencies of normal modes are only a few wavenumbers (Table 2). Also it should be noted that many of the fundamentals for the chair-axial conformer are predicted to be in near coincidence with the corresponding fundamentals of the chair-equatorial conformer. Therefore the assigned fundamentals for the less stable conformer (Table 3) are the only ones which could be confidently identified from their disappearance in the spectra of the solid with the exception of the SiH₃ torsion.

In the earlier electron diffraction investigation [27] of cyclohexyl silane, the uncertainty on the enthalpy difference $(482 \pm 203 \text{ cm}^{-1})$ between the two conformers is very large which made it difficult to compare with the corresponding quantity $(644 \pm 42 \text{ cm}^{-1})$ for cyclohexyl methane. However, in the present study the enthalpy difference determined for the liquid has a much smaller uncertainty. It is now clear that the conformational enthalpy difference for cyclohexyl silane is smaller than that for the cyclohexyl methane but much larger than the corresponding values for cyclohexyl halides. For this series, MP2 and B3LYP calculated results are in reasonable agreement with most of the previously reported experimental values. For the halogen series, it is clear from the data given in Table 1 that the conformational energy difference increases with increasing size as well as decreasing electronegativity of the substituent. When two substituent groups, one with larger size and higher electronegativity than the other, e.g. bromine

and methyl groups are compared, it becomes clear that the electronegativity of the substituent is a dominant factor and the steric factor plays a lesser role in determining the enthalpy difference in these mono-substituted cyclohexanes.

Second-order perturbation theory analyses of the interactions in NBO basis provide detailed comparisons of the donoracceptor delocalization among these mono-substituted cyclohexane molecules. These analyses were carried out by examining all possible interactions between donor Lewis-type NBOs and acceptor non-Lewis NBOs, and estimating their energetic importance by 2nd-order perturbation theory. For each donor NBO (i) and acceptor NBO (i), the stabilization energy E(2) associated with delocalization ('2e-stabilization') i \rightarrow *j* is estimated as $E(2) = \Delta E_{ij} = q_i \cdot [F(i,j)^2/(\varepsilon_j - \varepsilon_i)]$, where q_i is the donor orbital occupancy, ε_i , ε_i are diagonal elements (orbital energies) and F(i,j) is the off-diagonal NBO Fock matrix element [43]. Our NBO calculations are carried out at the MP2(full)/6-311+G(d,p) level. The major delocalization interactions among the series of mono-substituted cyclohexanes are listed in Table 6. These include the $\sigma_{C(4)-H(5)} \rightarrow \sigma^*_{C(16)-H(18)}$ $[\sigma_{C(4)-H(5)} \rightarrow \sigma^*_{C(17)-H(19)}], \sigma_{C(16)-H(18)} \rightarrow \sigma^*_{C(4)-H(5)} [\sigma_{C(17)-H(18)}]$ $H_{(19)} \rightarrow \sigma^*_{C(4)-H(5)}$ pair and the $\sigma_{C(4)-X(6)} \rightarrow \sigma^*_{C(10)-C(16)}$ $[\sigma_{C(4)-X(6)} \to \sigma^*_{C(11)-C(17)}], \ \sigma_{C(10)-C(16)} \to \sigma^*_{C(4)-X(6)} \ [\sigma_{C(11)-C(17)}]$ $_{C(17)} \rightarrow \sigma^*_{C(4)-X(6)}$ pair for the *chair-equatorial* conformer as well as the $\sigma_{C(4)-H(5)} \rightarrow \sigma^*_{C(10)-C(16)} [\sigma_{C(4)-H(5)} \rightarrow \sigma^*_{C(11)-C(17)}],$ $\sigma_{C(10)-C(16)} \rightarrow \sigma^{*}_{C(4)-H(5)} [\sigma_{C(11)-C(17)} \rightarrow \sigma^{*}_{C(4)-H(5)}] \text{ pair and the} \\ \sigma_{C(4)-X(6)} \rightarrow \sigma^{*}_{C(16)-H(18)} [\sigma_{C(4)-X(6)} \rightarrow \sigma^{*}_{C(17)-H(19)}], \ \sigma_{C(16)-H(16)} = \sigma^{*}_{C(16)-H(16)} [\sigma^{*}_{C(16)-H(16)} \rightarrow \sigma^{*}_{C(17)-H(16)}], \ \sigma_{C(16)-H(16)} = \sigma^{*}_{C(16)-H(16)} [\sigma^{*}_{C(16)-H(16)} \rightarrow \sigma^{*}_{C(17)-H(16)}], \ \sigma_{C(16)-H(16)} = \sigma^{*}_{C(16)-H(16)} [\sigma^{*}_{C(16)-H(16)} \rightarrow \sigma^{*}_{C(16)-H(16)}], \ \sigma_{C(16)-H(16)} = \sigma^{*}_{C(16)-H(16)} = \sigma^{*}_{C(16)-H(16)$ $_{\rm H(18)} \rightarrow \sigma^*_{\rm C(4)-X(6)} [\sigma_{\rm C(17)-H(19)} \rightarrow \sigma^*_{\rm C(4)-X(6)}]$ pair for the *chair*axial conformer. The sum of these four most significant pairs of donor-acceptor interactions gives the stabilization energy of the chair-axial over the chair-equatorial form of 0.94, 0.88 and 1.26 kcal/mol (329, 308 and 441 cm⁻¹), respectively, for the fluoride, chloride and bromide. These interactions give increasing favor to the *chair-axial* form further down the halogen group which largely offsets the increasing steric effect, and, thus, contributes to the relatively small differences in the ΔH values found for the halogen series. These donor-acceptor

Table 6

Difference in major delocalizing interactions among a series of mono-substituted cyclohexane molecules

			Energies in kca	al/mol, calculated	l at MP2(full)/6-3	B11 + G(d,p) level		
Conformation	Donor orbital	Acceptor orbital	Cyclohexane	Cyclohexyl silane	Cyclohexyl methane	Cyclohexyl fluoride	Cyclohexyl chloride	Cyclohexyl bromide
Chair-equatorial	$\sigma_{\mathrm{C}(4)-\mathrm{H}(5)}$	$\sigma^{*}_{C(16)-H(18)}, \sigma^{*}_{C(17)-H(19)}$	3.81	4.15	4.13	3.48	3.67	3.71
	$\sigma_{C(16)-H(18)}, \sigma_{C(17)-H(19)}$	σ [*] _{C(4)–H(5)}	3.81	4.01	4.04	3.72	4.18	4.32
	$\sigma_{C(4)-X(6)}$	$\sigma^*_{C(10)-C(16)}, \sigma^*_{C(11)-C(17)}$	3.49	3.97	2.41	1.27	2.51	3.01
	$\sigma_{C(10)-C(16)},$	$\sigma^{*}_{C(4)-X(6)}$	2.22	2.85	2.80	3.99	5.15	5.89
Chair-axial	$\sigma_{C(4)-H(5)}$	$\sigma^*_{C(10)-C(16)}, \sigma^*_{C(11)-C(17)}$	3.81	3.86	3.97	3.51	3.65	3.63
	$\sigma_{C(10)-C(16)},$ $\sigma_{C(11)-C(17)}$	$\sigma^*_{C(4)-H(5)}$	3.81	2.12	2.09	2.17	2.25	2.32
	$\sigma_{C(4)-X(6)}$	$\sigma^*_{C(16)-H(18)}, \sigma^*_{C(17)-H(19)}$	3.49	3.84	2.10	1.38	2.61	3.14
	$\sigma_{{ m C}(16)-{ m H}(18)}, \ \sigma_{{ m C}(17)-{ m H}(19)}$	$\sigma^*_{C(4)-X(6)}$	2.22	4.23	4.39	6.62	8.04	9.20

interactions are an order of magnitude weaker in cyclohexyl methane/silane. In cyclohexyl methane, the stabilization energy of the *chair-axial* form is only 0.11 kcal/mol (39 cm^{-1}) , whereas in cyclohexyl silane, the stabilization energy of the *chair-axial* form is negative with a value of -0.09 kcal/mol (-32 cm^{-1}) , indicating the delocalization interactions favor the chair-equatorial form. The differences in the stabilization energies between the halides and the methane/silane agree semiquantitatively with the experimental/theoretical conformational enthalpy differences. However, this does not explain the smaller ΔH value of the silane compared with that of the methane. Further analysis reveals that the difference in the interactions between the $\sigma_{C(4)-H(5)} \rightarrow \sigma^*_{Si(6)-H(7)} [\sigma_{Si(6)-H(7)} \rightarrow \sigma^*_{C(4)-H(5)}]$ pair of the silane and the $\sigma_{C(4)-H(5)} \rightarrow \sigma^*_{C(6)-H(7)} [\sigma_{C(6)-H(7)} \rightarrow$ $\sigma^*_{C(4)-H(5)}$ pair of the methane may be the answer. While these interactions are weak (less than 0.50 kcal/mol) in the chairequatorial conformer, they are much stronger in the chair-axial form where the net value of the $\sigma_{C(4)-H(5)} \rightarrow \sigma_{Si(6)-H(7)}$ interaction of the silane is 1.51 kcal/mol and that of the $\sigma_{\rm C(4)-}$ $_{\rm H(5)} \rightarrow \sigma^*_{\rm C(6)-H(7)}$ of the methane is only 0.79 kcal/mol. This interaction lends extra stability of the chair-axial form for the silane, hence contributing to the smaller conformational enthalpy differences compared with the methane, despite the significantly larger size of the silyl group.

The determined barrier of $684 \pm 3 \text{ cm}^{-1}$ to internal rotation of the SiH₃ group has a statistical uncertainty which is smaller than the difference usually found between the barriers obtained from microwave splitting and observed SiH₃ torsional transitions. For example, we recently completed a microwave and far infrared study [44] of CH₂FSiH₃ and the silyl rotation barriers obtained from the two methods differ by 5 cm⁻¹. Therefore, contribution to uncertainty from systematic method errors must be considered and we believe an uncertainty of 10 cm⁻¹ is more realistic so this is the value listed in (Tables 7 and 8) Table 9.

The SiH₃ barriers are listed for several molecules in Table 9 and the value of $684 \pm 10 \text{ cm}^{-1}$ for the *chair-equatorial* conformer of cyclohexyl silane is only slightly lower than the corresponding barriers in cyclopropyl silane [21], cyclopentyl silane [23], and the average barrier (709 cm⁻¹) of the *equatorial* and *axial* conformers of cyclobutyl silane [22]. For this latter molecule there is only 11 cm^{-1} difference between the barrier values obtained from the microwave splitting data [45] and the one determined from infrared spectrum [23]. There have been very few ab initio predicted barrier values for the silyl rotor but for ethyl silane the predicted value of 631 cm^{-1} (MP2(full)/6–31G(d) level) is

Table 7

Observed combination bands (cm^{-1}) of the SiH₃ torsion with the SiH₃ antisymmetric stretch in cyclohexyl silane

	Summation I	bands	Difference b	Difference bands			
Transition	Observed	obs2156	Observed	2156-obs.			
1←0	2286	130	2027	129			
2 ← 1	2278	122	(2034)	122			
3←2	2268	112					
4←3	(2258)	102					

Table 8 Observed and calculated SiH₂ to

Observed and calculated SiH_3 torsional frequencies (cm⁻¹) for cyclohexyl silane

Transition	Observed	Calculated ^a	Δ (obscalcd)
1←0	129.0	129.2	-0.2
2 ← 1	122.0	121.4	0.6
3←2	112.0	112.6	-0.6
4←3	102.0	101.3	0.7

^a Calculated with $F = 3.0208 \text{ cm}^{-1}$; $V_3 = 684 \pm 3 \text{ cm}^{-1}$.

between the barrier of $692 \pm 3 \text{ cm}^{-1}$ obtained from the microwave splitting [46] and 590 cm⁻¹ from infrared torsional data [47]. For this molecule the coupled rotor model [46] was used which has been questioned [23] whether it is applicable to the two different rotors in ethyl silane.

We have found that MP2(full)/6-31G(d) calculations predict the barriers of internal rotation of the methyl group reasonably well for a large number of molecules, particularly if it is attached to a carbon atom. In an attempt to find the optimal level of calculation for silvl rotation barriers, we calculated the SiH₃ barrier of the *chair-equatorial* form with MP2 and B3LYP methods utilizing several basis sets and the results are listed in Table 10. Among the calculated silvl barriers, the MP2(full)/6-31G(d) value of 669 cm⁻¹ is in closest agreement with the experimentally determined value of $684 + 10 \text{ cm}^{-1}$ which is an indication that calculation at this level might provide reasonable predictions on the values of the SiH₃ barriers where a silicon atom is attached to a carbon atom. We also predicted the SiH₃ barrier for the chair-axial conformer and the value (366 cm^{-1}) was nearly one-half the value of the barrier for the chair-equatorial conformer. Therefore, we tentatively assigned the 60 cm^{-1} sum and difference band on the SiH stretch to the SiH₃ torsion of the *chair-axial* form but

Table 9

Experimentally determined three-fold barriers to internal rotation for the SiH₃ group

Molecule	V_3		Method	Ref.
	cm^{-1}	cal/mol		
Methyl silane	587 <u>+</u> 7	1679 ± 20	IR	51
Ethyl silane	590	1687	IR	47
	692.2 ± 2.4	1979 ± 7	MW	46
	631	1804	MP2	46
Allyl silane	731	2090	IR	52
Cyclopropyl silane	692	1980	IR	21
Cyclobutyl silane (eq)	655	1873	IR	22
(ax)	763	2181	IR	22
	752	2150	MW	45
Cyclopentyl silane	718	2053	IR	23
Cyclohexyl silane (eq)	684 ± 10	1956 ± 30	IR	а
	669	1913	MP2	а
(ax)	336	961	MP2	а

^a This study.

Table 10 Calculated silyl rotational barriers (cm⁻¹) for the *chair-equatorial* and *chair-axial* conformers of cyclohexyl silane

Method/Basis set	Chair-equatorial	Chair-axial
RHF/6-31G(d)	610	417
RHF/6-31 + G(d)	620	430
MP2(full)/6-31G(d)	669	366
MP2(full)/6-31 + G(d)	643	393
MP2(full)/6-311G(d,p)	592	336
MP2(full)/6-311 + G(d,p)	601	338
MP2(full)/6-311G(2d,2p)	665	349
MP2(full)/6-311+G(2d,2p)	655	342
B3LYP/6-31G(d)	589	356
B3LYP/6-31+G(d)	565	365
B3LYP/6-311G(d,p)	594	385
B3LYP/6-311+G(d,p)	655	386
B3LYP/6-311G(2d,2p)	607	391
B3LYP/6–311+G(2d,2p)	606	391

the relative intensity is much larger than expected for such an assignment.

The structural parameters determined by electron diffraction [27] (Table 5) were obtained by two different models. In model 1 the three possible C-C distances were all assumed to be the same, the determined value was 1.542 ± 0.003 Å which led to $91 \pm 10\%$ abundance of the *equatorial* conformer at 75 °C with the same parameters for the axial form. In model 2 the C-C bonds adjacent to the Si atom were assumed to be 0.015 Å longer than the other two. This model gave the other two C-C distances with values of 1.535 ± 0.003 Å and the longer one adjacent to Si with a value of 1.550 ± 0.005 Å and both models gave the Si–C distance of 1.882 ± 0.006 Å. As can be seen from the data in Table 5 the assumed C-C difference is too large whereas the ab initio predicted differences are 0.007 and 0.009 Å for the equatorial and axial forms, respectively. The ab initio differences are expected to be much closer to the actual differences since errors in ab initio calculations are wellaccepted to be systematic.

To illustrate the quality of the MP2(full)/6–311+G(d,p) calculation for the predictions of the structural parameters, we recently carried out a study [48] of the Raman spectra and structural parameters of cyclohexane. The C–C, C–H_{eq} and C–H_{ax} distances were predicted to be 1.5299, 1.0959 and 1.0986 Å, respectively, which are in excellent agreement with the corresponding r_s parameters [49] of 1.5300(32), 1.0933(15) and 1.1013(39) Å. The predicted angles are equally good with all of them within the microwave structural uncertainties. These excellent predictions at the MP2(full)/6–311+G(d,p) level suggests that the same level is suitable for providing basis for the estimated structural parameters for cyclohexyl silane (Table 5).

In addition to the two *chair* conformers, three twist forms, equatorial, *axial* and III (Fig. 11) are predicted to be stable with all real calculated fundamental frequencies. However, the *twist* forms are predicted to be 2000–3000 cm⁻¹ higher in energy than the *chair* forms (Table 4). Therefore, one does not expect to find evidence for the *twist* form at ambient temperature. The *boat-equatorial* and boat-axial forms are first-order saddles



twist - III

Fig. 11. The twist-equatorial, twist-axial and twist-III forms of cyclohexyl silane.

points and their calculated energies are also listed in Table 4. It is interesting to point out that the *boat-equatorial* form is predicted with comparable energy to the *twist* forms whereas the *boat-axial* form is $3500-4000 \text{ cm}^{-1}$ higher in energy than the most stable conformation. The calculated potential function governing the ring inversion of cyclohexyl silane is given in Fig. 12.

In an earlier ab initio conformational analysis of cyclohexane [50] by MP2 correlation correction with triple zeta and polarization functions, a second minimum in addition to



Fig. 12. The potential function governing the ring inversion of cyclohexyl silane, calculated at MP2(full)/6-311G(d,p) level.

the lowest *chair* conformation was found to be a twist structure of D_2 symmetry. This form was found to be at a higher energy from the D_{3d} chair structure to have a value of 2413 cm⁻¹ (6.9 kcal/mol). The inter-conversion between the chair structures via the twist form is predicted to be accomplished through either of two transition states, one of C₂ symmetry and the other of C₁ symmetry with both transition states lying about 4200 cm⁻¹ (12 kcal/mol) above the *chair* form [50]. These values are similar to the predicted barriers to conformational interchange of cyclohexyl silane (Fig. 12) which indicates little effect of the barriers of cyclohexane by the silyl group.

Some additional conformational studies of cyclohexyl chloride and bromide in liquid rare gas solutions would be of interest, particularly since there is a significant spread in the experimentally determined enthalpy values for the chloride. Also, since both molecules have microwave rotational data, one expects to be able to obtain excellent structural parameters from the combination of these data with the ab initio predicted parameters.

5. Conclusion

In the present study, a thorough vibrational analysis of cyclohexyl silane was carried out by using the data obtained from infrared and Raman spectra as well as the theoretical calculations. This molecule was found to exist as a mixture of both chair-equatorial and chair-axial conformers in the fluid phases, with the equatorial conformer being more stable. In the polycrystalline solid phase, only the more stable chairequatorial conformer was found to exist. The conformational energy difference between the equatorial and axial conformers in the liquid phase was found to be $520+70 \text{ cm}^{-1}$ $(6.22\pm0.84$ kcal/mol). The series of combination band spectra arising between 2350 and 1950 cm^{-1} , which are attributed to the sum and difference bands of the SiH₃ torsion mode as well as two other low frequency bending modes combined with the Si-H stretching vibration, were used to determine the barrier to internal rotation of the silvl group of $684 \pm 10 \text{ cm}^{-1}$ (8.18 ± 0.12 kcal/mol). Effects of electronegativity and steric effect on the conformational stability are compared among a series of mono-substituted cyclohexanes by NBO analyses of the donor-acceptor delocalization interactions. The ab initio calculations predicted three stable *twist* forms: *twist-equatorial*, *twist-axial*, and *twist-III*. All three *twist* forms have much higher energies than the two *chair* conformers.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2005. 09.039.

References

- [1] P. Andersen, Acta Chem. Scand. 16 (1962) 2337.
- [2] L. Pierce, R. Nelson, J. Am. Chem. Soc. 88 (1966) 216.
- [3] L.H. Scharpen, J. Am. Chem. Soc. 94 (1972) 3737.
- [4] E.L. Eliel, R.J.L. Martin, J. Am. Chem. Soc. 90 (1968) 682.
- [5] F.A. Bovey, E.W. Anderson, F.P. Hood, R.L. Kornegay, J. Chem. Phys. 40 (1964) 3099.
- [6] P.S. Chu, N.S. True, J. Phys. Chem. 89 (1985) 5613.
- [7] D.E. Bugay, C.H. Bushweller, C.T. Danehey Jr., S. Hoogasian, J.A. Blersch, W.R. Leenstra, J. Phys. Chem. 93 (1989) 3908.
- [8] A.I. Fishman, W.A. Herrebout, B.J. Van der Veken, J. Phys. Chem. 106A (2002) 4536.
- [9] W. Caminati, F. Scappini, D. Damiani, J. Mol. Spectrosc. 108 (1984) 287.
- [10] D.J. Gardiner, C.J. Littleton, N.A. Walker, J. Raman Spectrosc. 18 (1987) 9.
- [11] Q. Shen, J.M. Peloquin, Acta Chem. Scand. A42 (1988) 367.

- [12] L. Dosen-Micovic, D. Jeremic, N.L. Allinger, J. Am. Chem. Soc. 105 (1983) 1723.
- [13] J. Stokr, B. Schneider, J. Jakes, J. Mol. Struct. 15 (1973) 87.
- [14] W. Caminati, D. Damiani, F. Scappini, J. Mol. Spectrosc. 104 (1984) 183.
- [15] F.R. Jensen, L.H. Gale, J. Org. Chem. 25 (1960) 2075.
- [16] J.E. Piercy, S.V. Subrahmanyam, J. Chem. Phys. 42 (1965) 4011.
- [17] H. Booth, J.R. Everett, J. Chem. Soc. Chem. Comm. (1976) 278.
- [18] K.B. Wiberg, J.D. Hammer, H. Castejon, W.F. Bailey, E.L. DeLeon, R.M. Jarret, J. Org. Chem. 64 (1999) 2085.
- [19] R.J. Abraham, D.S. Ribeiro, J. Chem. Soc. Perkin Trans. 2 (2001) 302.
- [20] E.L. Eliel, N.L. Allinger, S.J. Angyal, G.A. Morrison, Conformational Analysis, Interscience Division, Wiley, New York, N.Y., 1965.
- [21] J. Laane, E.M. Nour, M. Dakkouri, J. Mol. Spectrosc. 102 (1983) 368.
- [22] J.R. Durig, T.J. Geyer, T.S. Little, M. Dakkouri, J. Phys. Chem. 89 (1985) 4307.
- [23] J.R. Durig, W. Zhao, X. Zhu, T.J. Geyer, M. Dakkouri, J. Mol. Struct. 351 (1995) 31.
- [24] G.A. Guirgis, Y.E. Nashed, T.K. Gounev, J.R. Durig, Struct. Chem. 9 (1998) 265.
- [25] T.A. Mohamed, G.A. Guirgis, Y.E. Nashed, J.R. Durig, Struct. Chem. 9 (1998) 255.
- [26] J.R. Durig, C. Pan, G.A. Guirgis, Spectrochim. Acta 59A (2003) 979.
- [27] Q. Shen, S. Rhodes, J.C. Cochran, Organometallics 11 (1992) 485.
- [28] K.G. Penman, W. Kitching, W. Adcock, J. Org. Chem. 54 (1989) 5390.
- [29] R.J. Ouellette, D. Baron, J. Stolfo, A. Rosenblum, P. Weber, Tetrahedron 28 (1972) 2163.
- [30] R.J. Unwalla, S. Profeta Jr., F.K. Cartledge, J. Org. Chem. 53 (1988) 5658.
- [31] V.F. Kalasinsky, S.E. Rodgers, J.A.S. Smith, Spectrochim. Acta 41A (1985) 155.
- [32] C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618.
- [33] F.A. Miller, B.M. Harney, Appl. Spectrosc. 33 (1970) 291.
- [34] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A. Jr, Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda

Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A., GAUSSIAN 03, Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.

- [35] P. Pulay, Mol. Phys. 17 (1969) 197.
- [36] G.A. Guirgis, X. Zhu, Z. Yu, J.R. Durig, J. Phys. Chem. A 104 (2000) 4383.
- [37] M.J. Frisch, Y. Yamaguchi, J.F. Gaw, H.F. Schaefer III, J.S. Binkley, J. Chem. Phys. 84 (1986) 531.
- [38] R.D. Amos, Chem. Phys. Lett. 124 (1986) 376.
- [39] P.L. Polavarapu, J. Phys. Chem. 94 (1990) 8106.
- [40] G.W. Chantry, in: A. Anderson (Ed.), The Raman Effect 2, Marcel Dekker, New York, NY, 1971 (Chap. 2).
- [41] J.L. Duncan, J.L. Harvie, D.C. McKean, S. Cradock, J. Mol. Struct. 145 (1986) 225.
- [42] J.R. Durig, K.W. Ng, C. Zheng, S. Shen, Struct. Chem. 15 (2004) 149.
- [43] A.E. Reed, F. Weinhold, J. Chem. Phys. 83 (1985) 1736.
- [44] J. R. Durig, C. Pan, P. Groner, H. Nanaie, H. Bürger, P. Mority, J. Chem. Phys., Submitted
- [45] A. Wurstner-Rueck, H.D. Rudolph, J. Mol. Struct. 97 (1983) 327.
- [46] J.R. Durig, P. Groner, A.D. Lopata, Chem. Phys. 21 (1977) 401.
- [47] T.A. Mohamed, G.A. Guirgis, Y.E. Nashed, J.R. Durig, Struct. Chem. 9 (1998) 255.
- [48] A.E. Reed, F. Weinhold, J. Chem. Phys. 83 (1985) 1736.
- [49] J. R. Durig, C. Pan, P. Groner, H. Nanaie, H. Bürger, P. Mority, J. Chem. Phys., Submitted
- [50] D.A. Dixon, A. Komornicki, J. Phys. Chem. 94 (1990) 5630.
- [51] J.E. Griffiths, J. Chem. Phys. 38 (1963) 2879.
- [52] G.A. Guirgis, Y.E. Nashed, T.K. Gounev, J.R. Durig, Struct. Chem. 9 (1998) 265.