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Structures and Energetics of Axial and Equatorial 1-Methyl-1-silacyclohexane

Laura B. Favero,[†] Biagio Velino,[‡] Walther Caminati,*[,§] Ingvar Árnason,[⊥] and Ágúst Kvaran[⊥]

Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, Via Gobetti 101, I-40129 Bologna, Italy, Dipartimento di Chimica Fisica e Inorganica dell'Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy, Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy, and Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland

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The structural differences and the relative energies for the *axial* and *equatorial* forms of 1-methyl-1-silacyclohexane have been obtained from the rotational spectra of the normal, ^{29}Si, and all ^{13}C isotopologues of the *axial* and *equatorial* forms, observed by molecular beam Fourier transform microwave spectroscopy. The two species appear to have the same energy, within uncertainty limits, $\Delta E = 0.0 \pm 0.2$ kcal/mol. Structural parameters (r_0 and r_s) are given for the two forms. The main structural differences are discussed. Potential barriers for the methyl group internal rotations (V_3) have been determined for both conformers to be 1.26(1) and 1.48(2) kcal/mol for the axial and equatorial species, respectively.

Introduction

Equatorial−axial conformational equilibria and molecular structures of monosubstituted halo-derivatives of cyclohexane have been investigated extensively.[1−15] A general preference for the equatorial conformer is observed.[16] The reported energy differences show that the equatorial conformer is favored by about 0.3 kcal/mol over the axial one for fluorocyclohexane and likewise by about 0.5−0.7 kcal/mol for chloro-, bromo-, and iodocylohexane.[3,6,13,16] The rotational spectrum of methylcyclohexane has not been reported, whereas the equatorial form has been determined to be more stable by about 2 kcal/mol, from electron diffraction,[17] low-temperature nuclear magnetic resonance,[18] and ab initio[19] investigations.

Recently we have assigned rotational spectra of silacyclohexane[20] and 1-fluoro-1-silacyclohexane.[21] For the latter molecule we have shown that its axial/equatorial conformational behavior differs with respect to that of the corresponding cyclohexane derivative,[3] showing a slight preference for the axial conformer. The conformational equilibrium of 1-methyl-1-silacyclohexane has recently been reinvestigated by gas-phase electron diffraction (GED), low-temperature NMR, and quantum chemical calculations.[22] The equatorial form was found to be more stable by about 0.3−0.4 kcal/mol. Thus, it appears that the conformational pattern of monosubstituted silacyclohexanes is different from what is known for the analogous substituted cyclohexanes. The reasons for the different behavior of silacyclohexanes are not fully understood. Additional information on molecular structure and relative energies is therefore desirable. Now we have decided to do detailed rotational spectra studies of 1-methyl-1-silacyclohexane (MSCH) that can determine, with higher precision, the relative energies and the structural differences of the two conformers. The two conformers are shown in Figure 1, together with some parameters used throughout the text.

Results and Discussion

1. Rotational Spectra. Initial calculations to predict the spectra were based on the MP2/6-31G* geometries given in ref 22. First the spectrum of the equatorial conformer, recorded with a free jet absorption millimeter-wave (FJAMW) spectrom-

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* To whom correspondence should be addressed. E-mail: walther.caminati@unibo.it.

[†] ISMN, Sezione di Bologna.

[‡] Dipartimento di Chimica Fisica e Inorganica, Università di Bologna.

[§] Dipartimento di Chimica "G. Ciamician", Università di Bologna.

[⊥] University of Iceland.

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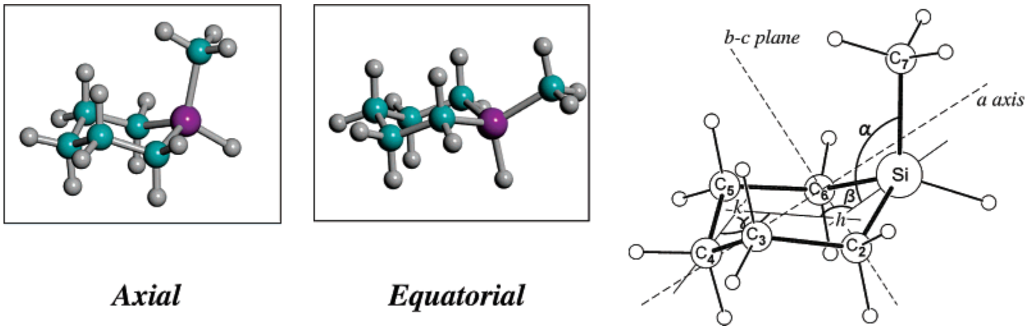

Figure 1. Axial and equatorial conformers of MSCH. To the right, structural parameters used throughout the text are indicated.

Table 1. Spectroscopic Constants of Axial and Equatorial MSCH for the Normal Molecular Species (A-reduction, I^r representation)

	axial	equatorial
A/MHz	2857.7316(8)[a]	3443.3346(7)
B/MHz	1855.2003(4)	1650.2745(3)
C/MHz	1474.9933(4)	1243.3791(4)
Δ_J/kHz	0.351(6)	0.084(4)
Δ_{JK}/kHz	−0.69(5)	0.10(2)
Δ_K/kHz	[0.0][b]	0.69(1)
δ_J/kHz	0.025(4)	0.050(7)
V_3/kcal mol^{-1}	1.26(1)	1.48(2)
I_α/μÅ^2	3.30(3)	3.07(3)
∠*(ai)*/deg[c]	58.6(3)	20(1)
∠*(ci)*/deg	31.4(3)	70(1)
σ/σ_{exp}[d]	1.42	0.93
N[e]	34	106

[a] Errors in parentheses are expressed in units of the last digit. [b] Quartic centrifugal distortion parameters Δ_K (for the *axial* conformer) and δ_k (both species) have been fixed to zero since not determined from the fit. [c] ∠*(bi)* has been fixed, by symmetry, to 90.0°. [d] Reduced standard deviation of the fit. [e] Number of fitted transitions.

eter as described in the Experimental Section, was assigned. Later the spectra of the axial conformer and the less abundant isotopologues (^{29}Si and ^{13}C) for both conformers, in natural abundance, measured by the more sensitive molecular beam Fourier transform millimeter-wave (MB-FTMW) technique, were assigned. Rotational transitions were found to be split, typically showing doublets, due to internal rotation of the methyl group. All measured lines are available as Supporting Information. A global fit to the absolute line positions of all component lines has been performed with the computer program XIAM,[23] using the combined axis method (CAM). A "rigid" limit set of rotational constants has been determined, common to both internal rotation A and the equatorial E sublevels. Furthermore, all quartic centrifugal distortion constants (A-reduction and I^r-representation[24]), the V_3 barriers, the angles ∠*ai* and ∠*ci* (angles between the axis of rotation of the methyl group and the principal axes of inertia; see Figure 1), and the I_α moments of inertia of the methyl group have been determined. The spectroscopic constants are reported in Table 1 for the normal species of both conformers.

For the less abundant isotopologues smaller numbers of experimental transitions are available. To fit the spectra, the centrifugal distortion and the methyl rotation constants were fixed to the values of the corresponding normal species. The spectroscopic constants of ^{29}Si and ^{13}C species are listed in Table 2.

Table 2. Rotational Constants for the Less Abundant Isotopologues of Equatorial and Axial MSCH[a]

	isotopic species	A/MHz	B/MHz	C/MHz	σ^b/ kHz	N^c
equatorial	^{29}Si	3440.307(2)	1644.0682(4)	1240.253 (1)	4	15
	^{13}C2	3392.306(4)	1650.1516(6)	1236.789(2)	5	12
	^{13}C3	3404.818(2)	1638.3663(3)	1231.795(1)	3	12
	^{13}C4	3440.007(2)	1626.4729(4)	1230.286(1)	3	13
	^{13}C7	3440.523(3)	1610.2853(4)	1220.897(1)	4	12
axial	^{29}Si	2853.924(6)	1845.3005(5)	1469.7524(2)	3	16
	^{13}C2	2818.162(3)	1853.2487(3)	1465.6799(1)	2	14
	^{13}C3	2829.115(4)	1843.7859(4)	1461.5461(2)	3	16
	^{13}C4	2857.514(8)	1827.7654(5)	1457.7151(3)	3	14
	^{13}C7	2839.225(7)	1817.8180(5)	1456.1076(3)	3	12

[a] Centrifugal distortion constants are fixed at the values of the corresponding main species. [b] Standard deviation of the fit. [c] Number of fitted transitions.

2. Structures of the Two Conformers. From the available rotational constants, 18 for each conformer, it is possible to obtain two kinds of structural information. First, the r_s coordinates, which are the *a*, *b*, and *c* coordinates of the atoms in the principal axes system of the normal species, can be determined. Their absolute values are easily obtained when the spectrum of the corresponding singly isotopic substituted species is available.[25] In the present case they have been determined for all heavy atoms (i.e., no hydrogen atoms). Second the r_0 geometries can be calculated by fitting the rotational constants of the ground states, supplying the molecular structures averaged over the vibrational ground state wave functions. The r_s structure is thought to be intermediate between the r_0 and the r_e (r_e correspond to the equilibrium, relative to a hypothetical vibrationless molecule) structures, since the vibrational effects are more or less the same for the normal and for the isotopically substituted species.

The substitution coordinates of the Si and C atoms are listed in Table 3.

The *a*-coordinates of the C2 atoms for both species are almost zero, hence poorly determined, according to the limitations that underline the Kraitchman procedure.[25] Nevertheless, we could obtain some r_s structural parameters, which are listed in Table 4 together with the r_0 data.

From the fit of the 18 rotational constants, we could determine nine r_0 structural parameters for each conformer. Due to the C_s symmetry of the molecule, these are sufficient to extract the structure of the frame constituted by the seven heavy atoms (C and Si). In the fitting procedure, we allowed these parameters to change, with respect to the ab initio values,[22] in "confidence intervals"[26] of 0.01 Å for the bond distances and of 2° for the valence angles, respectively. It was necessary to keep the structural parameters of the hydrogen atoms fixed to the ab initio values[22] (given in Table 5). This assumption little affects the heavy atoms' structural parameters, because the inertial effects

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Table 3. Substitution Coordinates (Å) for the Si, C2, C3, C4, and C7 Atoms of Axial and Equatorial MSCH

		axial					equatorial				
		Si	C2	C3	C4	C7	Si	C2	C3	C4	C7
$\|a\|$	expt	1.110(1)	0.10i[a]	1.227(1)	2.0223(7)	2.1070(7)	1.017(1)	0.10i[a]	1.478(1)	2.0866(7)	2.7426(6)
	calc[b]	1.119	0.045	1.228	2.0253	2.1091	1.020	0.015	1.484	2.0910	2.7437
$\|b\|$	expt	0.04i[a]	1.480(1)	1.288(1)	0.08i[a]	0.05i[a]	0.03i[a]	1.479(1)	1.288(1)	0.08i[a]	0.01i[a]
	calc[b]	0.0[c]	1.486	1.289	0.0[c]	0.0[c]	0.0[c]	1.484	1.291	0.0[c]	0.0[c]
$\|c\|$	expt	0.492(3)	0.554(3)	0.409(4)	0.15(1)	1.092(1)	0.363(4)	0.182(8)	0.179(8)	0.390(4)	0.352(4)
	calc[b]	0.499	0.548	0.415	0.138	1.097	0.366	0.177	0.173	0.386	0.367

[a] Imaginary value. [b] Calculated values with the partial r_0 geometry of Table 4. [c] Fixed to zero by molecular symmetry.

Table 4. Structural Parameters of Axial and Equatorial MSCH

	r_s[a]		r_0	
	equatorial	axial	equatorial	axial
r_{h-Si}/Å[b]			1.157(5)	1.151(3)
r_{h-C2}/Å[b]			1.4821(3)	1.4836(3)
r_{h-k}/Å[b]			1.533(4)	1.535(2)
r_{k-C3}/Å[b]			1.2888(5)	1.2864(3)
r_{k-C4}/Å[b]			0.831(3)	0.840(2)
Si−C7/Å	1.868	1.872	1.866(3)	1.873(1)
α/deg[b,c]			128.6(2)	125.0(1)
β/deg[b]	138.0	138.6	136.9(3)	138.2(2)
γ/deg[b]	123.2	123.6	123.0(2)	121.9(3)
Si−C2/Å	1.876	1.876	1.880(3)	1.878(2)[d]
C2−C3/Å	1.533	1.527	1.545(4)	1.548(2)[d]
C3−C4/Å	1.534	1.536	1.534(1)	1.536(1)[d]
C6−Si−C2/deg	104.0	106.1	104.1(2)	104.4(1)[d]
Si−C2−C3/deg	110.9	110.5	110.3(4)[d]	110.6(2)[d]
C2−C3−C4/deg	113.5	113.7	113.4(4)[d]	113.2(2)[d]
C3−C4−C5/deg	114.2	113.9	114.4(2)	113.7(1)[d]
C2−Si−C7/deg	112.9	110.4	112.6(3)[d]	110.6(1)[d]

[a] Some r_s values have been calculated by fixing to zero some slightly imaginary **a** or **b** coordinates of Table 3. [b] See Figure 1 for the definition of α, β, γ and of the *h* and *k* intersection points. [c] This parameter, α, is the *h*Si−C7 angle for both conformers (in Figure 1 it is defined only for the axial conformer). [d] Derived parameters, not required in the r_0 fit.

of the light hydrogen atoms are minor. The determined parameters, α, β, γ, r_{Si-C}, r_{hk}, r_{h-C2}, r_{k-C3}, r_{h-Si}, and r_{k-C4} (see Figure 1), are listed in Table 4. From these it was easy to derive standard geometrical parameters such as the C−C and C−Si bond lengths.

The differences between the structural parameters α and β (Figure 1) of the two conformers are found to be quite larger than the experimental uncertainties (see Table 4). On going from the axial to the equatorial form, α increases by 3.6°, whereas β decreases by 1.3°. This kind of difference is not outlined by the results of the GED investigation,[22] which supply the average values of the geometrical parameters. MW geometries are relative to the ground vibrational state, while the GED structure is averaged (weighted for the population) over several vibrational states. Then, a comparison of MW and GED structural data is an approximation and requires some cautions. However, the structural parameters of Table 4 agree with the GED values of Table 1 of ref 22 within the experimental error, considerably large for the GED geometry.

3. Conformational Energies. Rotational transitions of both conformers have been measured with the Fourier transform spectrometer only. Indications about the relative energies of the axial and the equatorial (Ax and Eq in the expression below, respectively) conformers could be obtained from those data.

Assuming that the "conformational temperature" (T_{conf}) is the temperature prior to supersonic expansion (e.g., room temperature, 25 °C), we calculated the conformational ground-state energy differences $(\Delta E_{0.0})_{Ax-Eq} = (E_{0.0})_{Ax} - (E_{0.0})_{Eq}$ by applying the following equation:

$$(\Delta E_{0.0})_{Ax-Eq} = kT_{conf} \ln[(I_{Eq}\mu_{c,Ax}\gamma_{Ax}\nu_{Ax}{}^{2})/(I_{Ax}\mu_{c,Eq}\gamma_{Eq}\nu_{Eq}{}^{2})] + [(E_{rot})_{Ax} - (E_{rot})_{Eq}]/kT_{rot} \quad (3)$$

The subscripts 0,0 hold for the $v = 0$ and $J = 0$ state. I_{Eq} and I_{Ax} are peak heights, $\mu_{c,Ax}$ and $\mu_{c,Eq}$ are the *c* dipole moment components, and γ_{Ax}, γ_{Eq}, ν_{Ax}, and ν_{Eq} are the line strengths and frequencies for the axial and equatorial conformers. We used *c*-type transitions only and made use of ab initio values for the μ_c dipole moment components ($\mu_{c,E} = 0.58$ and $\mu_{c,A} = 0.43$ D, respectively).[22] In the present case $T_{conf} = 298$ and $T_{rot} = 1$ K. Thus, we obtained $(\Delta E_{0.0})_{Ax-Eq} = 0 \pm 0.2$ kcal/mol.

Large uncertainties in the calculated values of the μ_c dipole moment components mainly are responsible for the big error limit obtained (±0.2 kcal/mol). More precise values of $\Delta E_{0.0}$ could be obtained if experimental values of the dipole moment components were available.

The axial/equatorial conformational energetics for MSCH differ significantly with respect to those of the cyclohexane homologue, methylcyclohexane. In the case of MSCH the two conformers have about the same energies in the gas phase, whereas the equatorial conformer is significantly favorable for methylcyclohexane. In Table 6 our results on the energetics are compared to those available in the literature. All of them are $\Delta G°$ values, which take into account also entropic effects. In this sense they are difficult to compare with our data, which is the energy differences between the ground (rotational and vibrational) states of the two conformers. In addition, the NMR data are relative to solutions, where the interactions with the solvent can overwhelm the slight conformational preference in the gas phase. All experimental and theoretical results from ref 22 give the equatorial species favored, but in contrast with previous NMR[27] and MM2[28] investigations. We performed MP2/6-311++G(d,p) calculations,[29] generally found to be reliable for this kind of conformational equilibrium. They gave a $\Delta E_{0,0}$ value of ca. zero (see Table 6), supporting our experimental result.

It is interesting to note that the barrier to the methyl group internal rotation (V_3) in MSCH is found to be considerably lower for the axial species compared to that for the equatorial species. Possibly the energy minimum of the axial species is destabilized by the interaction of the methyl hydrogen with the axial hydrogens in position 3 (Figure 1).

Experimental Section

MSCH was prepared according to a standard literature method,[30] and the sample was purified by preparative GLC prior to use.

Argon or helium (at least 99.99%), supplied by SIAD (Italy), was used as carrier gas. Two different experimental setups have been used: a free jet absorption millimeter-wave (FJ-AMMW) spectrometer and a coaxially oriented beam-resonator arrangement Fourier transform microwave (COBRA-FTMW) spectrometer, which provided complementary results.

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Table 5. MP2/6-31G* Structural Parameters[22] (see Figure 1) Relevant to the Hydrogen Atoms

bond lengths (Å)			valence angles (deg)			dihedral angles (deg)		
	axial	equat.		axial	equat.		axial	equat.
Si−H	1.4949	1.4971	*h*SiH	125.7	121.4	C4C3−C2H$_{eq}$	−179.9	−179.7
C2−H$_{eq}$	1.0971	1.0970	SiC2H$_{eq}$	111.4	111.2	C4C3−C2H$_{ax}$	63.6	62.2
C2−H$_{ax}$	1.0985	1.0991	SiC2 H$_{ax}$	109.1	109.3	SiC2−C3H$_{eq}$	−178.4	−178.7
C3−H$_{eq}$	1.0975	1.0976	C4C3H$_{eq}$	108.9	109.0	SiC2−C3H$_{ax}$	65.5	65.1
C3−H$_{ax}$	1.0989	1.0988	C4C3H$_{ax}$	108.6	108.6	*h*SiC7H$_{gauche}$	120.0	119.9
C4−H$_{eq}$	1.0972	1.0972	*k*C4H$_{eq}$	126.5	126.4			
C4−H$_{ax}$	1.0993	1.0993	*k*C4H$_{ax}$	127.2	127.3			
C7−H$_{trans}$	1.0942	1.0943	SiC7H$_{trans}$	111.4	110.9			
C7−H$_{gauche}$	1.0942	1.0942	SiC7H$_{gauche}$	111.1	111.3			

Table 6. Energy Differences ($\Delta G^0 = G_{ax} - G_{eq}$ or $\Delta E_{0,0} = E_{0,0-ax} - E_{0,0-eq}$) between the Equatorial and Axial Conformers for MSCH

$\Delta G°$ Data: Method and Value (kcal/mol)			
NMR (298 K)	−0.34[a]	HF/6-31G*	0.52[c]
MM2 (298 K)	−0.13[b]	MP2/6-31G*	0.46[c]
NMR (110 K)	0.23(2)[c]	B3LYP/6-31G*	0.60[c]
GED (298 K)	0.45(14)[c]	*m*PW1PW91/6-311G(2df,p)	0.56[c]
$\Delta E_{0,0}$ Data: Method and Value (kcal/mol)			
MW	0.0(2)[d]	MP2/6-311++G(d,p)	0.02[d]

[a] Ref 27. [b] Ref 28. [c] Ref 22. [d] This work.

a. Pulsed Jet Absorption Millimeter-Wave Spectroscopy (FJ-AMMW). The Stark modulated and FJ-AMMW spectrometer has already been described elsewhere.[31] Argon at a pressure of ca. 0.2 bar was flown over MSCH at room temperature, and the mixture was expanded through a nozzle with a diameter of 0.35 mm to 2 × 10^{-3} mbar. An estimated “rotational” temperature of about 10 K was reached. The accuracy of the frequency measurements is about 0.05 MHz.

b. Coaxially Oriented Beam-Resonator Arrangement Spectroscopy (COBRA-FTMW). The details of the COBRA-FTMW spectrometer,[32] which covers the range 6−18.5 GHz, have been described previously.[33] The spectrum was observed in the expansion of a gas mixture composed of approximately 1% of MSCH in He at a total backing pressure of 2 bar. Molecular pulses of ca. 0.40 ms duration followed by a MW polarization pulse of 10 mW at a pulse length of ca. 0.60 μs were found optimal. Frequencies were determined after Fourier transformation of the 8K data points’ time domain signals, recorded in a 40 ns sample interval. The pulsed molecular beam was introduced parallel to the axis of the Fabry-Pérot resonator, and consequently each observed transition appeared as a Doppler doublet. The line frequency was determined as the arithmetic mean of the frequencies of the two Doppler components. The accuracy of frequency measurements is estimated to be ca. 2 kHz.

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Supporting Information Available: Tables of rotational transition frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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