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1-Methoxy-1-silacyclohexane: Synthesis, molecular structure and conformational behavior by gas electron diffraction, Raman spectroscopy and quantum chemical calculations

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ABSTRACT

The synthesis and results of gas electron diffraction (GED), temperature-dependent Raman spectroscopy, along with detailed quantum chemical (QC) study of 1-methoxy-1-silacyclohexane **1** are reported. Within the series of the QC results, DFT(B3LYP, PBE0, M06, M062X), and MP2, the conformational preference predictions are rather contradictive. From the both GED and Raman experimental methods applied, the vapour and liquid phases of **1** were found to exist as a mixture of two conformers, *gauche*-axial and *gauche*-equatorial, with almost equal contributions, while the *trans*-forms are much less stable. In addition, theoretical calculations on the cyclohexane analog, methoxycyclohexane **2**, are performed in order to compare with the conformational properties of **1**. The latter is predicted not to diminish the axial/equatorial ratio, as contrasted to the expectations at switching the point of the substituent attachment from Si to C.

1. Introduction

Theoretical and experimental research of molecular structure of organosilicon compounds increases in the organic chemistry and stereochemistry. Investigation of conformational behavior and geometrical structure of silacyclohexane derivatives is an actual problem [1–8], since a substitution of a carbon atom by silicon changes physical and physiological properties of compounds [9–13].

A substituent attached to a silicon atom may occupy either axial or equatorial position relative to the six-membered ring frame. The effective volume of the substituent, its volume near the point of attachment to the cyclohexane ring, is of the decisive importance. However, it is not the single factor which determines the conformational energy of substituted cyclohexanes. The 1,3-*syn*-diaxial repulsion is most commonly considered as governing the conformational behavior but it has an intuitive character (see, for instance [14]). The anomeric effect is also frequently discussed in this connection, as well as the charge transfer from the ring to the substituent [14,15].

Conformational properties of 1-substituted silacyclohexanes were studied experimentally, by gas-phase electron diffraction (GED), NMR, IR and Raman spectroscopies, and theoretically applying high level quantum chemical approaches: (mono-substituted compounds) CH_3 [16], CF_3 [17], *t*-Bu [18], CN [19],F [20], Cl, Br, I [21], SiH_3 [22], Ph [23], (disubstituted) Me, Ph [24], F, Me; Me, CF_3 [25], (silaheterocyclohexanes) 1,3-Me2-3-silapiperedine [26], 3-Me-3-Ph-3-Silatetrahydropyran [27], 3-Me-3-Silathiane [28], 3-Me-3-silatetrahydropyran [29]. Some reviews on the silacyclohexanes structures are also available in literature, see for instance [30,31]. Conformational preference of a substituent is generally expressed by a conformational parameter, so called ‘conformational energy’— a Gibbs free energy difference between the axial and equatorial conformers.

1-Methoxy-1-silacyclohexane was investigated a decade ago [32] by performing RHF, B3LYP, and MP2 calculations, and complete basis set (CBS) estimation of electronic energies of the equatorial conformation relative to the axial position $\Delta E^{\mathrm{CBS}}_{\mathrm{CCSD(T)}} = 0.15$ kcal/

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mol were obtained, which means a slight preference of the axial conformer.

To our knowledge, no experimental studies on conformation properties of 1-methoxy-1-silacyclohexane **1** were reported in literature In addition to the axial-equatorial orientation of the entire methoxy-group, the O–C_{Me} bond orientation relative to the Si–O bond is also a question of specific interest.

In this paper, we report the synthesis of **1** and results of experimental, GED and temperature-dependent Raman spectroscopy, and quantum chemical (QC) study of 1-methoxy-1-silacyclohexane. In addition, we performed theoretical calculations on the cyclohexane analog, methoxycyclohexane **2**, in order to compare with the conformational properties of **1**.

2. Experimental

2.1. Synthesis

Standard Schlenk techniques and an inert atmosphere of dry nitrogen were used for all manipulations. 1-Chloro-1-silacyclohexane was prepared as previously reported [21]. *1-Metoxy-1-silacyclohexane*. Solution of triethylamine (30.0 g, 297.1 mmol), methanol (9.5 g, 297.1 mmol) and Et_2O (120 mL) was slowly added to chlorosilacyclohexane (20.0 g, 148.5 mmol) dissolved in Et_2O (400 mL) while stirring. After continued stirring overnight, the reaction mixture was filtered under nitrogen and reduced pressure and the salt was discarded. The solvent was then distilled off and the product was collected at 115–117 °C and 1 atm. Yield: 15.37 g (118 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.77–0.81$ (m, 4H, CH_2), 1.32–1.49 (m, 2H, $CH_{2(ax/eq)}$), 1.56–1.65 (m, 2H, $CH_{2(ax/eq)}$), 1.73–1.83 (m, 4H, CH_2), 3.49 (s, 3H, OMe), 4.50–4.51 (m, 1H, $^1J_{Si-H}$ = 197 Hz, SiH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 12.4, 23.7, 29.5 (CH_2), 51.8 (OMe). ^{29}Si NMR (79 MHz, $CDCl_3$): δ = 4.3 (dq, $^1J_{Si-H}$ = 197 Hz). MS (EI, 70 eV): *m*/*z* (%) 129 (100), 102.1 (64); HRMS: *m*/*z* calcd for $C_6H_{14}OSi$ 130.0814, found 130.0799.

2.2. GED/MS

The electron diffraction patterns and the mass spectra of **1** were recorded simultaneously using the combined GED/MS unit EMR-100/APDM-1 described previously [33–36]. Two series of GED/MS experiments at two camera distance, L_1 = 598 and L_2 = 338 mm, were performed. Since the compound is volatile even at room temperature, its vapour was let in from an external vessel via a dosing valve and an inlet system pipe into effusion cell. All operations were carried out on open air.

In the course of the GED/MS experiments, the stainless steel effusion cell was kept at 275(5) K as measured by a W/Re-5/20 thermocouple. Accurate wavelength of electrons was calibrated against the diffraction patterns of polycrystalline ZnO. Optical densities were measured by a computer-controlled MD-100 (Carl Zeiss, Jena) microdensitometer [37]. More experimental details are given in the Supporting information.

The most intensive peaks in the electron ionization mass spectra (U_{ioniz} = 50 V) corresponded to the molecular ion $C_5H_{10}Si(H)OCH_3^+$ ($m/z = 130$, 58%), and fragment ions, such as: $C_5H_{10}SiH_2^+$($m/z = 100$, 32%), $C_3H_8Si^+$($m/z = 74$, 42%), $SiOCH_3^+$ ($m/z = 59$, 100%). The ratio of ionic current intensities did not change during the experiments, no ions with a mass greater than that of the molecular ion were detected.

2.3. Low-temperature NMR experiment

A 250 MHz NMR spectrometer (Bruker AC 250) was used for the NMR experiments. A solvent mixture of CD_2Cl_2, $CHFCl_2$, and CHF_2Cl in a ratio of 1:1:3 was used for low-temperature ^{13}C measurements of the title compound. We have previously used this Freon mixture to freeze the conformational equilibria of monosubstituted silacyclohexanes [16,17,20,21].

In the present case we were able to record NMR spectra down to 109 K but no signal splitting was achieved.

2.4. Raman experiment

Raman spectra were recorded with a Jobin Yvon T64000 spectrometer equipped with a triple monochromator and a CCD camera. The samples were filled into 1 mm capillary glass tubes and irradiated by the green 532 nm line of a frequency doubled Nd-YAG Laser (Coherent, DPSS model 532-20, 10 mW). Spectra were recorded from pure compound and in heptane and THF solution. A continuous flow cryostat, Oxford instruments OptistatCF™, using liquid nitrogen for cooling was employed for the low temperature measurements.

2.5. Computational details

All QC calculations were performed with Gaussian09 suit of programs [38]. Geometries and harmonic vibrational frequencies were calculated using the DFT (with B3LYP, PBE0, M06, M062X functionals) and the MP2 methods with cc-pVTZ basis set. The results are summarized in Tables 1 and 2.

Potential energy surfaces (PES) were scanned with 10° step at all geometrical parameters optimized. The PESs of internal rotation of $-OCH_3$ group and the relative energies for six possible rotamers of axial and equatorial conformers are plotted in Fig. 1; the PESs for the methyl group rotation are given in Fig. 6.

Results of calculations for the cyclohexane analog, methoxycyclohexane **2**, at M062X/6-311G** and M062X/cc-pVTZ levels are represented in Table 5 and Fig. 7.

Table 1
Full energies ΔE, free Gibbs energies ΔG°_T and mole fractions of conformers *X* of **1**[a,d].

	Conformer	Method					
		PBE0	M06	M062X	B3LYP	MP2	GED
ΔE	**I**	−0.05	−0.76	−0.40	−0.02	−0.38	
	II	1.61	1.39	1.34	1.62	1.52[b]	
	III	0	0	0	0	0	
	IV	0.76	0.95[b]	0.80	0.77	0.85	
ΔG^{o}_T	**I**	0.09	0.23	−0.23	0.18	−0.27	−0.20(28)
	II	1.96	0.57	1.55[b]	1.91	1.09	–
	III	0	0	0	0	0	0
	IV	0.57	−0.15[b]	0.29[b]	0.64	0.53	–
X [c]	**I**	42	30	50	39	53	59(12)
	II	1	6	2[b]	1	4[b]	–
	III	50	45	33	54	33	41(12)
	IV	7	19[b]	15[b]	6	10	–

[a] Energies in kcal/mol. Mole fractions in %. Theoretical conformer ratios *X* were evaluated from the ΔG^{o}_{298} values; the experimental ΔG^{o}_{275} were calculated from the refined vapour composition.

[b] Values for the structures for "*quasi-trans*" conformers of C_1 symmetry with the C–Si–*O*–H7 angles of ca. 172° (**II**, **IV** from MP2 and M06) and ca. 155° **II**, 177° **IV** from M062X method.

[c] Degeneracy degree of conformers: 2(**I**), 1(**II**), 2(**III**),1(**IV**).

[d] See also Raman spectroscopy results in the relevant section below.