The conformational behavior and structure of monosubstituted 1,3,5-trisilacyclohexanes.
Part III: 1-Methyl-1,3,5-trisilacyclohexane

Liubov E. Kuzmina,[#] Ingvar Arnason,[†] Nanna R. Jonsdottir,[†] Sergey A. Shlykov*[#]

[#] *Ivanovo State University of Chemistry and Technology, Sheremetievskiy ave., 7, Ivanovo 153000, Russian Federation*

† Science Institute, University of Iceland, Dunhaga 3, IS-107Reykjavik, Iceland.

* To whom correspondence should be addressed: shlykov@isuct.ru

ABSTRACT

1-Methyl-1,3,5-trisilacyclohexane was synthesized and its structure and conformational properties have been determined by gas electron diffraction (GED) and quantum chemical (QC) calculations. The molecule may exist in two forms differing from each other by the substituents' position. QC results shows that the equatorial conformer is predicted to be slightly more stable than the axial conformer, note that one method (M06-2X) with basis set 6-311G** shows an equal amount of Ax and Eq conformers: ratio (Ax/Eq) = (30-50) : (70-50)% (depending on method and basis set). From the GED data, the molar fractions of the conformers were found to be Ax:Eq=54(10):46(10) at 280(5) K. A temperature-dependent Raman experiment resulted in an Ax:Eq ratio of 58(4):42(4). Conformational properties are compared in series of analogous 1-X-1- (hetero)cyclohexanes.

Keywords: 1-methyl-1,3,5-trisilacyclohexane, molecular structure, combined gas-phase electron diffraction/mass spectrometry, low-temperature Raman spectroscopy, quantum chemical calculations

INTRODUCTION

With this paper, we finalize our series of conformational and structural studies of silacyclohexane derivatives extensively studied theoretically by various quantum chemical (QC) methods and experimentally by combinations of NMR, Raman and IR spectroscopies and gas-phase electron diffraction (GED). In the last decade, results were reported by a team of authors of variable content, on 1-X-1-silacyclohexanes with X=Hal [1,2], CN [3], SiH_3 [4], *t*Bu [5] OMe [6], NMe_2 [7], Ph [8]. Several doubly substituted, 1-X-1-Y-silacyclohexanes, and 1-X-silaheterocyclohexanes were also investigated: In the first one, 1-F-1-Me and 1-Me-1-CF_3-silacyclohexane a nice additivity of the conformational properties by the substituents was found, which is not shown by the analogous cyclohexanes [9]. Further examples include 1-Ph-1-Me- [10], 1-Ph-1-NMe_2- [11], 3-Methyl-3-Phenyl-3-Silatetrahydropyran [12], etc., in which a conformational concurrency of the substituents were of the main interest or a shift to the axial position due to a heteroatom (N, S, O) implemented into the silacyclohexane ring observed. Reviews on the silacyclohexanes structures and properties are available in the literature [13,14]

Our two latest publications were devoted to 1-X-1,3,5-trisilacyclohexanes, where X were a dimethylamino –NMe_2 [7] and methoxy –OMe [15] substituents. Both groups appeared to occupy, in addition to axial and equatorial positions, *gauche*- and *trans*-orientations of their fragments relative to the six-membered cycle. In case of 1–OMe-1,3,5-trisilacyclohexane, it was found to be represented by three conformers while in the singly-silicon substituted 1–OMe-1-silacyclohexane [6] by only two.

In this paper, we report the conformational and structural characteristization of 1-Methyl-1,3,5-trisilacyclohexane **1** by QC, GED, and Raman methods and discuss some features by comparison with data for the parent compound 1,3,5-trisilacyclohexane [16], 1-methyl substituted cyclohexane [17,18], and silacyclohexane [19] as well as with other 1-X-1-sila- and 1-X-1,3,5-trisilacyclohexanes.

EXPERIMENTAL SECTION

Synthesis

All synthesis stages of **1**were carried out in absence of oxygen and moisture under an inert atmosphere of nitrogen gas employing standard Schlenk techniques for all manipulations. All solvents were dried using appropriate drying agents and were distilled prior to use. The preparation of the title compound **1** has been reported previously [20] . In this work we have used a different approach.

1,3,5-trisilacyclohexane (2) was purchased from JSI Silicone and used without further purification.

1-Bromo-1,3,5-trisilacyclohexane (3): A solution of bromine (7.5 mL, 145.6 mmol) in 50 mL of pentane was added dropwise into a solution of 1,3,5-trisilacyclohexane **1** (19.0 g, 143.5 mmol) in 75 mL of pentane at –50 °C under stirring. The brown color of the bromine solution disappeared instantly when the drop reacted with **2**. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The solvent was distilled off and the product was collected at 75–79 °C at 10 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03–0.07 (m, 2H, CH_2), 0.45–0.52 (m, 2H, $CH_{2(ax/eq)}$), 0.57–0.64 (m, 2H, $CH_{2(ax/eq)}$), 3.98–4.06 (m, 2H, $SiH_{2(ax/eq)}$), 4.19–4.26 (m, 2H, $SiH_{2(ax/eq)}$), 5.07 (m, 1H, Si*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ –10.96, –1.13. ^{29}Si NMR (79 MHz, $CDCl_3$): δ –36.7 (*Si*H_2), –9.2 (*Si*HBr).

1-Methyl-1,3,5-trisilacyclohexane (1): A solution of 40 mL of 0.79 M MeMgI (31.60 mmol) in diethylether was slowly added to **3** (6.44 g, 30.48 mmol) in 75 mL of diethylether, while stirring at 0 °C. The reaction mixture was stirred overnight at room temperature. The solvent was removed by distillation and the product was isolated from the remaining salt by a condensation onto a $N_2(l)$ cold finger in vacuo. A second purification step using repeated condensation yielded 1.04 g 23% **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ –0.18–(–)0.10, (m, 2H, CH_2), –0.06–(–)0.01 (m, 2H, C $H_{2(ax/eq)}$), –0.01–0.06 (m, 2H, C $H_{2(ax/eq)}$), 0.23 (d, 3H, $^3J_{H\text{-}H}$ = 3.56 Hz, CH_3), 3.99–4.06 (m, 2H, Si$H_{2(ax/eq)}$), 4.07–4.13 (m, 2H, Si$H_{2(ax/eq)}$), 4.15–4.22 (m, 1H, Si*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ –10.48 (CH_3), –6.22, –1.53. ^{29}Si NMR (79 MHz, $CDCl_3$): δ –35.61 (*Si*H_2), –13.29 (*Si*HCH_3). The NMR spectra are plotted in SI.

GED/MS experiment

The diffraction patterns were recorded during a combined gas-phase electron diffraction and mass spectrometric (GED/MS) experiment carried out using the EMR-100/APDM-1 unit at ISUCT [21,22]. Due to a high volatility of **1**, an inlet system with dosing valve was applied though which a vapour flow of the compound passed into a stainless steel outlet effusion cell filled with shavings of the same material and kept at 280(5) K in the course of the experiments. The conditions of the GED/MS experiment and data refinement details are given in Supporting Information, **Table S2(a)** and related chapters. In the EI (50 eV) mass spectra recorded simultaneously with the diffraction patterns, the most intense peaks were 145$[M]^+$, 100 and 131$[M\text{-}Me]^+$, 80. No ions with mass heavier than that of $[M]^+$ were detected. Relative intensities of other peaks are summarized in **Table S2(b**) in SI. A series of MS runs at lowered ionization energies resulted in a simplification of the mass spectra – only $[M]^+$ ion left at *ca.* 10 eV. This is to be considered as evidence that all other ions are products of dissociative ionization of the same parent molecule, $[M^+]$.

Low-temperature Raman experiment

Raman spectra of liquid **1** 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).

Computational details

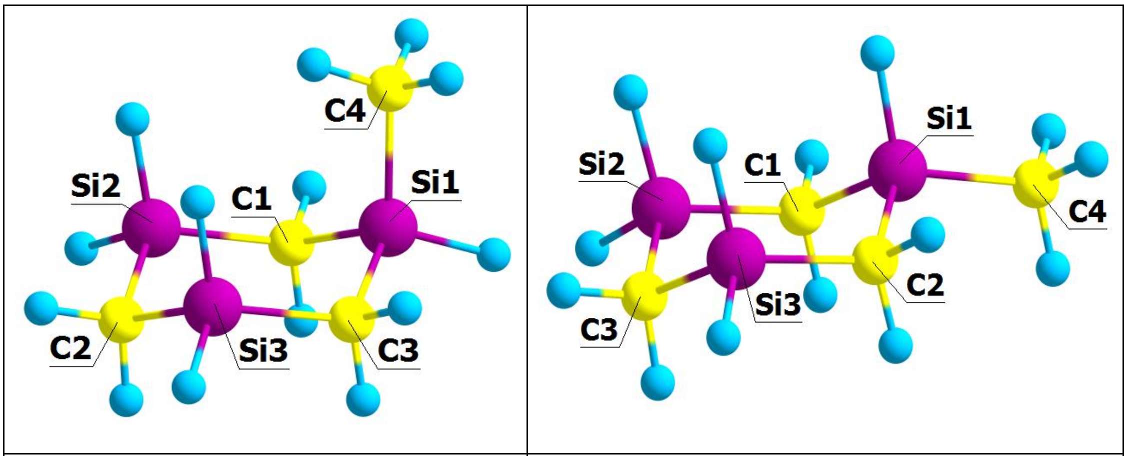
All calculations of **1** were performed with Gaussian 09 program suite [23]. The geometry and vibrational calculations were performed using the MP2 and DFT (with B3LYP, B3LYP-D3 and M06-2X functional) methods with the 6-311G** and cc-pVTZ basic sets. The potential energy surface (PES) profiles were obtained by calculations of ring inversion from equatorial and axial forms at M06-2X/6-311G** level.

The heavy atoms, Br and I, in halogen-substituted 1,3,5-trisilacyclohexanes were described using the effective core potential with cc-pVTZ-PP basis sets while H, C and Si atom were described by cc-pVTZ basis sets, all taken from database [24].

RESULTS AND DISCUSSION

Energies

The methyl group in molecule **1** may occupy two different positions: axial and equatorial (**Figure 1)**. Both of the conformers correspond to a local minimum of potential energy, which is confirmed by the calculation of harmonic vibration frequencies.



Ax

Eq

Figure 1. *Chair* conformers of compound **1**.

It is well known that for the cyclohexane-based rings three different forms, at least, may be relevant: *chair*, *boat* and *twist*. In this work, we explored a possibility for the free molecule of **1** to exhibit all of them, in addition to the most favorable *chair*-shaped conformers Ax and Eq. For this, a ring inversion PES was obtained by synchronous scanning of two opposite dihedral angles of the ring, Si1–C1–Si2–C2 and Si1–C3–Si3–C2, at M06-2X/6-311G** level with a step of 10^{o} (**Figure**). Thus, the molecule exists in two forms: **Ax**, **Eq**, which correspond to the minima on the 3D presentation and its projection of the relative energy surface. As follows from **Figure** , the energy barrier for **Ax** → **Eq** process is *ca*. 4 kcal/mol. The pathway lies via the *twisted-boat* structures. The latter are less stable than the *chair*-forms and their contribution in the vapor at 298 K is predicted to not exceed 7%, see Table S1 in SI, and were therefore not taken for further consideration.

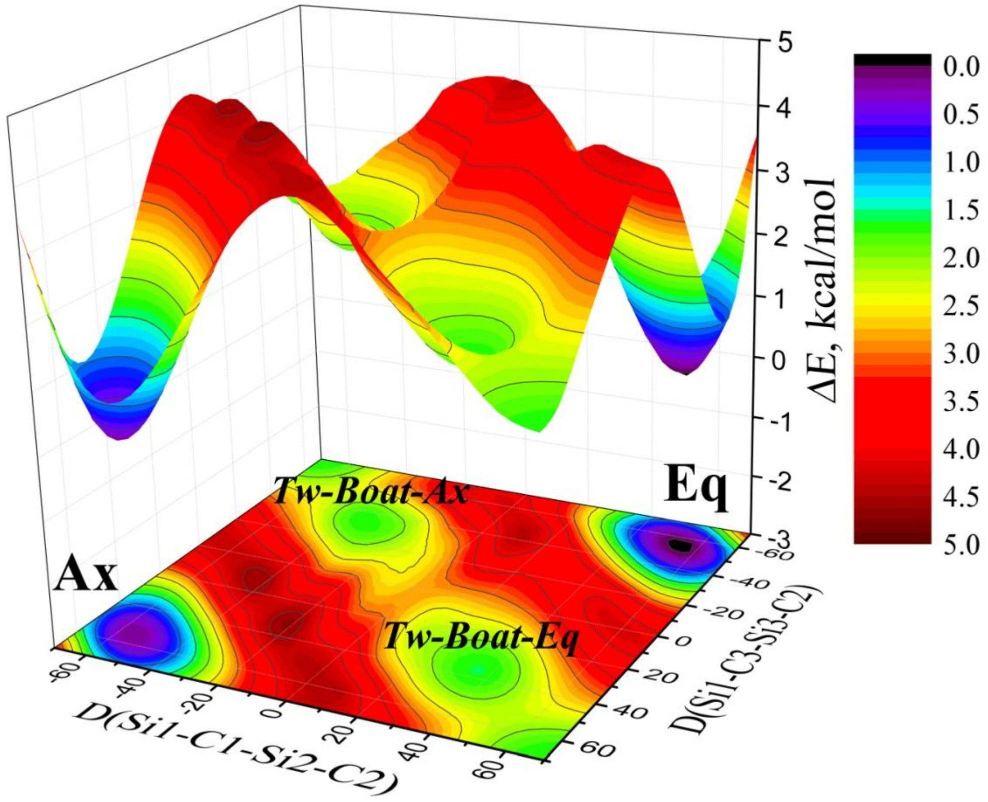


Figure 2. 3D presentation and its projection of the relative energy surface of **1** calculated at the M06-2X/6-311G** level of theory, shown as a function of two dihedral angles; the iso-energy contours are drawn with 0.5 kcal/mol step.

Theoretical relative total energy, Gibbs free energy, and the molar fraction of the conformers are summarized in **Table 1**. Almost all theoretical methods predict the Eq conformer as somewhat more energetically stable than Ax in gas phase at 298 K. The ratio of axial and equatorial forms varies in the range Ax:Eq =(30-50) : (70-50)%. Interestingly, we can divide the results by the DFT functionals into two groups. Both the M06-2X and the B3LYP-D3 functionals are known to be able to take into account dispersion interactions contrary to the widely used B3LYP functional [25]. As shown in Table 1, the ΔG^{o}_{298K} values by using the M06-2X and B3LYP-D3 functionals fall in a narrow range of 0.00 to 0.15 kcal/mol whereas the two B3LYP values give 0.49 and 0.51 kcal/mol as results. The one MP2 calculation results in an intermediate value of 0.32 kcal/mol.

Table 1. Relative total electron energies ΔE, Gibbs free energies ΔG (kcal/mol) and contributions X (mol.%) of conformers of **1**.

Method/basis set	ΔE(a)	ΔE+ZPE(a)	ΔG^{o}_{298K}(b)	$(X_{Ax}:X_{Eq})_{298}$(c)
QC				
B3LYP/6-311G**	0.44	0.47	0.49	30:70
B3LYP-D3/6-311G**	-0.13	-0.06	0.07	47:53
M06-2X/6-311G**	-0.14	-0.01	0.00	50:50
MP2(FC)/6-311G**	0.54	0.61	0.32	37:63
B3LYP /cc-pVTZ	0.48	0.50	0.51	30:70
B3LYP-D3/CC-pVTZ	-0.10	-0.06	0.05	48:52
M06-2X/ cc-pVTZ	-0.12	0.02	0.15	44:56
Experiment				
GED, 280(5) К			–0.09(13)	54(10):46(10)
Raman, liquid, 300–220K		ΔH=–0.17(4)[b]		58(4):42(4)(d)

(a) $\Delta E = E_{Ax} - E_{Eq}$, ZPE – zero-point energy correction for 298 K,

(b) ΔG and ΔH for the Eq ⇄ Ax equilibrium

(c) Mole fractions X derived from the ΔG values

(d) Mole fraction X derived from the ΔH value

GED analysis

The diffraction intensities were averaged from 6 photographic films for both long and short camera distances, respectively, and were used for further data processing. Total scattering intensities and background curves are given in **Figure S2** and **Table S3** in Supporting Information. The total intensities were transformed into molecular intensity curves sM(s) by background elimination, see formula (1) in Supporting Information. All refinements were done using two intensity curves, long and short camera, simultaneously; experimental and theoretical sM(s) curves are plotted in **Figure 5**.

The GED data were analyzed using the UNEX program [26]. Refinements were performed assuming all located *chair* conformers **Ax** and **Eq** possess a C_s symmetry of equilibrium structure as it follows from the QC calculations.

The following independent geometric parameters were used to describe the geometry for the compound **1** (Figure **1**): 17 bond distances, 5 groups, the groups shown in square brackets: [*r*(X–X), *r*(C3–Si3), *r*(C3–Si1), *r*(C2–Si3), *r*(C4–Si1)], [*r*(C3–X)], [*r*(Si3–X)], [*r*(H–Si1), *r*(H$_{eq}$–Si2), *r*(H$_{ax}$–Si2)], [*r*(H$_{ax}$–C1), *r*(H$_{eq}$–C1), *r*(H$_{ax}$–C2), *r*(H$_{eq}$–C2), *r*(H–C4), *r*(H–C4), *r*(H–C4)]; 10 bond angles, 2 group: [∠(H$_{ax}$–C2–X), ∠(H$_{eq}$–C2–X), ∠(H$_{ax}$–C1–Si2), ∠(H$_{eq}$–C1–Si2), ∠(H$_{ax}$–Si2–C2), ∠(H$_{eq}$–Si2–C2), ∠(H–C4–Si), ∠(H–C4–Si), ∠(H–C4–Si)] and [∠(C4–Si1–X)] for Eq conformer; dihedral angles, 2 groups [∠(Si1–C3–C1–Si2)] and [∠(C2-Si3-Si2-C1)] see **Table S4** (Supporting Information). The differences between parameters within a group were adopted from M06-2X/6-311G** calculations.

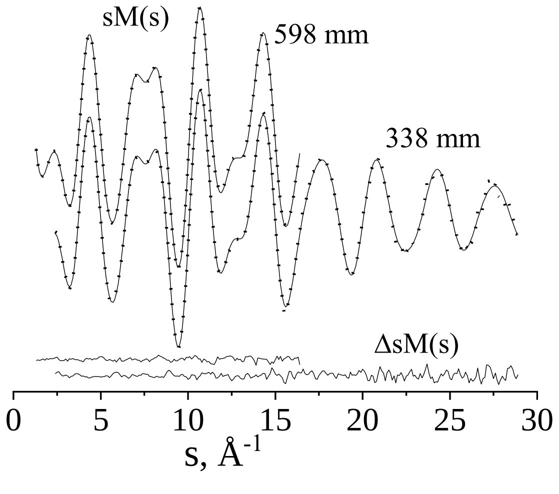
Vibrational amplitudes for all three conformers were refined in 7 groups according to the specific regions in the radial distribution: 0–1.3; 1.3–1.65; 1.65–2.2; 2.2–2.76; 2.76–3.4; 3.4–4.2; 4.2–8.0 Å for compound **1**, see f(r) graphs in **Figure 5.** The ratios between the amplitudes within each group were constrained to the calculated values. Vibrational corrections $\Delta r = r_{h1} - r_a$ and starting root-mean square amplitudes were calculated with the Vibmodule program [27] using the so-called second approximation, in which a harmonic approach with nonlinear relation between Cartesian and internal coordinates was applied on the basis of the force field estimated in the QC calculations at the M06-2X/6-311G** level.

The mole fraction ratio X_{Ax}:X_{Eq} of the conformers was also refined along with the geometric and vibrational parameters.

Correlation coefficients between structural parameters in the least-squares analyses are provided in **Table S7** (Supporting Information). The correlations above 0.9: Xmol – Xmol (-0.919); for two pairs of parameters these coefficients are between 0.8 and 0.9: X_{mol} – Scale (0.884), X_{mol} – Scale (0.857), for three pairs of parameters these coefficients are between 0.7 and 0.8: AMPLGROUP – Si3X2 (0.781), X_{mol} – Scale (-0.722), AMPLGROUP – Si3X2 (0.720). Other correlations were below 0.7.

The least-squares refinement converged at the conformers ratio Ax:Eq of 54(6):44(6) mol.% with the uncertainty specified as $3\sigma_{LS}$. Another estimation of the error was performed by applying the Hamilton's criterion approach [28] which resulted in 54(10):44(10) mol.%, **Figure 6**.

The resulted experimental and theoretical molecular scattering intensities sM(s) and radial distribution curves f(r) with the corresponding differences “Experim.–Theor.” are plotted in **Figure 5**.



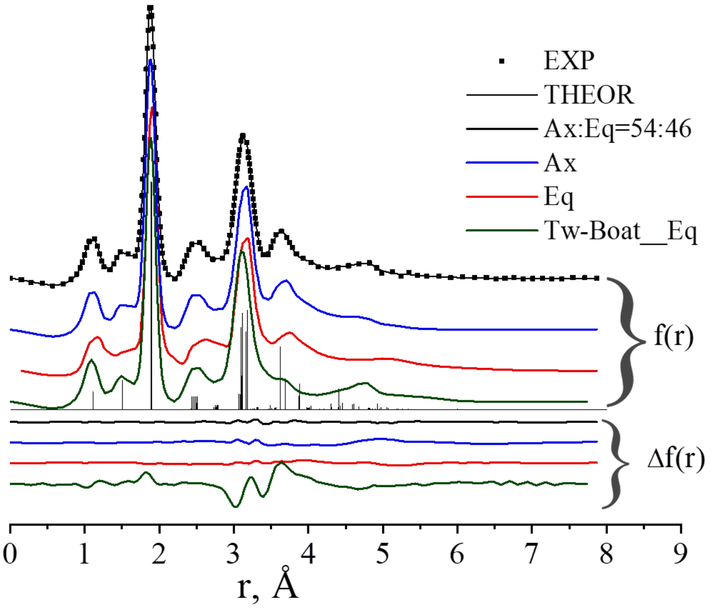


Figure 5. Molecular scattering intensities sM(s) (upper) and radial distribution curves f(r) (lower): experimental (dots) and theoretical (black line) for refined mixture of two most stable conformers Ax:Eq =54(6):46(6)% for **1**; colored lines correspond of the individual conformers including the *twisted-boat*-Eq conformer (green lines); the differences "Experim.-Theor." are given at the bottom.

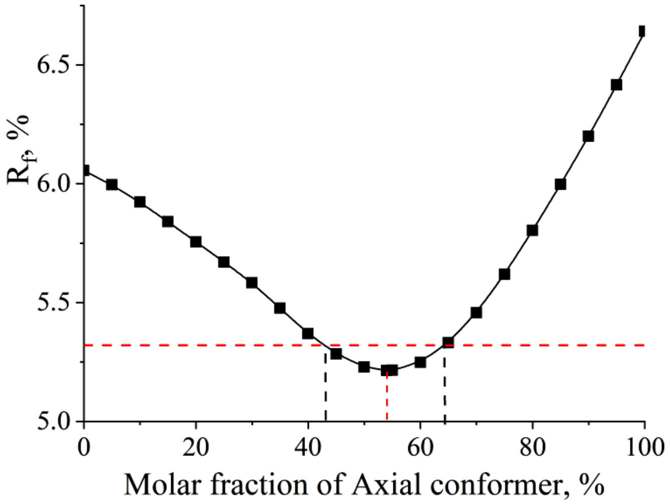


Figure 6. R_f *vs* axial conformer contribution under molecular parameters refinement. The horizontal line corresponds to the Hamilton's criterion [28] at 0.05 confidential level.

It is worthwhile to mention that a fit of the *twisted-boat* conformer to the experimental GED data was tested. The green lines in Figure 5 show a significant mismatch which confirmed a low, ≤7%, contribution of this conformers predicted by QC calculations, see **Table S1** in SI.

In order to collate the conformational contributions, a temperature dependence of Ax:Eq ratio calculated in a 'rigid rotor - harmonic oscillator' approximation realized in the VibModule program [27] along with the GED (280 K) and Raman spectroscopy (220-300 K interval) data are plotted in Figure 7. Noticeably diverged below 500 K, the QC predictions demonstrate a tendency to converge at higher temperatures at ca. 45% of Ax. B3LYP and MP2 show a domination of Eq at low temperatures while the other theoretical approximations reveal a somewhat less pronounced dependence. The M06-2X and B3LYP-D3 coincide with the GED data.

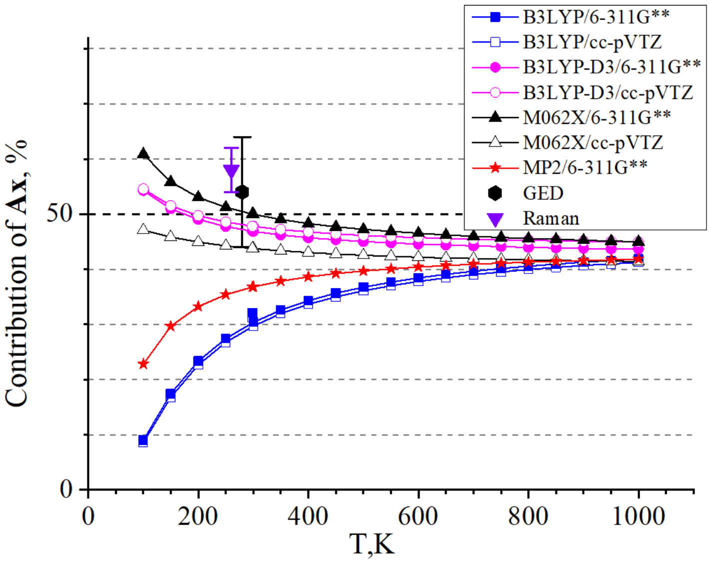


Figure 7. Calculated temperature dependence of the Ax conformer contribution of **1** along with experimental GED (gas) and Raman (liquid) data; the latter was derived from the ΔH value.

Selected experimental (GED) and calculated (QC) geometric parameters of the three most stable conformers are compiled in **Ошибка! Источник ссылки не найден.**.

In the quantum chemical calculations at M06-2X/6-311G** level there is a good agreement with the GED values (bond distances, bond angles and torsion angles). However, the Si-H and C-H bond from GED analysis are somewhat longer than those from QC calculations. The complete set of experimental and theoretical structural (geometric and vibrational) parameters of the conformers are summarized in Supporting Information, **Tables S5-S6**.

Table 2. Selected theoretical (with 6-311G** basis set) and experimental GED geometric parameters[a] of the two most stable conformers of **1**

Conformer	**Ax**					**Eq**				
Method	B3LYP	B3LYP-D3	M06-2X	MP2	GED[b]	B3LYP	B3LYP-D3	M06-2X	MP2	GED[b]
Bond distance, Å										
Si1-C1	1.896	1.893	1.884	1.885	1.884 (4)	1.894	1.892	1.883	1.883	1.883 (4)
Si2-C1	1.889	1.888	1.880	1.881	1.880 (4)	1.890	1.889	1.881	1.881	1.880 (4)
Si2-C2	1.891	1.890	1.882	1.882	1.881 (4)	1.891	1.890	1.882	1.882	1.882 (4)
Si1-C_{Me}	1.886	1.885	1.878	1.878	1.878 (4)	1.887	1.885	1.878	1.878	1.878 (4)
Si1-H(aver.)	1.493	1.492	1.487	1.485	1.496 (7)	1.492	1.491	1.487	1.486	1.497 (7)
C-H(aver.)	1.096	1.096	1.097	1.097	1.105(2)	1.096	1.096	1.095	1.097	1.105(2)
Bond angle, °										
C1-Si1-C3	108.8	108.8	108.6	108.6	110.2 (23)	108.9	108.8	108.6	108.5	110.2 (23)
Si1-C1-Si2	115.6	114.8	114.2	114.9	115.1 (8)	114.9	114.6	113.7	114.4	114.7 (8)
Si2-C2-Si3	114.3	114.2	113.2	114.0	112.0 (16)	114.5	114.2	113.2	114.1	112.0 (16)
C1-Si1-C_{Me}	111.0	110.4	110.0	110.4	109.2 (12)	111.3	111.0	111.0	111.2	111.1 (18)
H-Si1-C_{Me}	108.2	108.8	109.0	108.7	109.0 [f]	108.6	109.1	109.4	109.0	108.2 [f]
Torsion angle, °										
Si1-C1-Si2-C2	-52.6	-53.7	-55.3	-54.2	-52.5 (16)	-53.0	-53.9	-55.7	-54.7	-53.0 (20)
H-Si1-C_{Me}-H	59.7	59.9	59.9	59.8	59.4 [d]	59.9	60.1	60.1	60.1	60.1 [d]
Flap(Si1)[c]	44.9	46.7	47.7	46.6	43 (3)	46.6	47.3	48.8	47.9	44.1 (28)
Flap(C2)[c]	48.5	49.1	51.3	50.3	49 (4)	48.0	49.1	51.5	50.1	49.3 (42)
φ[e]	83.1	80.1	78.1	80.1	82.8[f]	4.8	4.7	3.4	3.9	6.8[f]

[a] r_{h1} values ($r_{h1}=r_a+\Delta r$) are given for GED results. The vibrational corrections Δr were calculated by the Vibmodule program [27] using the so called second approximation, in which harmonic approach with nonlinear relation between Cartesian and internal coordinates were applied on the base of the force field estimated in the quantum chemical calculations at M06-2X/6-311G** level.

[b] Values in parentheses for the GED data are full errors estimated as $\sigma(r_{h1})=[\sigma_{scale}^2+(2.5\sigma_{LS})^2]^{½}$, where σ_{scale} = 0.002r and σ_{LS} is a standard deviation in least-squares refinement for internuclear distances and as $3\sigma_{LS}$ for bond angles. The place-value is such that the last digit of the uncertainty lines up with the last digit of the nominal value.

[c] Flap (Si) and flap (C) are the angles between the Si3C3… C1Si2 plane and the C1Si1C3 and Si2C2Si3 triangles, respectively, Figure 1.

[d] Dependent parameter

[e] Inclination angle of the Si-C4 bond to the Si3C3… C1Si2 plane: the bond has a towards-to-plane direction in I and the Si-C4 vector approaching the continuation of the plane.

[f] Fixed parameter

Raman spectroscopy

Raman spectroscopy may be used to analyze the ratio of axial and equatorial conformers of monosubstituted six-membered rings. The application of the method has been described in detail in other publications [4,29]. Therefore only a brief description will be given here. Temperature-dependent Raman spectra of compounds are typically analyzed using the van´t Hoff relation $\ln(A_1/A_2) = -\Delta H/RT + constant$, where A_1 and A_2 are the intensities of the vibrational bands belonging to two different conformers of the molecule. Either the heights or areas of the bands can be used for the A_1/A_2 ratio. The relation is correct under the assumption that ΔH and the Raman scattering coefficients are temperature independent.

Low-temperature spectra were recorded for pure **1** at temperatures varying from 300 to 220 K at 20 K intervals. The Raman spectrum of pure **1** at variable temperatures is shown in Figure 3 (upper part). The calculated Raman spectrum using B3LYP/6-31G* calculations and the ORCA program system is shown in Figure 3 (lower part). At 544 (axial) and 552 (equatorial) cm^{-1}, respectively, a pair of separated bands is detected, that correspond to symmetric stretching modes of C1–Si1–C3 and Si2–C2–Si3 of the ring conformers. These bands correspond very well with experimental bands at 544 and 554, hence the latter were used for a van´t Hoff plot as shown in Figure 4. The obtained $\Delta H = H_{\mathrm{ax}} - H_{\mathrm{eq}}$ corresponds to –0.17(4) kcal mol^{-1}, **Table 1**.

. According to the Raman experiment, compound **1** has a slight preference for the axial conformer based on the enthalpy, see Table 1.

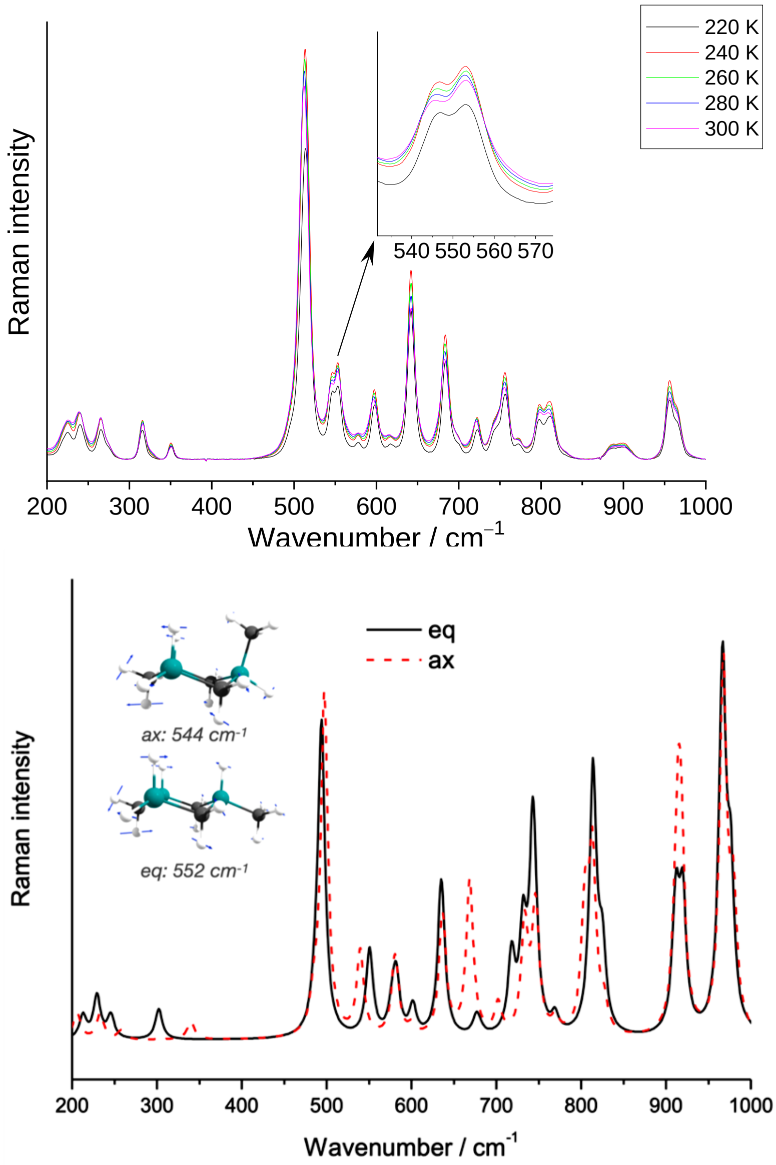


Figure 3. Raman spectra of **1**: (upper) experimental of pure compound at variable temperatures from 300 to 220 K in the wavenumber range 200–1000 cm^{-1}; (lower) calculated (gas, B3LYP/6-31G*) for equatorial and axial conformers

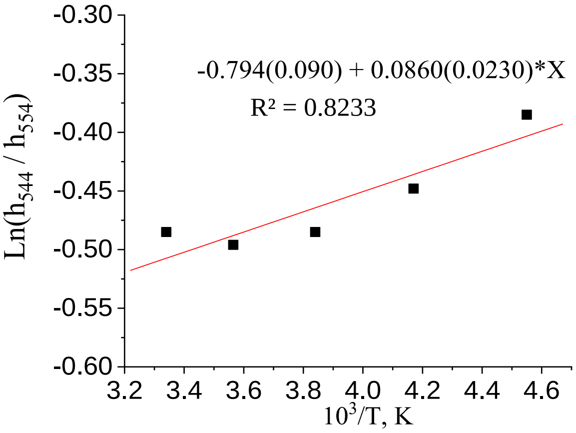


Figure. 4. Van´t Hoff plot of the band pair 544/554 cm^{-1} using band heights. The derived enthalpy value $\Delta H = H_{ax} - H_{eq} = -0.17(4)$ kcal mol^{-1}.

In addition, attempts to measure low temperature ^{13}C-NMR spectra of **1** were undertaken but did not succeed. In a 1:2:2 solvent mixture of CD_2Cl_2, CHF_2Cl and CF_3BR most of the compound had crystallized when the temperature reached 152 K and thus prevented a successful DNMR measurement.

Comparison of 1-X-1,3,5-trisilacyclohexanes with monosubstituted six-membered cyclic compounds

The larger 1,3,5-trisilacyclohexane ring relative to those of cyclohexane and silasyclohexane is a possible prerequisite for conformers priority as well as for geometry of the cycle itself. The measured (GED) flap(C) angle in **1** demonstrate the Si-C-Si fragment to lie closer to the plane of the six-membered cycle frame than in 1-Me-1-silacyclohexane [19]: 49 (4)° *vs*. 56(2)°, that can be caused by the Si atoms proximity in **1**. This tendency is supported by QC and GED, also in 1-OMe-1,3,5-trisila- [15] and 1-NMe_2-1,3,5-trisilacyclohexane [7].

In earlier work [3], the Eq-Ax priority was compared in the series of X=halogen and CN for 1-X-1-silacyclohexanes. Here, we supplemented that series with the Me-analog as well as with such series for 1-X-1,3,5-trisilacyclohexanes, Figure 8.For the 1-X-1-silacyclohexanes, the GED and QC data were taken from [1–3,19,30–32].

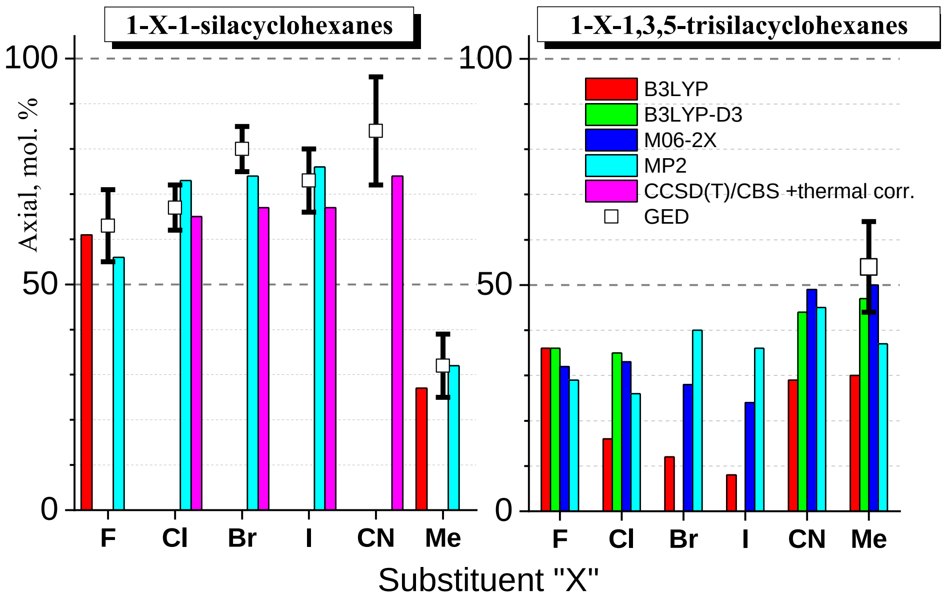


Figure 8. Contribution of Ax conformers in 1-X-1-silacyclohexanes (literature data, see text above for references) and 1-X-1,3,5-trisilacyclohexanes (this work, see section Computational details)

In the series 1-Me-substituted piperidine→ cyclohexane → silacyclohexane → germacyclohexane, the axial conformer presence noticeably grows, see Table 3, that is caused by, predominantly, bond lengthening.

Table 3. Contribution of Ax conformers in the 1-methyl substituted cyclohexane derivatives

Compound/Method	QC	Raman	GED	NMR
1-Me-piperidine	≈0 [33]			
1-Me- cyclohexane	≈0 [18]	≈0 [18]	4 [17]	
1-Me- silacyclohexane	27-32 [19]		32(7) [19]	26(1) [19]
1-Me- germacyclohexane	≈50 [34]			≈50 [34]

Another comparison may be done when change from the methyl to silyl substituent which accompanied again by increase of the cycle-to-substituent bond length and, consequently, increase of the Ax conformer contribution: 10(10) % GED [35] and 12.7±1% MW [36] in 1-SiH_3-cyclohexane and 57(7)% GED [4] in 1-SiH_3-1-silacyclohexane. The latter is very close to the conformational ratios in **1** and 1-Me-1-germacyclohexane.

CONCLUSIONS

A monosubstituted-1,3,5-trisilacyclohexane, 1-Methyl-1,3,5-trisilacyclohexane **1** was synthesized and the molecular structure was investigated by gas electron diffraction and quantum chemical calculations. From the GED analysis a ratio Ax:Eq conformers was found 54(10):46(10)% at 280(5) K. A Raman experiment resulted in an Ax:Eq ratio of 58(4):42(4) based on ΔH. Excellent agreement with the experimental values was achieved using DFT functionals (B3LYP-D3 and M06-2X that take into account dispersion interactions. The B3LYP functionals without D3 did considerably worse, whereas a MP2 result took a medium place.

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