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КОНФОРМАЦИОННОЕ ПОВЕДЕНИЕ И СТРУКТУРА МОНОЗАМЕЩЕННЫХ 1,3,5-ТРИСИЛАЦИКЛОГЕКСАНОВ. ЧАСТЬ II: 1-МЕТОКСИ-1,3,5-ТРИСИЛАЦИКЛОГЕКСАН

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Настоящая работа является продолжением нашего систематического комплексного изучения строения производных 1,3,5-трисилациклогексанов - соединений с чередующимися атомами углерода и кремния в каркасе шестичленного цикла. Недавно мы опубликовали первый результат по конформационным свойствам и структуре монозамещенного 1,3,5-трисилациклогексана, изученного методами газовой электронографии и квантовой химии, а именно 1-N,N-диметиламино-1,3,5-трисилациклогексана. В данной работе был синтезирован 1-метокси-1,3,5-трисилациклогексан, и были определены его структура и конформационные свойства с помощью газовой электронографии и теоретических расчетов. Шестичленный цикл имеет конфигурацию «кресло», а промежуточные минимумы между аксиальными и экваториальными конформерами соответствуют структурам twist-boat-Eq. Энергетический барьер для процесса g-Ax →twist-boat-Eq составляет около 1.0 ккал/моль. Молекула может существовать в 3 или 4 формах (в зависимости от метода и базисного набора), отличающихся друг от друга положением заместителей. Результаты квантово-химических расчетов показывают, что конформеры gouch с “внешней” ориентацией группы MeO, g-Ax (I) и g-Eq (III), более стабильны, чем транс-формы с “внутренней” ориентацией, tr-Ax (II) и tr-Eq (IV); соотношение (I + III):(II + IV) = (80-69) : (20-31)% (в зависимости от метода и базисного набора). Из данных электронографии было установлено, что мольные доли конформеров составляют g-Ax:g-Eq:tr-Eq=54(13):35(15):11(15)% при T=287(3) K. Конформационные свойства были сопоставлены в серии аналогичных 1-OMe-1-(гетеро)циклогексанов. Также была предпринята попытка выявить конформационное проявление в растворе методом ЯМР. Попытка «заморозить» конформационное равновесие (спектры ^{13}C ЯМР) не увенчалась успехом, скорее всего, из-за низкого барьера инверсии колец системы 1,3,5-трисилацилогексановых колец.

Ключевые слова: 1-Метокси-1,3,5-трисилациклогексан, молекулярная структура, объединенная газовая электронография/масс-спектрометрия, ^{13}C ЯМР-спектроскопия, ^{1}H ЯМР-спектроскопия, ^{13}C ЯМР-спектроскопия при низких температурах

THE CONFORMATIONAL BEHAVIOR AND STRUCTURE OF MONOSUBSTITUTED 1,3,5-TRISILACYCLOHEXANES. PART II: 1-METHOXY-1,3,5-TRISILACYCLOHEXANE

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This work is a continuation of our systematic comprehensive study of the structure of derivatives of 1,3,5-trisilacyclohexanes - compounds with alternating carbon and silicon atoms in the framework of a six-membered cycle. Recently we have published the first result on the conformational properties and structure of monosubstituted 1,3,5-trisilacyclohexane studied by gas-phase electron diffraction and quantum chemistry, namely 1-N,N-dimethylamino-1,3,5-trisilacyclohexane. In this work, 1-methoxy-1,3,5-trisilacyclohexane was synthesized, and its structure and conformational properties were determined using electron diffraction and theoretical calculations. The six-membered cycle has a "chair" configuration, and the intermediate minima between axial and equatorial conformers correspond to the structures of twist-boat-Eq. The energy barrier for the g-twist-boat-Eq process is about 1.0 kcal/mol. The molecule can exist in 3 or 4 forms (depending on the method and the basic set), differing from each other in the position of substituents. The results of quantum chemical calculations show that gouch conformers with the "external" orientation of the MeO group, g-Ax (I) and g-Eq (III), are more stable than trans-forms with the "internal" orientation, tr-Ax (II) and tr-Eq (IV); the ratio (I + III): (II + IV) = (80-69) : (20-31)% (depending on the method and the basic set). From the electron diffraction data, it was found that the molar fractions of conformers are g-Ax:g-Eq:tr-Eq=54(13):35(15):11(15)% at T=287(3) K. The conformational properties were compared in a series of similar 1-OMe-1-(hetero)cyclohexanes. An attempt was also undertaken to identify the conformational manifestation in solution by NMR. An attempt to "freeze" the conformational equilibrium (^{13}C NMR spectra) was unsuccessful, most likely due to the low ring inversion barrier of the 1,3,5-trisylacylhexane ring system.

Key words: 1-Methoxy-1,3,5-trisilacyclohexane, molecular structure, combined gas-phase electron diffraction/mass spectrometry, ^{13}C-NMR spectroscopy, ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy at low temperatures

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INTRODUCTION

Cyclohexane is known to be an important cornerstone in organic stereochemistry, and the conformational behavior of numerous derivatives of it have been studied for a long time using various experimental and theoretical methods [1], but at the beginning of this century, much less was known for its silicon analogues, even the simplest case of silacylohexane, were one carbon atom in the ring skeleton has been replaced by a Si atom. During the past two decades, several publications on conformational properties of 1-Si monosubstituted silacylohexanes have appeared. The conformational equilibrium has been studied experimentally by gas-phase electron diffraction (GED), dynamic NMR, temperature-dependent Raman as well as IR spectroscopies, and theoretically applying high level quantum chemical approaches. In the case of monosubstituted cyclohexanes, the general rule is a predominance of the equatorial conformer. Conformational preference of a substituent is generally expressed by a conformational parameter, so called “conformational energy” – the Gibbs free energy difference between the axial and equatorial conformers. Monosubstituted silacyclohexanes, when compared to the analogous monosubstituted cyclohexanes either show a considerably lower equatorial preference CH_3 [2], Ph [3], *t*-Bu [4], or even more often a preference for the axial conformer, F [5], Cl, Br, I [6], CF_3 [7, 8], SiH_3 [9], CN

[10], NMe$_2$ [11], OMe [12]. Some reviews on the silacyclohexanes structures and properties are available in the literature [13, 14].

Another interesting six-membered silicon-containing ring system is 1,3,5-trisilacyclohexane with alternating carbon and silicon atoms in the ring skeleton. The chemistry of carbosilane molecules with alternating carbon and silicon atoms has been reviewed in a monograph [15]. Recently we published a first result on conformational properties and structure of a monosubstituted 1,3,5-trisilacyclohexane as studied by gas-phase electron diffraction (GED), namely 1-N,N-dimethylamino-1,3,5-trisilacyclohexane [16]. Earlier GED and quantum chemical (QC) study of the parent compound, 1,3,5-trisilacyclohexane reported in [17] resulted in experimental geometry and calculated energy difference between the *chair* and *twisted boat* conformers to be 2.2 kcal·mol^{-1} that may witness for a complete domination of the former in gas phase at ambient temperatures.

In this paper, we report detailed GED/MS and QC study of structure and conformational properties of 1-Methoxy-1,3,5-trisilacyclohexane in the gas phase.

EXPERIMENTAL SECTION

Synthesis

All syntheses 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. 1,3,5-trisilacyclohexane was purchased from JSI Silicone and used without further purification.

Compound **2**, 1-bromo-1,3,5-trisilacylohexane, was prepared according to a previous publication [16]. A solution of triethylamine (6.3 g, 62 mmol), methanol (2.0 g, 62 mmol) and 50 mL of diethyl ether was added dropwise into a flask containing **2** (6.54 g, 31.0 mmol) and 175 mL of diethyl ether. White precipitate was immediately formed and the solution turned light grey. Stirring was continued overnight and the precipitate was filtered off. The solvent was distilled off and NMR spectra confirmed the remaining clear liquid to be 1-methoxy-1,3,5-trisilacyclohexane (3.08 g, 19.0 mmol, 61%). ^{1}H NMR (400 MHz, CDCl$_3$): δ –0.01–0.04 (m, 2H, C*H2*), 0.12–0.18 (m, 4H, C*H2*), 3.5 (s, 3H, C*H3*), 3.95–4.15 (m, 4H, Si*H2*), 4.73 (m, 1H, Si*H*). ^{13}C NMR (101 MHz, CDCl3): δ –10.68, –4.16, 51.54 (C*H3*). NMR spectra are shown in the Figures **S(1)-S(2)** in the Supporting Information. Small signals of an impurity can be detected in the NMR spectra. The purity of the title compound **1** is estimated to be 96% or better.

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 [18, 19]. 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 287(3) K in the course of the experiments. The conditions of the GED/MS experiment and data refinement details are given in Supporting Information, Table **S1(a)** and related chapters.

The mass spectra (EI, 50 eV) of the molecular beam taken synchronously with the GED experiments showed the major peaks and their intensities: m/z (%) 162 [M]$^{+}$ (100), 147 [M-Me]$^{+}$ (57), 131 [M-OMe]$^{+}$ (63), see Table **S1(b)** for details. With a decrease of ionizing electrons energy, a relative contribution of fragment ions decreased; the only peak representing the mass spectrum at less than 9 eV was the molecular ion [M]$^{+}$.

Low temperature ^{13}C-DNMR

A 400 MHz NMR spectrometer (Bruker Avance 400) was used for the NMR experiments. A solvent mixture of CD$_2$Cl$_2$, CHFCl$_2$, and CHF$_2$Cl 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 successfully to freeze the conformational equilibria of monosubstituted silacyclohexanes [20-23]. ^{13}C-DNMR was measured for **1** at the temperature range from 177 K down to 115 K. Further cooling to 112 K resulted in a repetitive loss of the lock signal that prevented measurements at lower temperatures. Upon cooling the spectra show broadening of all the signals which was most pronounced for the two equivalent carbons (2) adjacent to the substituted silicon atom. Expanded spectra for carbons (2) at temperatures in the range from 177 K to 115 K are shown in Figure **S3** in the Supporting information. The bandwidth at 115 K is nearly five times larger than at 177 K and the slope at the right side is clearly steeper than at the left side. This might indicate that a second, smaller, signal would be formed on the left side of the main signal upon further cooling. Calculated values indicate that the energy barrier required for ring inversion of the 1,3,5-trisilacylohexane ring system is as low as 5.5 kcal/mol [24]. We note that a second monosubstituted derivate of 1,3,5-trisilacylohexane also escaped the detection of a frozen equilibrium using ^{13}C NMR at low temperatures [16].

Computational details

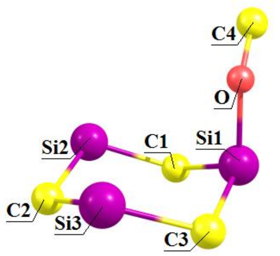
All calculations of **1** were performed with Gaussian 09 program suite [25]. The geometry and vibrational calculations were performed using DFT (with

B3LYP, B3LYP-D3 and M062X functionals) and MP2 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 M062X/6-311G** level.

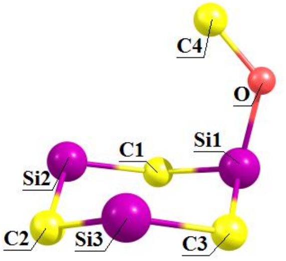
RESULTS AND DISCUSSION

Energies

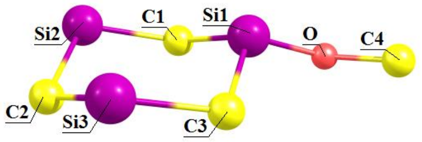
Scanning the potential energy surface profile for internal rotation of the methoxy group rotation around the Si – O bond by the M06-2X/6-311G** combination, Fig. 1, showed that the molecule has four conformers: two axial conformers in *gauche*-(g-Ax, I) and *trans*-(tr-Ax, II) positions and two equatorial in *gauche*-(g-Eq, III) and trans-(tr-Eq, IV) positions, (Fig. 2) differing from each other by the position of the substituent. All of them correspond to the minima of potential energy, which is confirmed by the calculation of harmonic vibration frequencies.



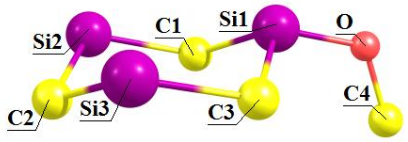
g-Ax, I



tr-Ax, II



g-Eq, III



tr-Eq, IV

Fig. 1. Possible conformers of compound **1**; hydrogens omitted for easier view. The trans and gauche orientations of the methoxy group are considered relative the hydrogen atom at Si

Рис. 1. Возможные конформеры соединения **1**; водороды опущены для облегчения просмотра. *Транс*- и *гош*-ориентации метоксигруппы рассматриваются относительно атома водорода при атоме Si

According to the calculations performed, all located conformers possess a C_1 symmetry of equilibrium structure, except the case of the *trans*-axial **II** structure when using B3LYP and B3LYP-D3 functionals with 6-311G** and cc-pVTZ basis sets which resulted in C_s symmetry (see Fig. 2 (a)).

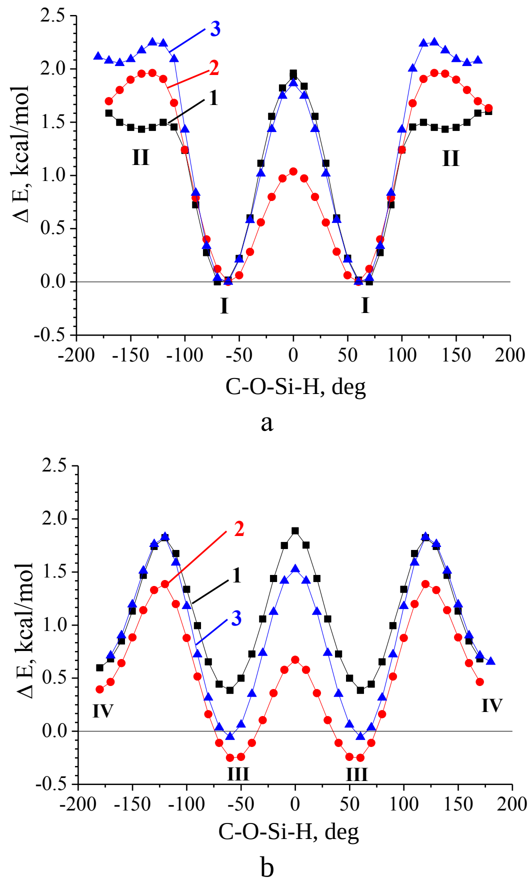


Fig. 2. Potential energy surfaces (PES) profiles of the 1-methoxy-1,3,5-trisilacyclohexane obtained by scanning by rotating the –OCH_3 group around the Si – O bond for axial (a) and equatorial (b) conformers of **1** (see also Fig. 1) calculated by different methods with 6-311G** basis set. Both plots have the same ordinate axes scale. 1– M062X, 2– B3LYP, 3– MP2

Рис. 2. Профили поверхностей потенциальной энергии (PES) 1-метокси-1,3,5-трисилациклогексана, полученные сканированием путем вращения группы –OCH_3 вокруг связи Si–O для аксиальных (a) и экваториальных (b) конформеров **1** (см. также Рис. 1), рассчитанных различными методами с базисным набором 6-311G**. Оба графика имеют одинаковый масштаб осей ординат. 1– M062X, 2– B3LYP, 3– MP2

Moreover, 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 M062X/6-311G** level with a step of 10° (Fig. 3). Thus, the molecule exists in three forms: *g*-**Ax**, *g*-**Eq**, *tr*-**Eq**, which correspond to the minima on the 3-D presentation and its projection of the relative energy surface. The intermediate minima between correspond to *twist-boat*-**Eq** structures. As follows from Fig. 3, the energy barrier for *tr*-**Eq** → *twist-boat*-**Eq** process is ca. 1.0 kcal/mol.

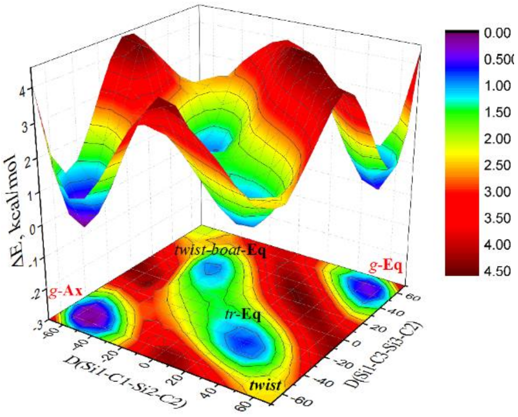


Fig. 3. A 3-D presentation and its projection of the relative energy surface of **1** calculated at the M062X/6-311G** level of theory, shown as a function of two dihedral angles; the iso-energy contours are drawn with 0.5 kcal/mol step

Рис. 3. Трехмерное представление и его проекция относительной энергетической поверхности **1**, рассчитанной на уровне теории M062X/6-311G**, показанные как функция двух двугранных углов; изоэнергетические линии представлены с шагом 0,5 ккал/моль

Differences between energies of *boat* and *twist* conformers with respect to *g*-**Eq** are as follows: the boat has an energy of less than 1.0 kcal/mol, which corresponds to about 10%; twist conformer has a higher energy of 2.0-2.3 kcal/mol.

Theoretical relative total energy, Gibbs free energy, and the molar fraction of the conformers are summarized in Table 1. All theoretical methods show that the *g*-**Ax** and *tr*-**Ax** conformers (with an “outer” orientation of the MeO group) are more energetically stable than *g*-**Eq** and *tr*-**Eq** (with an “inner” orientation MeO group). Note that zero point correction were not applied. The ratio of equatorial and axial forms is (*g*-**Ax** + *tr*-**Ax**) : (*g*-**Eq** + *tr*-**Eq**) = (80-69):(20-31)%. It is obvious that 1,3-diaxial repulsion between the substituent and the ring destabilizes the *trans*-conformers. At the same time, the orbital interaction between the lone pair of the O atom with the Si orbitals stabilizes to some extent the *trans* conformers. Interestingly, the MP2(FC) method with the 6-311G ** basic sets showed the absence of the II conformer (*tr*-Ax).

Table 1

Relative total electron energies Δ*E*, Gibbs free energies Δ*G* and contributions X of all conformers of 1

***Таблица 1.* Относительные полные электроные энергии Δ*E*, свободные энергии Гиббса Δ*G* и вклады X всех конформеров 1**

	Δ*E*, kcal/mol				Δ*G*°(298K), kcal/mol				X(298K), %			
Method/basis set	**I**	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**
B3LYP/6-311**	0.00	1.66	-0.26	0.39	0.00	1.44	-0.44	0.19	26	2	54	18
B3LYP-D3/6-311G**	0.00	1.21	0.28	0.65	0.00	0.42	-0.04	0.46	33	16	36	15
M062X/6-311G**	0.00	1.56	0.43	0.73	0.00	1.54	0.09	0.33	40	3	34	23
MP2(FC)/6-311G**	0.00	1.94	-0.18	0.64	0.00	2.73	-0.17	0.33	34	0	46	20
B3LYP-D3/CC-pVTZ	0.00	1.21	0.31	0.69	0.00	0.73	0.11	0.54	40	12	33	15

GED analysis

The diffraction intensities were averaged from 6 photographic films for long and short camera distances, respectively, and were used for further data processing. Total scattering intensities and background curves are given in Fig. S4 and Table S2 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 simultaneously. The conformers contribution in the LS-refinement was sought in two ways: (i) as a in independent parameter and (ii) by scanning at fixed contributions while all structural parameters were refined (Fig. 4). The experimental and theoretical molecular scattering intensities sM(s) and radial distribution curves f(r) with the corresponding differences “Experim.–Theor.” are plotted in Fig. 5.

The GED data were analyzed using the UNEX program [26]. Refinements were performed assuming C_1 symmetry of the molecule for the *trans*-conformers and for the *gauche*-conformers.

Depending on the ‘method/basis set’ combination of the QC calculations, three or four conformers located – among various calculations performed, some, though not all, of them predict the conformer **II** as not favorable (see Table 1). For this reason in the GED data refinement the conformer **II** was excluded from consideration.

The following independent geometric parameters were used to describe the geometry: for compound 1 (Fig. 1): 22 bond distances, 4 groups, the groups shown in square brackets: [*r*(C1–Si1), *r*(C1–Si2), *r*(C2–Si2), *r*(C2–Si3), *r*(C3–Si3), *r*(C3–Si1)], [*r*(H–Si1), *r*(C4–O), *r*(H_{ax}–Si2), *r*(H_{eq}–Si2), *r*(H_{ax}–Si3), *r*(H_{eq}–Si3)], [*r*(O–Si1)], [*r*(H_{ax}–C1), *r*(H_{eq}–C1), *r*(H_{ax}–

C2), *r*(H_{eq}–C2), *r*(H_{ax}–C3), *r*(H_{eq}–C3), *r*(H–C4), *r*(H–C4), *r*(H–C4)]; 19 bond angles, 3 groups: [∠(C–Si–C), ∠(Si2–C2–Si3), ∠(Si3–C3–Si1)], [∠(O–Si–C)], [∠(C–O–Si)]; dihedral angles, 3 groups [∠(C4–O–Si–C1)] for conformers **I**, as a separate group, [∠(C4–O–Si–C1)] for conformer **III**, [∠(C4–O–Si–C1)] for conformer **IV** see in Table S3 (Supporting Information) http://journals.isuct.ru/ctj/workflow/index/4116/5. The differences between parameters with a group were adopted from M062X/6-311G** calculations.

Vibrational amplitudes for all three conformers were refined in 8 groups according to the specific regions in the radial distribution: 0–1.2; 1.2–1.5; 1.5–1.7; 1.7–2.2; 2.2–3.4; 3.4–4.0; 4.0–4.8; 4.8–9.1 Å for the compound **1**, see the f(r) plots in Fig. 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 M062X/6-311G** level.

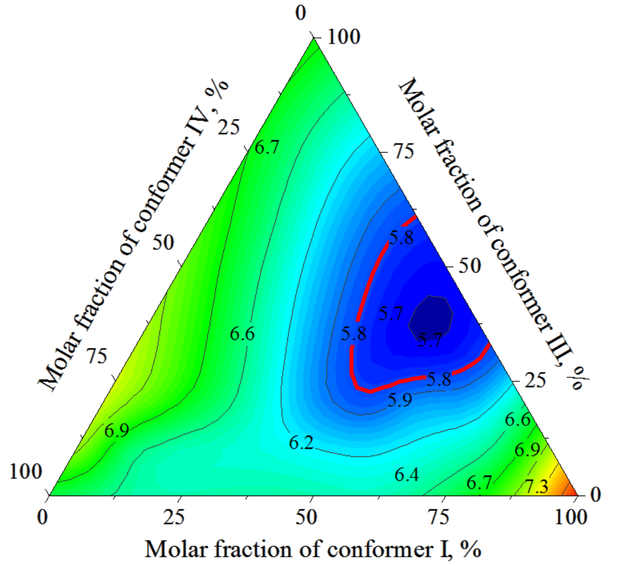


Fig. 4. Agreement factor R_f as a function of molar fraction of the most stable conformers of compound **1**. All geometric and vibrational parameters were refined, see text above. Hamilton's criterion [28] was applied for the $R_f/R_{f(min)}$ ratio of roughly 1.03 to estimate the uncertainties in the conformers' contribution was applied (see bold red contour)

Рис. 4. Коэффициент согласования Rf как функция молярной доли наиболее стабильных кон-формеров соединения **1**. Все геометрические и колебательные параметры варьировались, см. текст выше. Критерий Гамильтона [28] был применен для отношения $R_f/R_{f(min)}$, равного примерно 1,03, для оценки неопределенности вклада конформеров (см. жирный красный контур)

Correlation coefficients between structural parameters of the least-squares analyses are provided in Table S7 (Supporting Information). No correlation above 0.8 occurred; for five pairs of parameters these coefficients are between 0.6 and 0.8: tCOSiC - Xmol (-0.76), AMPLGROUP - Scale 0.74), aCSiC – rCSi1 (-0.71), aOSiC - Xmol (-0.68), aCSiC – Xmol (-0.64).

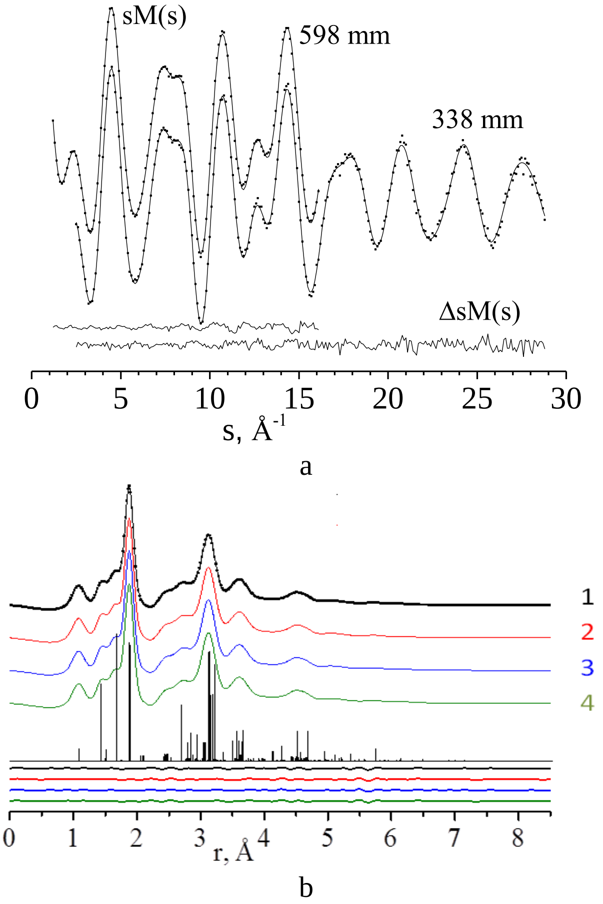


Fig. 5. Molecular scattering intensities sM(s) (upper) and radial distribution curves f(r) (lower): experimental (dots) and theoretical (black line) for refined mixture of three most stable conformers **I:III:IV**=54(13):35(15):11(15)% for **1** (line 1); colored lines correspond to refinement of all parameters under assumptions of the individual conformers: 2 – **I**, 3 – **III**, 4 – **IV**. The differences “Experim.-Theor.” are given at the bottom

Рис. 5. Интенсивности молекулярного рассеяния sM(s) (вверху) и кривые радиального распределения f(r) (внизу): экспериментальные (точки) и теоретические (черная линия) для оптимальной смеси трех наиболее стабильных конформеров **I:III:IV**=54(13):35(15):11(15)% для соединения **1** (строка 1); цветные линии соответствуют варьированию всех параметров в предположении присутствия только отдельных конформеров: 2 – **I**, 3 – **III**, 4 – **IV**. Разностные линии “Экспер.– Теор.” приведены внизу

Geometry

Selected experimental (GED) and calculated (QC) geometric parameters of the three most stable conformers are compiled in Table 2.

Table 2

Selected theoretical (with 6-311G basis set) and experimental geometric parameters[a] of three most stable conformers of 1**

Таблица 2. **Выбранные теоретические (с базисным набором 6-311G**) и экспериментальные геометрические параметры[a] трех наиболее стабильных конформеров 1**

Con-former	*g*-Ax, I					*g*-Eq, III					*tr*-Eq, IV				
Method	B3LYP	B3LYP-D3	M062X	MP2	GED[b]	B3LYP	B3LYP-D3	M062X	MP2	GED[b]	B3LYP	B3LYP-D3	M062X	MP2	GED[b]
Bond distance, Å															
Si1-C1	1.874	1.872	1.874	1.864	1.875(4)	1.885	1.883	1.862	1.874	1.862(4)	1.885	1.883	1.874	1.875	1.875(4)
C1-Si2	1.893	1.893	1.884	1.884	1.885(4)	1.893	1.891	1.882	1.883	1.882(4)	1.893	1.891	1.883	1.883	1.883(4)
Si2-C2	1.893	1.893	1.881	1.884	1.881(4)	1.890	1.890	1.882	1.881	1.882(4)	1.891	1.890	1.882	1.882	1.882(4)
Si1-O	1.666	1.666	1.662	1.665	1.669(6)	1.667	1.666	1.660	1.664	1.666(6)	1.666	1.666	1.659	1.664	1.666(6)
O-C4	1.419	1.420	1.412	1.419	1.432(5)	1.419	1.420	1.413	1.420	1.432(5)	1.417	1.419	1.411	1.417	1.430(5)
Si1-H (aver.)	1.494	1.492	1.486	1.485	1.506(5)	1.493	1.491	1.488	1.486	1.507(5)	1.482	1.481	1.477	1.476	1.497(5)
Bond angle, °															
C1-Si1-C3	110.0	109.9	109.8	109.6	110.1(2)	109.9	109.9	109.8	109.6	110.1(2)	108.3	108.3	107.7	107.6	108.0(2)
Si1-C1-Si2	115.0	113.6	111.9	113.7	112.3(2)	114.6	114.0	113.3	114.0	114.2(2)	114.5	114.3	113.2	113.9	113.6(2)
Si2-C2-Si3	115.3	115.5	114.8	115.5	116.9(2)	114.4	114.0	113.2	114.0	115.2(2)	114.4	113.9	113.2	114.0	115.2(2)
C1-Si1-O	105.7	105.3	109.1	105.4	105.6(14)	106.9	107.2	107.7	107.4	103.9(14)	112.3	111.7	111.7	112.3	107.9(14)
Si1-O-C4	125.8	125.1	122.1	121.5	120.3(9)	125.1	124.1	121.9	121.0	120.0(9)	126.6	124.8	123.0	122.5	121.2(9)
H-Si1-O	109.0	109.5	109.1	109.3	105.5(6)	109.0	109.2	109.0	109.2	105.5(6)	103.7	104.3	105.0	104.2	101.5(6)
Torsion angle, °															
Si1-C1-Si2-C2	-52.0	-52.7	-55.6	-53.6	-54.6(9)	-52.8	-53.8	-54.9	-54.4	-53.8(9)	-54.1	-54.7	-56.8	-55.7	-55.7(9)
H-Si1-O-C4	-57.8	-66.7	64.9	63.6	53.3(11)	-55.9	-59.7	61.5	60.7	61.4(11)	180.0	180.0	180.0	180.0	145.4(11)
C1-Si1-O-C4	-62.7	-54.2	-60.0	-57.3	-63.6(13)	175.4	179.5	178.4	179.4	177.8(13)	-61.2	-60.7	-60.3	-60.7	-98.8(13)
Flap(Si1-C1-C3-Si3)[c, d]	46.4	50.4	51.7	49.9	51.6	46.1	47.1	48.6	47.4	48.4	48.5	48.6	51.3	50.1	51.1
Flap(Si1-C3-C1-Si2)[c, d]	46.3	49.7	52.4	49.7	52.3	46.5	47.3	48.2	47.8	48.1	48.5	48.6	51.2	50.1	51.1
Flap(C2-Si2-Si3-C3)[c, d]	47.7	47.9	49.4	48.7	49.4	48.1	49.7	51.5	49.9	51.5	47.8	49	50.8	49.6	50.8
Flap(C2-Si3-Si2-C1)[c, d]	47.5	47.2	50.1	48.5	50.1	48.4	49.9	51.2	50.4	51.2	47.8	49	50.7	49.6	50.7

Notes: [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 M062X/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 vibration amplitudes. 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 CSi1C and Si2CSi3 triangles, respectively (Fig. 1)

[d] Dependent parameter

Примечания: [a] Для результатов GED приведены значения r_{h1}, где ($r_{h1}=r_a+\Delta r$). Колебательные поправки Δr были рассчитаны с помощью программы Vibmodule [27] с использованием так называемого второго приближения, в котором применесь гармоническое приближение с нелинейной связью между *де*-картовыми и внутренними координатами на основе силового поля, оцененного в квантово-химических расчетах на уровне M062X/6-311G**

[b] Значения в скобках для GED данных – это полные погрешности, оцениваются как $\sigma(r_{h1})=[\sigma_{scale}^2+(2.5\sigma_{LS})^2]^{½}$, где σ_{scale} = 0.002r и σ_{LS} стандарт-ное отклонение процедуры наименьших квадратов для межъядерных расстояниях и, как $3\sigma_{LS}$ для амплитуд колебаний.

[c] Углы Flap (Si) and flap (C) - это углы между плоскостью SI3C3... C1 C2 и треугольниками CSi1C C и Si2CSi3 соответственно (рис. 1).

[d] Зависимый параметр.

[c] Углы Flap (Si) and flap (C) - это углы между плоскостью SI3C3... C1 C2 и треугольниками CSi1C C и Si2CSi3 соответственно (рис. 1).

[d] Зависимый параметр.

The results of quantum chemical calculations at M062X/6-311G** level are in good agreement with the GED values (bond distances, bond angles and torsion angles). However, the O-C4 and Si1-H (aver.) bonds length from GED analysis is longer by than that from QC calculations. Experimental and theoretical geometric and vibrational parameters of all conformers are summarized in Supporting Information, Tables S4-S6.

Comparison of conformational preferences in a series of analogous 1-OMe-(hetero)cyclohexanes

Conformational preferences in gas-phase of 1-(OMe,X)-1-(Y)cyclohexanes and 1-OMe-1,3,5-trisilacyclohexane are compiled in Table 3. As one could expect from steric suggestions, the longer Y-O bond length (where Y is a heteroatom introduced into the six-membered cycle) results in a less repulsion and, thus, in a richer contribution of conformers with axial position of the methoxy group – this is clearly manifested in the series of Y= N,C,Si, see compounds **6**, **5** and **3**. Moreover, a more spacious cycle, in case of triply silicon implemented 1,3,5-trisilacyclohexanes (**1**), could seems to produce a similar tendency in comparison with a single silicon heteroatom (**3**), but it does not evidently follow from the both, theoretical and experimental results, represented in Table 3, though a variety of the species contributing increases. Addition of a substituent adjacent to the OMe-group, such as a highly conjugated phenyl group (**4**) somewhat 'suppressed' the OMe-axial species abundance. A serious dissimilarity is to be noted for 1-methoxy-piperidine **6** which is represented in gas phase by, almost exclusively, equatorial form, with the outer direction of the methoxy group, *cis*-form.

Table 3

Comparison of conformation contributions (mol.%) of 1-methoxy-(hetero)cyclohexanes

Таблица 3. **Сравнение вкладов конформеров (мол.%) 1-метокси-(гетеро)циклогексанов**

Method	Ref.	QC				GED			
Compound [a]		g-Ax	tr-Ax	g-Eq	tr-Eq	g-Ax	tr-Ax	g-Eq	tr-Eq
1 (OMe-1,3,5-Si)	This work	26-40	0-16	33-54	15-23	54(13)	–	35(15)	11(15)
3 (OMe--Si)	[12]	30-53	1-6	33-54	6-19	59(12)	–	41(12)	–
4 ((OMe, Ph)--Si)	[29]	24-39	5-7	28-53	2-28	30(15)	–	60(15)	10(15)
5 [b] (OMe-C)	[12]	40-54	–	46-60	–	N/A	N/A	N/A	N/A
6 (OMe-N)	[30]		3-14 (*c*-Ax)		86-97 (*c*-Eq)	N/A	N/A	N/A	N/A

Notes: [a] - 1-Methoxy-1,3,5-trisilacyclohexane (**1**), 1-Methoxy-1-silacyclohexane (**3**), 1-methoxy-1-phenyl-1-silacyclohexane (**4**), methoxy-cyclohexane (**5**), methoxy-piperidine (**6**)

[b] – only M062X/6-311G** and M062X/cc-pVTZ results

Примечания: [a] -1-метокси-1,3,5-трисилакиклогексан (**1**), 1-метокси-1-силакиклогексан (**3**), 1-метокси-1-фенил-1-силакиклогексан (**4**), метокси-циклогексан (**5**), метокси-пиперидин (**6**)

[b] - только результаты M062X/6-311g** и M062X/cc-pVTZ

CONCLUSIONS

In this contribution, we have presented a study of the title compound, 1-Methoxy-1,3,5-trisilacylohexane **1**. Our main focus has dealt with geometry and energetics of its various conformers. The substituent may be axially or equatorially oriented and it may be *trans* or *gauche* relative to the hydrogen atom at the substituted Si atom. From the GED analysis a ratio *g*-**Ax**:*g*-**Eq**:*tr*-**Eq** conformers was found 54(13):35(15):11(15)% at 287(3) K. At the same time, the (*g*-**Ax** and *g*-**Eq**):(*tr*-**Ax** and *tr*-**Eq**) ratio is (80-69):(20-31)% from QC results, that excellently agrees with experimental values. The studies reported in last decades demonstrated the GED method in combination with QC calculations as a powerful tool for gas-phase molecular structure determination even for relatively bulky and flexible species with 'rich conformeric variety', for example, amino acids [31].

An attempt to freeze the conformational equilibrium (13C NMR spectra) has been undertaken. Unlike many other successful cases of silacyclohexane derivatives ([2,3,5-10], etc.), in this it failed, most likely because of the low ring inversion barrier of the 1,3,5-trisilacylohexane ring system. However, our results presented herein will inspire us to examine more examples of that ring system.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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