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1-Methylthio-1-phenyl-1-silacyclohexane: Synthesis, Conformational Preferences in Gas and Solution by GED, NMR and Theoretical Calculations

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ABSTRACT:

1-Methylthio-1-phenyl-1-silacyclohexane **1**, the first silacyclohexane with the sulfur atom at silicon, was synthesized and its molecular structure and conformational preferences studied by gas-phase electron diffraction (GED) and low temperature ^{13}C and ^{29}Si NMR spectroscopy (LT NMR). Quantum-chemical calculations were carried out both for the isolated species and solvate complexes in gas and in polar medium. The predominance of the **1**-MeS$_{ax}$Ph$_{eq}$ conformer in gas phase (**1**-Ph$_{eq}$:**1**-Ph$_{ax}$ = 55:45, $\Delta G°$ = 0.13 kcal/mol) determined from GED is consistent with that measured in the freon solution by LT NMR (**1**-Ph$_{eq}$:**1**-Ph$_{ax}$ = 65:35, $\Delta G°$ = 0.12 kcal/mol), the experimentally measured ratios being close to that estimated by quantum chemical calculations at both the DFT and MP2 levels of theory.

Keywords: 1-Methylthio-1-phenyl-1-silacyclohexane; Conformational analysis; Gas phase electron diffraction; Low-temperature ^{13}C and ^{29}Si NMR; DFT and MP2 calculations.

1. Introduction

Nowadays, a large number of silacyclohexanes, mono and disubstituted at silicon, and silaheterocyclohexanes has been studied experimentally from the viewpoint of their conformational preferences both in gas phase and in a freon solution, as reviewed in 2016[1] and reported later.[2–13] Among these sila(hetero)cyclohexanes the Si−Ph compounds, which possess a second substituent at silicon such as H, Me,[14–18,] OR,[4, 7] F, Cl, Br,[19] Me_2N,[20] are of special interest for the present work because the conformational energies of substituents in silacyclohexanes are additive (in the parent cyclohexanes they are much more distinct but non-additive), and because steric and electrostatic effects in the two series are of different importance.[21]

The conformational analysis of Si−Ph silacyclohexanes having as the second substituent at silicon the O, N, F, Cl, Br heteroatoms[4,19,20] showed that in the gas phase at room temperature they exist predominantly as $Si{-}Ph_{ax}$ conformers (GED), but in a freon solution at low temperature the $Si{-}Ph_{eq}$ conformers predominate (LT NMR, ~100 K). The latter result is in agreement with the conformational equilibria of the cyclohexyl derivatives and the mono- and di-Si-substituted silacyclohexanes. Although the C−Si bonds are considerably longer than the C−C bonds in the cyclohexyl analogues, the more bulky substituent still goes into the equatorial, whereas the less bulky and more polar substituents into the axial position; the differences are much less distinct as in the corresponding cyclohexyl derivatives but clearly indicated.

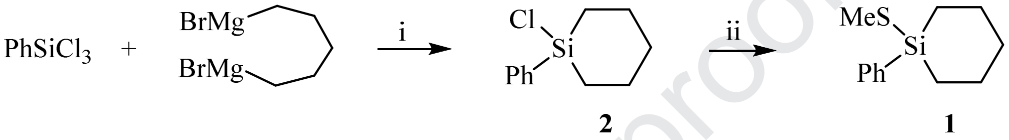
The above set of substituents includes heteroatoms O, N and Hal, which all are more electronegative than carbon. The only available heteroatom having electronegativity close to carbon is sulfur (2.50 and 2.44), but no sila(hetero)cyclohexanes with exocyclic sulfur atom at silicon were known in the literature. Therefore, our first task was to synthesize 1-methylthio-1-phenyl-1-silacyclohexane, as the simplest representative, and then to investigate it in gas phase (by GED method), in the freon solution (at low temperature by LT NMR spectroscopy) and theoretically at the DFT and MP2 levels of theory.

2. Results and discussion

2.1 Synthesis.

The simplest way to the target 1-methylthio-1-phenyl-1-silacyclohexane **1** is substitution of chlorine in 1-chloro-1-phenyl-1-silacyclohexane **2** with sodium methanethiolate. Compound **2** was synthesized by the known procedure employing the reaction of the Grignard reagent prepared from 1,5-dibromopentane with phenyltrichlorosilane.[22] The reaction of **2** with suspension of MeSNa in benzene was performed in an inert atmosphere under dry conditions in the presence of dibenzo-18-crown-6 as phase-transfer catalyst. Pure **1** was isolated in 55% yield by vacuum distillation (**Scheme 1**).

Scheme 1. Synthesis of heterocycle **1**. Reagents and conditions: (i) Et_2O, reflux for 5 h under Ar; (ii) MeSNa, benzene, dibenzo-18-crown-6 (0.10 mol %), reflux for 3 h under Ar.



2.2 Quantum chemical calculations.

The PES profiles of molecule **1** were obtained by scanning the $C_{ipso}SiSC$ (φ) and $C_{orth}C_{ipso}SiS$ (θ) dihedral angles describing the rotation of the methylthio group about the Si–S bond and the phenyl ring about the Si–C_{ipso} bond are plotted in **Figure 1**. As follows from these profiles, rotation of the two groups is strongly correlated, which is typical for gear motion in molecular motors as was demonstrated in our recent works on related compounds, 1-X-1-phenyl-1-silacyclohexanes with X= Me,[3] MeO, HO[4, 7] and Me_2N.[6] In order to clarify this influence, we have calculated the PES profiles at the M062X/6-311G** level for both axial and equatorial conformers on a grid of points corresponding to the torsion angles about the Si–C_{ipso} and Si–S bonds scanned with a step of 10º, the rest of the molecule being optimized (**Figure 2**).

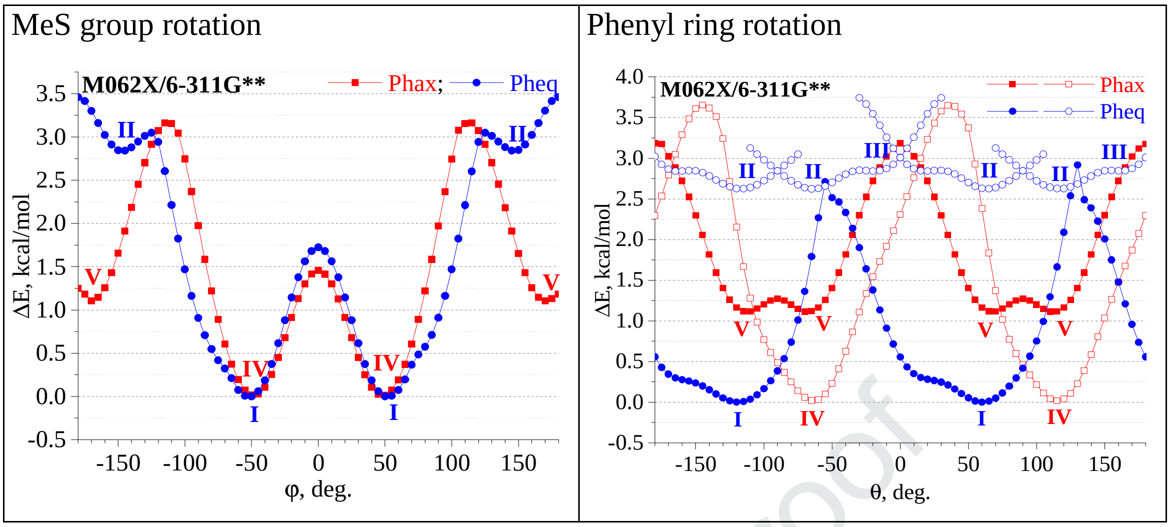


Figure 1. Lowest energy pathways for **1**-Ph$_{ax}$ and **1**-Ph$_{eq}$ conformers by rotating the MeS group about Si–S bond (left) and the phenyl ring about Si–C$_{ipso}$ bond (right) calculated at M062X/6-311G** level.

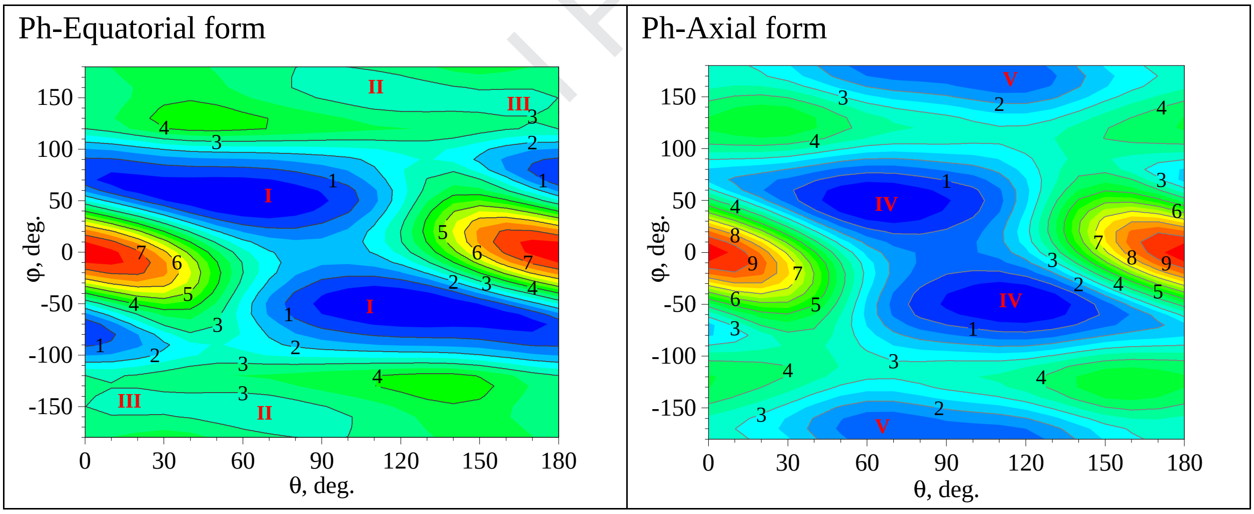


Figure 2. PES profiles of **1** obtained by synchronous scanning two angles, θ and φ, M062X/6-311G**, energy in kcal/mol.

The M062X calculations show that this compound has five possible conformers (neglecting the rotamers) with C$_1$ symmetry, see **Figure 3**. Note that the energy barriers for the phenyl ring rotation between conformers **III→II** is very low, 0.01 kcal/mol, and conformer **III** has the lowest frequency of 18 cm^{-1}, corresponding to the phenyl ring rotation. At the same time, from the B3LYP and MP2 results, conformer **III** is unstable and readily converges to conformer **II** when being optimized. Thus, molecule **1** has only four conformers: two **1**-Ph$_{eq}$

and two **1**-Ph$_{ax}$. Compared to the 1-methoxy- and 1-hydroxy-1-phenyl-1-silacyclohexanes, the **1**-Ph$_{ax}$ conformer, in which the phenyl ring lies in the bisect plane of the silacyclohexane frame, does not exist due to orbital interaction and steric repulsion between the two substituents at silicon.

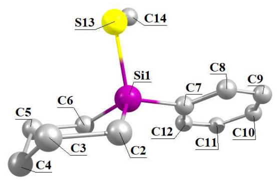
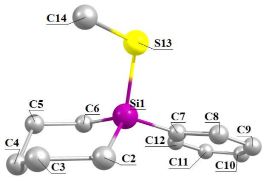
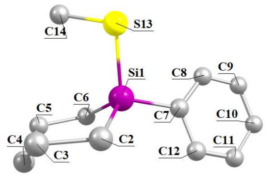
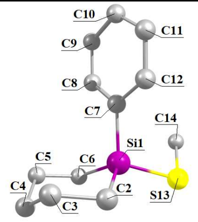
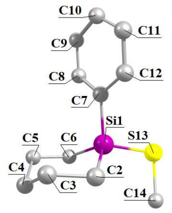
				
I	**II**	**III**	**IV**	**V**

Figure 3. Conformers of compound **1**, hydrogen atoms are omitted.

As a rule, for the series 1-X-1-Ph-1-silacyclohexanes (X = Me, MeO, HO, Me$_2$N), in molecule **1** the methylthio group rotation induces the phenyl ring rotation in Ph$_{eq}$ forms, whereas the phenyl group rotation does not noticeably affect the methylthio group orientation. From the M062X/6-311G** results, the energy barriers for the MeS group rotation between conformers **I**→**II** and **IV**→**V** are *ca*. 3.0 and 3.2 kcal/mol, respectively. Comparing to 1-methoxy-1-phenyl-1-silacyclohexane, replacement of methoxy group at silicon[4] by the bulkier methylthio group increases the repulsion between the two substituents and, hence, the energy barrier.

The relative total electron and Gibbs free energies (kcal/mol) of all conformers are given in **Table 1**. As follow from QC calculations, the conformers **I** and **IV** are most stable, the Δ*E* and Δ*G* values of conformer **II** are higher by 2.20 and 2.47 kcal/mol, respectively, relative to conformer **I**. According to all the DFT/6-311G** calculations, conformers **I** and **IV** have very similar Δ*E* values and are more stable than others. It should be noted, that the use of more sophisticated basis set cc-pVTZ leads to the increase of Δ*E* value of conformer **IV** by 0.22 kcal/mol. Since the phenyl group is a bulkier substituent than the methylthio group, the Ph$_{eq}$ conformers are entropically more preferable, hence, the molar fraction of Ph$_{eq}$ conformer is higher than of Ph$_{ax}$. It is to be noted that the Δ*G*° values from DFT calculations show conformer **IV** to be less preferable than **I** by 0.5–0.6 kcal/mol. Of the QC computational methods employed, the DFT calculations predict conformer **I** to be the most stable. Total contribution of the Ph_{ax} conformers summed over all its rotamers varies within 31–39% at the DFT level. At the same time, at the MP2/6-311G** level of theory, conformer **IV** is lower in energy *E* by 0.43 kcal/mol and in free energy *G*° only 0.02 kcal/mol higher in energy than conformer **I**, suggesting the predominance of **1**-Ph_{ax} conformer (from ΔE) or practically equal contribution of the two conformers (from $\Delta G°$). However, the use of a higher-level basis set cc-pVTZ for MP2 calculations inverts this result so that the most stable rotamers of **1**-Ph_{ax} and **1**-Ph_{eq} conformers become practically identical in energy (ΔE = 0.023 kcal/mol in favor of **1**-Ph_{eq}). Vibrational calculations at MP2/cc-pVTZ level are too costly, so the ZPE and entropy corrections to ΔE were taken from MP2/6-311G** calculations resulting in $\Delta G°$ for equation (1) of –0.47 kcal/mol and the **1**-Ph_{eq}:**1**-Ph_{ax} ratio of 64:36 (Table 1). This ratio virtually coincides with the calculated at various DFT levels (Table 1) as well as with those measured experimentally in gas phase [**I**:**IV**:**V**=55(15):35(15):10(10), GED] and in the freon solution (**1**-Ph_{eq}:**1**-Ph_{ax} = 65:35, LT NMR) – *vide infra*.

Table 1. Relative total electron energies ΔE [E(**1**-Ph_{ax}) – E(**1**-Ph_{eq})] and Gibbs free energies $\Delta G°$ [$G°$(**1**-Ph_{ax}) – $G°$(**1**-Ph_{eq}), kcal/mol] and predicted contribution X of conformers of **1**.

	$-\Delta E$					$-\Delta G°$ (298 K)					X, %
Method/basis set	**I**	**II**	**III**	**IV**	**V**	**I**	**II**	**III**	**IV**	**V**	**I:IV:V**
B3LYPD3/6–311G**	0	2.20	–	–0.01	0.84	0	2.47	–	0.47	1.17	63:28:9
B3LYPD3/cc–pVTZ	0	2.32	–	0.22	0.95	0	2.60	–	0.45	1.06	61:29:10
M062X/6–311G**	0	2.62	2.84	0.02	1.11	0	3.16	3.40	0.45	1.41	64:30:6
M062X/cc–pVTZ	0	2.68	2.70	0.22	1.14	0	3.38	3.34	0.62	1.39	69:24:7
MP2/6–311G**	0	2.70	–	–0.43	0.59	0	2.80	–	0.02	0.87	46:44:10
MP2/cc–pVTZ	0	–	–	0.023	–	0	–	–	(0.47)	–	64:36

2.3 Gas Electron Diffraction (GED) analysis.

Based on the $\Delta G°$ values in **Table 1**, conformer **I** is favorable with respect to conformers **IV** and **V** because of strong steric repulsion between the phenyl and silacyclohexane ring (1,3-diaxial interactions). Conformers **II** and **III** are much higher in terms of ΔE and $\Delta G°$ values and, thus, may be excluded from further consideration. For this reason, we assume the investigated vapor over liquid at 333(3) K to consist of three conformers, namely **I**, **IV** and **V** (*cf.* **Figure 3**).

The following independent geometric parameters were used to describe the geometry: bond distances Si–C2, C2–C3, C7–C8, Si–S, C–S and C2–H; bond angles SiC2C3, C7SiC2, C8C7Si, SSiC2, CSSi, HC2Si, HC2C3, HC8C7, HCS and HC14H; dihedral angles SiC2C3C4, C2C3C4C5, C8C7SiC2, CSSiC7 and HCSSi for conformer **I**; C8C7SiC2 and CSSiC7 for conformers **IV** and **V**. All other geometrical parameters for the conformers were described by parameters analogous to those in conformer **I** and corrected by adding the differences adopted from M062X/6-311G** calculations. For the three studied conformers, the benzene ring was fixed to be planar since the QC calculations showed very small deviations from planarity.

The experimental and theoretical molecular scattering intensities sM(s) and radial distribution curves f(r) with the corresponding differences “Experim.–Theor.” are plotted in **Figure 4**. Vibrational amplitudes for all three conformers were refined in nine groups according to the specific regions in the radial distribution: 0–1.20; 1.20–1.70; 1.70–2.02; 2.02–2.30; 2.30–2.64; 2.64–3.02; 3.02–3.91; 3.91–6.06 and 6.06–10.0 Å. The differences between the amplitudes within each group were constrained to the calculated values. Vibrational corrections $\Delta r = r_{h_1} - r_a$ and starting root-mean square amplitudes were calculated with the Vibmodule program[23] 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.

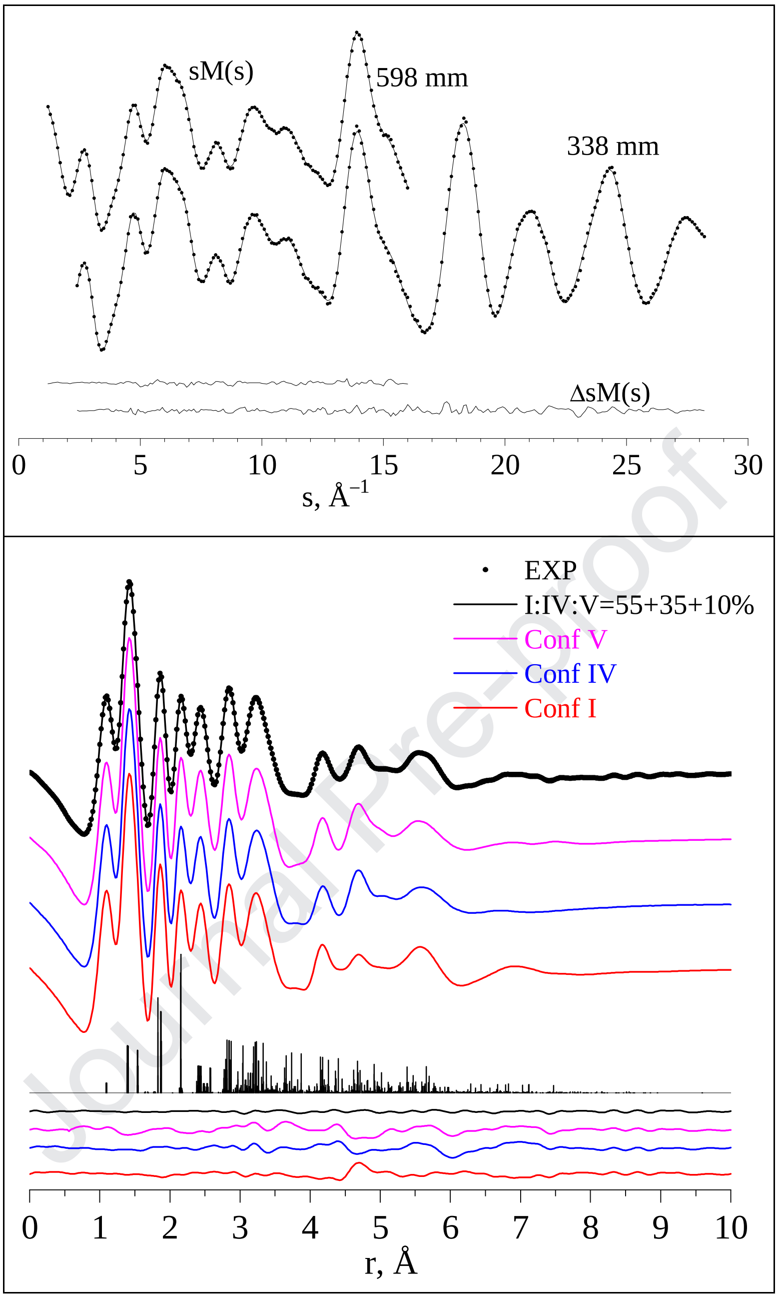


Figure 4. Molecular scattering intensities sM(s) (above) and radial distribution curves f(r) (below): experimental (dots) and theoretical (black line) for refined mixture of the conformers **I**:**IV**:**V**=55(15):35(15):10(10)%; colored lines correspond to refinement of all parameters under assumptions of individual conformers; the differences "Experim.-Theor." are given at the bottom.

The optimal conformer ratio of compound **1** was found to be **I**:**IV**:**V**=55(15):35(15):10(10)% [Ph_{ax}:Ph_{eq}=55(15):45(15)%] with the uncertainty estimated using Hamilton's criterion at 0.05 significance level ($R_{f,min}$= 4.17%), see **Figure 5**. Thus, from GED analysis, relative Gibbs free energies between the Ph_{ax} and Ph_{eq} conformers were estimated as $\Delta G°(333K) = G°_{ax} - G°_{eq}$ = 0.13(40) kcal/mol [the values of ΔG(333K) of conformers **I**:**IV**:**V** are 0:0.30:1.13 kcal/mol]. Clearly, the theoretical results very well agree with experimental GED data. For comparison, the ratios Ph_{eq}:Ph_{ax} of 1-phenyl-1-(X)-silacyclohexanes are 62(10):38(10), 42(15):58(15), 20(15):80(15), 30(15):70(15) and 50(20):50(15) for X of H,[14] Me,[14] Me_2N,[6] MeO[4] and HO group,[4] respectively.

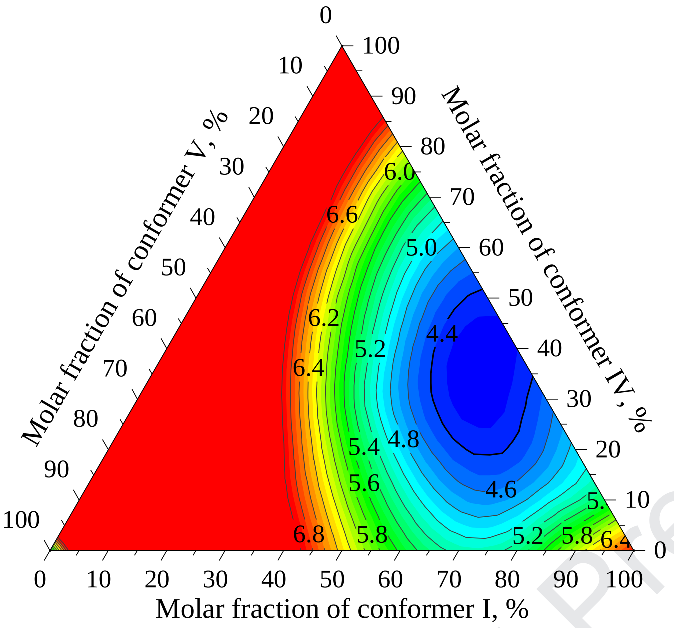


Figure 5. Agreement factor R_f as a function of molar fraction of the most stable conformers of compound **1**.

In addition, a goodness of fit was checked by running the KCED program with no refinement of geometry and vibrational parameters of all three conformers of the compounds for the theoretical models built on the M062X/6-311G** calculations; the tests resulted in the following R-factors: 7.1, 8.1 and 12.4% in the case of individual conformers **I**, **IV** and **V**, respectively.

Geometry and NBO analysis. Selected experimental (GED) along with the calculated (QC) geometric parameters of the three most stable conformers **I**, **IV** and **V** of compound **1** are compiled in **Table 2**. As follows from QC results, the C–C bond distances of silacyclohexane ring do not depend on position and orientation of the substituents. Due to steric repulsion between the two rings, the Si–C_{ipso} bond distance in conformer **IV** is longer by 0.005 Å than that in conformer **I**. The MP2 method predicts shorter Si−S and S−C bond distances by 0.008-0.009 Å and longer C−C bond distances of phenyl ring by 0.007-0.010 Å than the M062X calculations. In conformers **I** and **IV**, the steric repulsion between the methyl group and two rings leads to increase of the C(7)−Si−S bond angle by *ca*. 3º. The θ angles of both Ph_{ax} conformers **IV** and **V** differ by 4–6º, i.e. the rotation of the methylthio group does not strongly influence the orientation of the phenyl ring.

The calculated bond distances and bond angles are in good agreement with the GED values. The MP2 calculations very well predict Si–S, S–C and sesquialteral C–C bond distances. The experimental dihedral angles φ and θ were refined for the conformers **I**, **IV** and **V** with big uncertainty, in agreement with the theoretical predictions. The Si–S bond is not perpendicular to the phenyl ring plane in the axial and equatorial forms. The bond length of the term Si−S, despite low multiplicity, was derived reliably with high precision (standard deviation 0.0008 Å) due to it is quite well resolved in the radial distribution, see **Figure 4** at *ca*. 2.15Å and **Table 2**. Experimental and theoretical geometric and vibrational parameters of all conformers are summarized in *Supplementary data, Tables S4–S6*.

As follows from the NBO analysis, the orbital interaction between the electron lone pairs of sulfur atom and Si–C_{ipso} bond leads to the Si–C_{ipso} bond distance elongation in conformer **IV** by 0.005 Å, comparing to that in conformer **V**. This orbital interaction LP(S)→ σ*(Si–C7) also leads to stability of conformers **I** and **IV**. In addition, the NBO analysis shows that the steric effect stabilizes the equatorial form **I** at M062X/6-311G** level of theory. However, as concluded from the MP2/6-311G** results, the steric effect stabilizes the axial conformer **IV**.

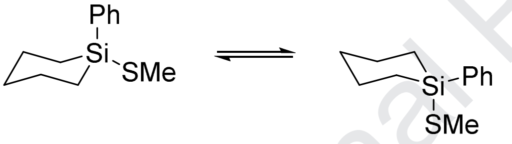
Table 2. Theoretical (with 6-311G** basis set) and experimental parameters,[a] the second-order perturbation energy $E^{(2)}$ LP(S)→σ*(Si–C), relative total steric energy $\Delta E^{(ST)}$ at the M062X and MP2 levels with 6-311G** basis set of three conformers (MP2/cc-pVTZ values are given in brackets).

Conformer	I			IV			V		
Method	M062X	MP2	GED	M062X	MP2	GED	M062X	MP2	GED
	Bond distance, Å								
Si–C2	1.875	1.874 (1.878)	1.872(4)	1.874	1.873 (1.877)	1.871(4)	1.879	1.878	1.876(4)
Si–C7	1.875	1.873 (1.876)	1.872(4)	1.881	1.877 (1.879)	1.878(4)	1.876	1.872	1.872(4)
Si–S	2.157	2.148 (2.150)	2.158(5)	2.151	2.143 (2.145)	2.152(5)	2.152	2.143	2.152(5)
C2–C3	1.542	1.542 (1.538)	1.542(3)	1.542	1.543 (1.539)	1.542(3)	1.542	1.543	1.543(3)
C7–C8	1.401	1.408 (1.404)	1.406(4)	1.399	1.408 (1.404)	1.404(4)	1.399	1.409	1.404(4)
C–S	1.831	1.824 (1.827)	1.828(4)	1.832	1.825 (1.828)	1.829(4)	1.831	1.825	1.828(4)
	Bond and torsion angles, º								
C7SiS	108.4	108.9 (108.3)	106.8(8)	108.5	108.7 (108.3)	108.1(8)	105.7	105.7	111.1(8)
SiSC	98.9	98.4 (98.5)	99.5(6)	99.0	98.7 (98.5)	99.5(6)	100.0	99.8	100.6(6)
φ	52.1	52.4 (54.6)	48(17)	48.1	46.5 (49.8)	58(25)	170.1	171.5	152(57)
θ	60.2	65.4 (43.8)	59(13)	63.8	68.3 (61.5)	55(32)	68.0	74.2	85(30)
	Second-order perturbation energy and total steric energy, kcal/mol								
LP(S)→ σ*(SiC6)	9.76	11.30		10.69	12.46		10.02	11.32	
LP(S)→ σ*(SiC7)	6.83	7.91		6.29	6.85		–	–	
ΔE^{ST}	0	0		–0.75	1.15		–0.50	–0.11	

[a] See Figure 3 for atom numbering and text above for angles φ and θ definition. Values in parentheses for the GED data are full errors estimated as $\sigma(r_{h1})=[\sigma_{scale}^{2}+(2.5\sigma_{LS})^{2}]^{½}$ and as $3\sigma_{LS}$ for angles, where σ_{scale} =0.002r and σ_{LS} is a standard deviation in least-squares refinement for internuclear distances

2.4 Low-temperature dynamic NMR study.

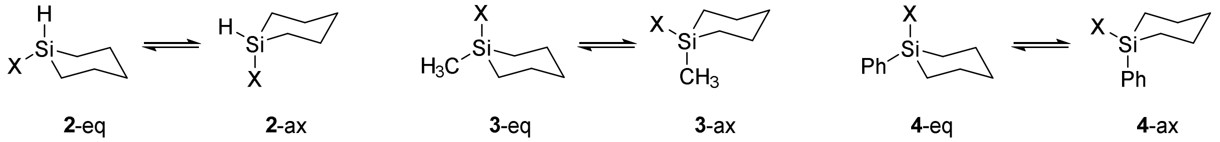
Room temperature ^{1}H, ^{13}C and ^{29}Si NMR spectra of compound **1** in CD_2Cl_2 confirm the structure of the compound (see *Supplementary Data*). The dynamic ring interconversion of the silacyclohexane ring is fast on the NMR time scale; thus, averaged ^{1}H/^{13}C signals and a single ^{29}Si signal of conformers **1**-Ph$_{ax}$ and **1**-Ph$_{eq}$ are observed. On cooling the solution of compound **1** in the freon mixture CD_2Cl_2 : $CHFCl_2$: CHF_2Cl = 1 : 1 : 3, which remains liquid below 100 K, the dynamic silacyclohexane ring interconversion process gets slow on the NMR time scale; the ^{1}H, ^{13}C and ^{29}Si NMR signals partly or completely split into separate signals of conformers **1-Ph$_{ax}$,SMe$_{eq}$** and **1-Ph$_{eq}$,SMe$_{ax}$** (*cf.* **Scheme 2**). This allowed full conformational analysis to be performed. Note, that until very recently the ^{29}Si NMR was not used for conformational analysis of silacyclohexane or any related Si-containing compounds. The first and so far the only example is our recent work on (1,1′-phenyl-1,1′-silacyclohex-1-yl)disiloxane.[24]



1-Ph$_{ax}$,SMe$_{eq}$ **1-Ph$_{eq}$,SMe$_{ax}$**

Scheme 2. Conformational equilibrium of 1-Methylthio-1-phenyl-1-silacyclohexane **1**.

1-Methylthio-1-phenyl-1-silacyclohexane **1** is the first compound which can be employed to study the influence of the $C_2{-}Si{-}S{-}CH_3$ motif on both the barrier to ring interconversion and on the conformational equilibrium of the Si-disubstituted silacylohexanes. So far, monosubstituted silacyclohexanes (X = Me, CF_3, SiH_3, CN, F, Cl, Br, I, OMe, NMe_2) **2**,[8−10, 12, 25−30] disubstituted analogues **3** containing a methyl group at silicon (X = F, CF_3) [31] and disubstituted silacyclohexanes **4** (H, CH_3, F, Cl, OMe, NMe_2) with the phenyl group at silicon[2, 4, 6, 14,17] have been studied (*cf.* **Scheme 3**); the corresponding conformational equilibria have been investigated in the gas phase by GED, otherwise in solution by vibrational spectroscopy and/or low temperature NMR spectroscopy.



Scheme 3. Conformational equilibria of various mono- and di-Si-substituted silacyclohexanes.

In series **2**, CH_3, SiH_3 and C≡N prefer the equatorial conformation. The substituents F, CF_3, Cl, Br, I, OMe and NMe_2 in **2**, however, were found as preferred axial conformers (unlike in the corresponding cyclohexanes, where they still remain equatorial). This trend is continuing in the di-substituted derivatives **3**: the methyl group remains in the equatorial, the more polar substituents (CF_3, F and Cl) change to the axial position. Finally, the phenyl analogues **4**: Depending on temperature in the gas phase (GED) and in the freon solution (LT NMR spectroscopy) the conformational preferences may be different. At room temperature in the gas phase the $\mathbf{Ph_{ax}}$ conformer is the preferred one, whereas in the freon solution at ca. 100 K the corresponding $\mathbf{Ph_{eq}}$ conformer predominates. The latter result is in agreement with the evident trend of a more bulky substituent (Ph) to occupy the equatorial position and the other substituent – less bulky and/or more electronegative – to go to the axial position; the differences are much less distinct as in the corresponding cyclohexyl derivatives but clearly indicating.

First, we calculated the free energy of activation of the silacyclohexane ring interconversion ($\Delta G^{\neq}$) of compound **1**. In **Figure 6** are given the relevant ^{13}C NMR data for the C_{ipso} carbon signal. The coalescence temperature (T_c) was found at 123 K, the chemical shift difference ($\Delta\nu$ = 317 Hz) of the ^{13}C NMR signals of the two conformers was measured at 98 K, the lowest temperature obtained with the local NMR facility. Together with the rate constant $k_c = \pi\ \Delta\nu/\sqrt{2} = 704.2$ *via* $\Delta G^{\neq} = 19.14\ T_c\ (10.32 + \log T_c/k_c)$ the barrier to ring interconversion of 5.8 kcal/mol was obtained, quite normal for the ring interconversion in the so-far studied Si-disubstituted silacyclohexanes.[2–19]

The barrier to the 6-membered ring interconversion was also calculated by the same procedure examining the ^{29}Si NMR signal, and the ^{13}C NMR signals of $C^{3,5}$ and of the SMe carbon of **1**. As to the ^{1}H NMR spectra, in spite of splitting of some signals at low temperature (not the SMe singlet), even at 98 K there are too many poorly resolved and overlapping signals, so that the assignments could not be easily done (see *Supplementary data*).

Theoretical estimation of the barrier to ring inversion by calculating the transition state (TS) at the same MP2 level as for conformers of **1** are too time-consuming, so, it was done at the MP2/6-311G**//MP2/6-31G** level, that is, on the geometry optimized with a slightly smaller basis set. The energy of TS is higher than that of conformers **1-Ph$_{ax}$,SMe$_{eq}$** and **1-Ph$_{eq}$,SMe$_{ax}$** by 3.9 and 3.4 kcal/mol, respectively, which is in satisfactory agreement both with the experiment and the barriers for the previously studied related silacyclohexanes.[21] However, it must be mentioned that the imaginary frequency from MP2/6-31G** vibrational calculations is as low as –41 cm^{-1} and, moreover, this vibrational mode corresponds not only to the distortion of the silacyclohexane ring from the chair conformation but mainly to rotational vibrations of the phenyl ring about the Si–C$_{ipso}$ bond, so, it cannot be considered as a reliable TS for the ring interconversion.

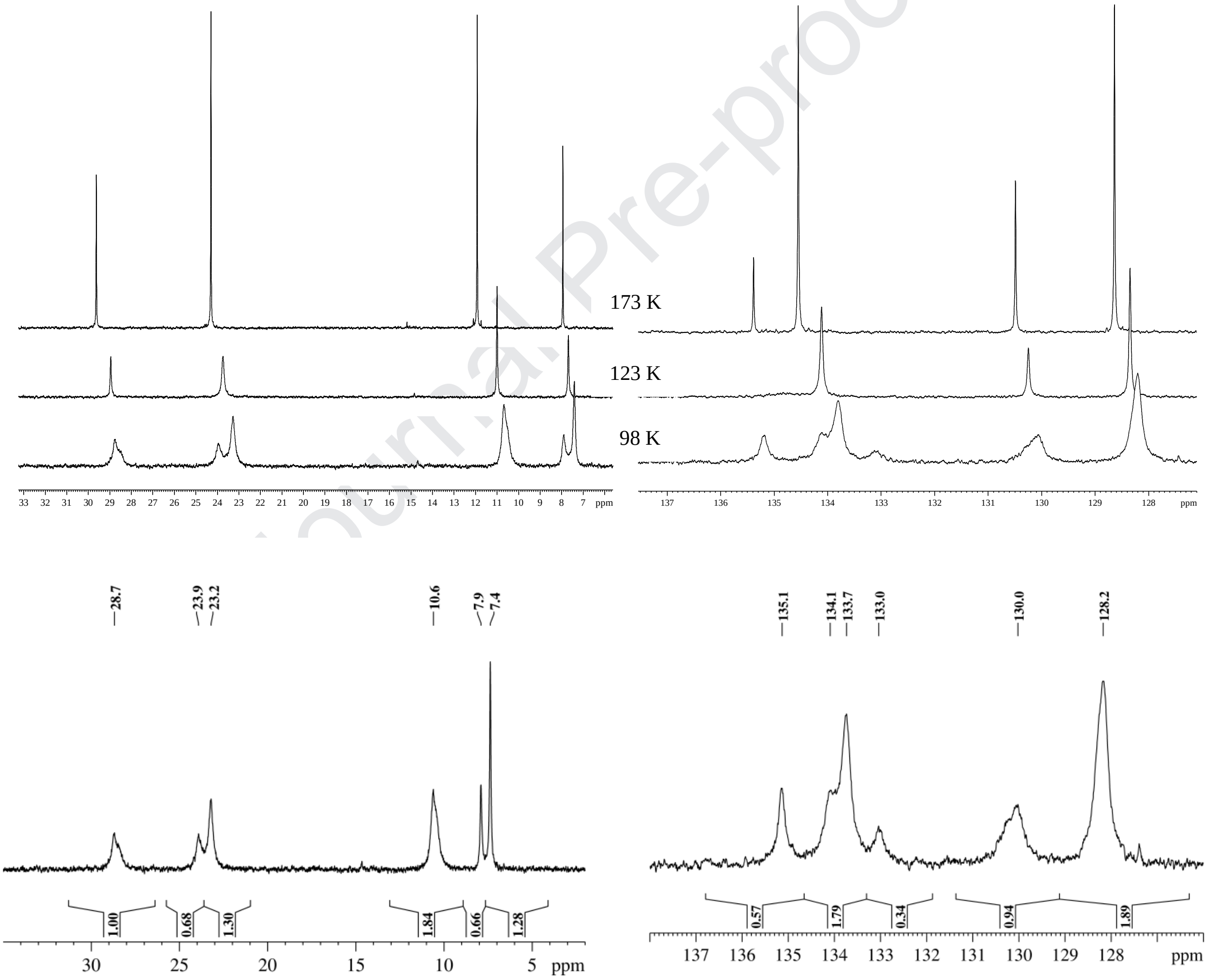


Figure 6. ^{13}C NMR spectra of 1-phenyl-1-SMe-1-silacylohexane **1** at various temperatures (above: 173 K, 123 K, 98 K; below: at 98 K, all in the freon solution).

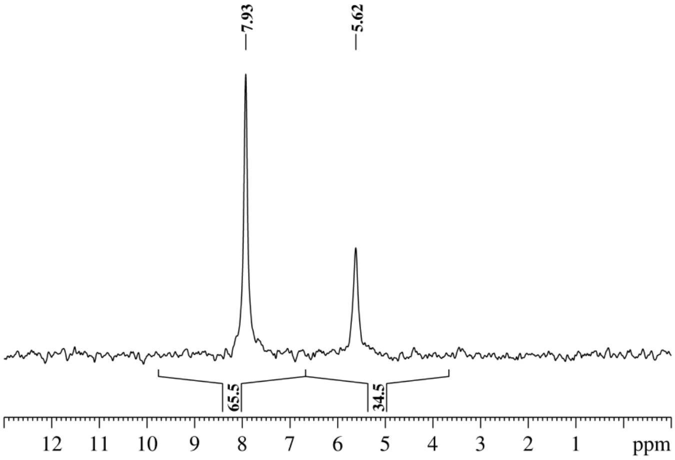


Figure 7. ^{29}Si NMR spectrum of 1-methylthio-1-phenyl-1-silacyclohexane **1** at 98 K in the freon solution.

Second, the different contribution of the two conformers in the present conformational equilibrium was determined. The ^{29}Si (*cf.* **Figure 7**), ^{13}C signals of C_{ipso}, $C^{3,5}$ and the SMe carbon atom at 98 K (*cf.* **Figure 6**) were integrated (K = [65.7]/[34.3] = 1.90 and evaluated accordingly $-\Delta G° = RT_c \ln K = \pm 0.12$ kcal/mol). To determine the sign of $\Delta G°$ and, hence, the structure predominating in the conformational equilibrium (*cf.* **Scheme 2**), it is necessary to assign the ^{13}C and ^{29}Si signals in the low temperature NMR spectra to specific conformers. Based on the comparison of theoretically calculated and experimental chemical shifts (**Table 3**), as well as on the above brief analysis of conformational preferences of the Si(Ph,X) disubstituted silacyclohexanes, the major conformer was assigned to the **1**-Ph_{eq} conformer (65.5%, $\Delta G°$ = 0.12 kcal/mol). This is in agreement with the conformational equilibria of the other so far studied disubstituted silacyclohexanes as obtained by low temperature NMR spectra. The differences in $\Delta G°$ are only minor: for 1-X-1-Ph-silacyclohexanes (X = Me, F, Cl, OMe, NMe_2, SMe) they vary from −0.15 to −0.1 kcal/mol, but, as compared with the cyclohexyl analogues, there are parallel conformational dependences. The most bulky substituent Ph goes into the equatorial position (the **1**-Ph_{eq} conformer predominates), the others go into the axial position. (ii) In doing so, the most bulky among the other substituents (Me) shows the lowest percentage of **1**-Ph_{eq} conformer (63%), while and the least bulky and most polar ones (H, F, Cl) – the highest percentage of **1**-Ph_{eq} (76−82%). In between are X = NMe_2 (77%), OMe (69%) and SMe (66% of **1**-Ph_{eq} conformer), which are unsymmetrical rotors and can adopt the least hindered conformation by rotating their methyl group(s) away from the ring. (iii) When comparing X = OMe and SMe, a slightly larger axial preference of more polar OMe group is evident (69 vs. 66%). So, all together, the conformational behavior of substituted cyclohexanes persists for the same substituents in silacyclohexanes; the effects are only less pronounced due to the longer C−Si bond distances.

Table 3. Calculated (MP2/6-311G**) and experimental (**bold**) ^{29}Si and ^{13}C chemical shifts, δ, of **1**-Ph$_{ax}$ and **1**-Ph$_{eq}$ conformers$^{a)}$ of compound **1** and their difference $\Delta_{eq–a}$ (ppm).

Conformer	^{29}Si	$\Delta_{eq–ax}$	C$_{ipso}$	$\Delta_{eq–ax}$	C$_{meta}$	$\Delta_{eq–ax}$	C^{3,5}	$\Delta_{eq–ax}$	SCH$_3$	$\Delta_{eq–ax}$
1-Ph$_{ax}$	12.19		134.3		130.3		29.7		8.5	
	5.62	0.84	**133.0**	2.6	**135.1**	–0.4	**23.9**	–1.0	**7.9**	–0.6
1-Ph$_{eq}$	13.03	**2.31**	136.9	**1.1**	129.9	**–1.4**	28.7	**–0.7**	7.9	**–0.5**
	7.93		**134.1**		**133.7**		**23.2**		**7.4**	

$^{a)}$ The remaining carbon atoms (C$_{ortho}$, C$_{para}$, C^{2,4,6}, as well as all ^{1}H NMR signals] do not split at 98 K.

In **Table 3**, the most convincing evidence of correct assignment is the calculated values of $\Delta_{eq–ax}$, which vary in parallel with the experimental ones and prove the predominance of the **1**-Ph$_{eq}$ conformer. Note, that the relative Gibbs free energies in Table 1 cannot strongly depend on the polarity of the medium because the **1**-Ph$_{eq}$ and **1**-Ph$_{ax}$ conformers have very close calculated dipole moments differing by ~0.1 D (depending on the method used). Therefore, the predominance of the **1**-Ph$_{eq}$ conformer in gas phase, which is retained in the Freon mixture used should probably retain in other solvents of different polarity.

3. Conclusions

In conclusion, we have synthesized 1-methylthio-1-phenylsilacyclohexane **1**, the first silacyclohexane with the sulfur atom at silicon and performed its conformational analysis by GED, low-temperature NMR and theoretical calculations. In gas phase, the three lowest-lying conformers were found to be **1**-Ph$_{eq}$ and **1**-Ph$_{ax}$ (two rotamers about the Si–S bonds) in the ratio of 55:45% corresponding to $\Delta G°$(333K) = 0.13 kcal/mol. In the freon solution, LT NMR spectroscopy showed decoalescence of some ^{13}C and ^{29}Si signals at ca. 100 K, allowing to measure a somewhat larger **1**-Ph$_{eq}$:**1**-Ph$_{ax}$ ratio of 65:35% corresponding to $\Delta G°$(98K) = 0.12 kcal/mol. The signals were assigned to specific conformers based on quantum-chemical calculations, including both the energy and NMR calculations, as well as by comparison to the earlier studied analogues. The dynamic NMR analysis also allowed to determine the barrier to interconversion of the silacyclohexane ring ($\Delta G^{\neq}$ = 5.8 kcal/mol), which is typical for barriers measured by us earlier for other silacyclohexanes. Theoretical calculations are consistent with the experiment, proving a higher stability of **1**-Ph_{eq} conformer by up to 0.5 kcal/mol depending on the method and basis set used.

4. Experimental Section

4.1 General.

IR spectra were taken on a Bruker Vertex 70 instrument. Chemicals and technical grade solvents (hexane, triethylamine) were distilled prior to use over CaH_2. Room temperature ^{1}H, ^{13}C and ^{29}Si NMR spectra were registered on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 100 (^{13}C) and 79 MHz (^{29}Si) in $CDCl_3$. Low temperature ^{29}Si and ^{13}C NMR spectra were recorded on a Bruker AVANCE-600 instrument (at 119.2 MHz and 150.95 MHz, respectively). Chemical shifts were determined relative to residual $CHCl_3$ (^{1}H, 7.27 ppm), internal $CDCl_3$ (^{13}C, 77.0 ppm), and internal CD_2Cl_2 (^{13}C, 53.73 ppm). Analysis and assignment of the ^{1}H NMR data were supported by homonuclear (COSY) and heteronuclear (HSQC and HMBC) correlation experiments. A solvent mixture of CD_2Cl_2, $CHFCl_2$, and CHF_2Cl in a ratio of 1:1:3 was employed for the low temperature measurements because of being still liquid at around 100 K. The probe temperature was calibrated by means of a thermocouple PT 100 inserted into a dummy tube. The low temperature measurements were estimated to be accurate to ±1°. EI mass spectra (70 eV) were obtained on a GC-MS-QP5050A Shimadzu chromatomass spectrometer with quadruple mass analyzer, capillary column Ultra 2, 0.2 mm × 50 m, gas carrier – helium. Solvents were purified and dried by standard procedures and stored over molecular sieves 4Å. All reactions were performed in flame-dried glassware under argon atmosphere.

4.2 Synthesis.

Three-neck flask equipped with condenser, dropping funnel, thermometer and protected from air moisture was filled with argon and charged with 1 g (0.014 mol) of MeSNa (Acros Organics), 1.061 g (0.10 mol%) of dibenzo-18-crown-6 and 15 ml of benzene. Then, 3.011 g (0.014 mol) of 1-chloro-1-phenyl-1-silacyclohexane **2** was added dropwise during 15 min at vigorous stirring, the mixture refluxed for 3 h, cooled to room temperature, concentrated in vacuum (45 mm Hg). The residue was treated with hexane and filtered through

Schott filter under Ar. After vacuum distillation 1.745 g (55%) of 1-methylthio-1-phenyl-1-silacyclohexane **1** (b.p. 148–9 ^{o}C/1 mm Hg) was isolated. IR spectrum (film), ν, cm^{-1}: 3062 (Ph), 2919 (CH_2), 2852, 1433 ($SiCH_2$), 1109 (SiPh). ^{1}H NMR, δ, ppm: 1.13 dd (2H, SiCH^{A}, *J* 5.2, 1.9 Hz), 1.16 d (2H, SiCH^{B}, *J* 6.1 Hz), 1.44 dtt (1H, CH^{4A}, *J* 13.6, 9.1, 3.0 Hz) 1.55–1.65 m (1H, CH^{4B}), 1.73–1.87 m (4H, $CH_2^{3,5}$), 1.90 s (3H, SMe), 7.41–7.43 m (3H, H^{m,p}), 7.65–7.67 m (2H, H^{o}). ^{13}C NMR, δ_C, ppm: 8.20 (SMe), 12.63 ($C^{2,6}$), 24.12 ($C^{3,5}$), 29.62 (C^4), 127.99 (C^p), 129.75 (C^m), 134.06 (C^o), 135.10 (C^i). ^{29}Si NMR, δ_{Si}: 6.61 ppm. Mass spectrum, *m/z* (I_{rel}, %): 222(83) $[M]^+$, 175(100) $[M–CH_3S]^+$, 145(68) $[M–Ph]^+$, 121(70) $[C_6H_5SiHCH_3]^+$, 105 (86) $[PhSi]^+$, 96(80) $[C_5H_{10}Si]^+$. Found, %: C, 64.25; H, 7.91; Si, 12. 80; S 14.23. $C_{12}H_{18}SSi$. Calculated, %: C, 64.63; H, 8.05; Si, 12.61; S 14.41.

4.4 GED-MS experiments.

The diffraction patterns were recorded during a combined gas-phase electron diffraction and mass spectrometric experiment carried out using the EMR-100/APDM-1 unit at ISUCT.[32, 33] The samples were loaded into molybdenum effusion cell filled with crushed pieces of Schott filter (the details of the experiment see in the *Supplementary data*) and kept at 333(3) K in the course of the experiments for compound **1**. All operations with the sample were done in a glove box under argon atmosphere. The conditions of the GED/MS experiment and data refinement details are given in *Supplementary data, Table S1* and related chapters.

The EI mass spectra recorded simultaneously with the diffraction patterns showed at $U_{ioniz.}$ = 50 V, a noticeable molecular peak *m/z* = 222 a.m.u.(36), and a set of fragmented ions, such as: [M–SMe], *m/z* = 175 (90), [M–Ph] *m/z* = 146 (62), $[C_6H_5SiH]$, *m/z* = 106 (100), see also Table S3 in *Supplementary Data*. In order to check whether the daughter ions originated from the same molecule **1**, a set of mass spectra were recorded at lower electron energies: the molecular ion was left the only species at $U_{ioniz.}$ as low as ca.10 V.

4.5 Computational details.

All calculations were performed with Gaussian 09 program suite.[34] The geometry and vibrational calculations were performed using DFT (with 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 scanning C_{orth}–C_{ipso}–Si–S (θ) and C_{ipso}–Si–S–C (φ) dihedral angles with a step of 5^o and optimization of all other geometrical parameters at the M062X/6-311G** level of theory. Also, the energies at the M062X/6-311G** level for both conformers have been calculated on a grid of points corresponding to the Si–C_{ipso} and Si–S torsion angles varied with a step of 10^o with optimizations of all other geometric parameters.

The Natural Bond Orbital (NBO) analysis was performed at the M062X/6-311G** levels using the GenNBO program version 5.0.[35]

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi ...

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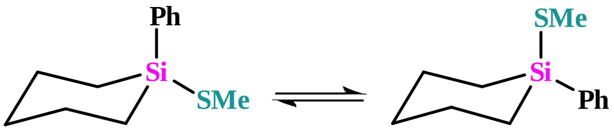
1-Methylthio-1-phenylsilacyclohexane: Synthesis, Conformational Preferences in Gas and Solution by GED, NMR and Theoretical Calculations

Bagrat A. Shainyan,* Elena N. Suslova, Tran Dinh Phien, Sergey A. Shlykov, Matthias Heydenreich and Erich Kleinpeter*

Graphical Abstract



$Ph_{ax}MeS_{eq}$ $Ph_{eq}MeS_{ax}$

	GED	NMR	Theory
$Ph_{ax}MeS_{eq}$: $Ph_{eq}MeS_{ax}$	45 : 55	35 : 65	33 : 67

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Highlights

- 1-Methylthio-1-phenylsilacyclohexane **1**, the first silacyclohexane with the sulfur atom at silicon was synthesized.
- The conformational analysis of **1** was performed by GED, low-temperature NMR spectroscopy and theoretical calculations.
- In gas phase, the three lowest-lying conformers were found to be **1**-Ph_{eq} and **1**-Ph_{ax} (two rotamers about the Si–S bons) in the ratio of 55:45% corresponding to $\Delta G°(333K) = 0.13$ kcal/mol.
- In a freon solution, LT NMR spectroscopy showed at ca. 100 K a conformational equilibrium **1**-Ph_{eq}:**1**-Ph_{ax} ratio of 65:35% corresponding to $\Delta G°(98K) = 0.12$ kcal/mol.
- The dynamic NMR analysis also allowed to determine the barrier to interconversion of the silacyclohexane ring ($\Delta G^{\neq} = 5.8$ kcal/mol).
- Theoretical calculations are consistent with the experiment, proving a higher stability of **1**-Ph_{eq} conformer by up to 0.5 kcal/mol depending on the method and basis set used.

1-Methylthio-1-phenyl-1-silacyclohexane: Synthesis, Conformational Preferences in Gas and Solution by GED, NMR and Theoretical Calculations

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ABSTRACT:

1-Methylthio-1-phenyl-1-silacyclohexane **1**, the first silacyclohexane with the sulfur atom at silicon, was synthesized and its molecular structure and conformational preferences studied by gas-phase electron diffraction (GED) and low temperature ^{13}C and ^{29}Si NMR spectroscopy (LT NMR). Quantum-chemical calculations were carried out both for the isolated species and solvate complexes in gas and in polar medium. The predominance of the **1**-MeS$_{ax}$Ph$_{eq}$ conformer in gas phase (**1**-Ph$_{eq}$:**1**-Ph$_{ax}$ = 55:45, $\Delta G°$ = 0.13 kcal/mol) determined from GED is consistent with that measured in the freon solution by LT NMR (**1**-Ph$_{eq}$:**1**-Ph$_{ax}$ = 65:35, $\Delta G°$ = 0.12 kcal/mol), the experimentally measured ratios being close to that estimated by quantum chemical calculations at both the DFT and MP2 levels of theory.

Keywords: 1-Methylthio-1-phenyl-1-silacyclohexane; Conformational analysis; Gas phase electron diffraction; Low-temperature ^{13}C and ^{29}Si NMR; DFT and MP2 calculations.

Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

~~☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:~~