1,3-Dimethyl-3-silapiperidine: Synthesis, Molecular Structure, and Conformational Analysis by Gas-Phase Electron Diffraction, Low Temperature NMR, IR and Raman Spectroscopy, and Quantum Chemical Calculations

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ⓈSupportingInformation

ABSTRACT: The first Si−H-containing azasilaheterocycle, 1,3-dimethyl-3-silapiperidine **1**, was synthesized, and its molecular structure and conformational properties were studied by gas-phase electron diffraction (GED), low temperature NMR, IR and Raman spectroscopy and quantum chemical calculations. The compound exists as a mixture of two conformers possessing the chair conformation with the equatorial NMe group and differing by axial or equatorial position of the SiMe group. In the gas phase, the SiMe$_{ax}$ conformer predominates (GED: ax/eq = 65(7):35(7)%, ΔG = 0.36(18) kcal/mol; IR: ax/eq = 62(5):38(5)%, ΔG = 0.16(7) kcal/mol). In solution, at 143 K the SiMe$_{eq}$ conformer predominates in the frozen equilibrium (NMR: ax/eq = 31.5(1.5):68.5(1.5)%, ΔG = −0.22(2) kcal/mol). Thermodynamic parameters of the ring inversion are determined ($\Delta G^{‡}$ = 8.9−9.0 kcal/mol, $\Delta H^{‡}$ = 9.6 kcal/mol, $\Delta S^{‡}$ = 2.1 eu). High-level quantum chemical calculations (MP2, G2, CCSD(T)) nicely reproduce the experimental geometry and the predominance of the axial conformer in the gas phase.
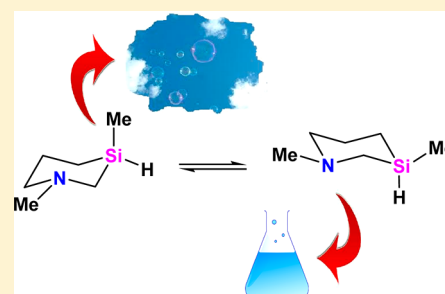
INTRODUCTION

The conformational analysis of saturated six-membered cyclic compounds has been one of the most active fields of research in stereochemistry for a long time.[1,2] A large body of experimental and theoretical studies has been carried out to rationalize the factors that control stereochemical preferences in substituted cyclohexanes and heterocyclohexanes. Of all the substituents that have carbon bonded to the cyclohexane ring, the methyl group is considered as a benchmark substituent in the conformational analysis of cyclohexanes. The conformational energy of the methyl group $-\Delta G°$ (or "A value") of 1.76 kcal/mol shows its strong equatorial preference.[3,4] Unfavorable 1,3-steric repulsion between an axial methyl group and axial ring hydrogens is usually considered to be the major factor in destabilizing the axial conformer of methylcyclohexane.[1,2] It was also suggested that the main factor destabilizing the axial conformation is repulsive steric interaction between an axial methyl group and the ring carbons, including the gauche torsional interaction.[3] The opposite opinion was voiced by Ribeiro and Rittner, who believed that steric effects cannot be the sole determinant of the conformational equilibrium of methylcyclohexane.[5] The relative role of steric and hyperconjugation effects was the subject of several studies,[5,6] and the

question is still open. The only thing that can be stated unequivocally is that there is a delicate balance between steric, electrostatic and hyperconjugation effects in heterocyclohexanes, which in turn depends on the presence, nature, and relative position of heteroatoms.[7]

To date, a great deal is known about the conformations of monomethylated heterocyclohexanes (oxanes,[8] thianes,[9,10] piperidines[10,11]). Considering only steric effects, the replacement of one or two methylene group(s) in the 3- or 3,5-positions of methylcyclohexane by a heteroatom must lead to a decrease of the equatorial preference, and this is the case for C-methylated heterocycles[8,12−14] (Chart 1). Note that, although the preference of the equatorial conformers of 3-methylheterocyclohexanes is lower than in methylcyclohexane, they still strongly predominate over the axial conformers (>95%).
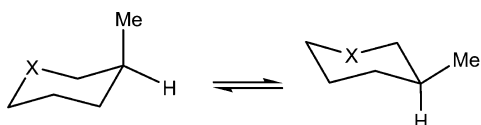
On going to 1-methyl-1-silacyclohexane[15−17] and 3-methyl-3-silathiane,[7] the equatorial preference of the methyl group drastically diminishes (Chart 2).

The increased population of the axial conformer and the decrease of the ring inversion barrier in these heterocycles as

Chart 1

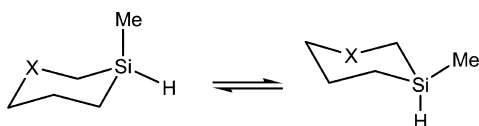| X	$A = -\Delta G^o$(eq - ax), kcal mol^{-1} [Ref.]
CH_2	1.76 [3]
NH	1.60 [12]
NMe	1.60 [12]
O	1.43 [13]
SiH_2	1.66 [14], 1.87 (our MP2/6-311G** calculations)
S	1.40 [8]

Chart 2

X	A, kcal mol^{-1} [Ref.]
CH_2	0.23 [15]
S	0.35 [7]
NMe	?

compared to the carbocyclic analogues (5−6 vs 10−11 kcal/mol) was explained by the longer endocyclic Si−C bond (1.904 Å) compared to the C−C bond (1.534 Å),[15,16] although stereoelectronic effects were also suggested to play an important role.[18−20] Two areas of the conformational energy A can be envisioned: for the C-methylated compounds (Chart 1) and the Si-methylated heterocycles (Chart 2). It is worth mentioning that the presence of silicon atom in the ring does not ensure itself a low A value, but only when the methyl group is attached to it (cf. 3-methyl-1-silacyclohexane in Chart 1 and 1-methyl-1-silacyclohexane in Chart 2). As follows from the literature data, the only two compounds that allow correct estimation of the conformational energy of the methyl group attached to silicon are 1-methyl-1-silacyclohexane and 3-methyl-1,3-thiasilinane. Recently we have studied a series of 3-silapiperidines (1,3-azasilinanes) bearing two substituents at silicon and different N-alkyl groups.[21−24] However, the lack of a reference point (here, 1,3-dimethyl-3-silapiperidine) does not allow us to analyze the conformation energies A in various silaheterocyclohexanes as a function of the nature of the heteroatom and the substituent at silicon. With this in mind, the goal of the present study was to synthesize the first Si−H-

containing azasilaheterocycle, 1,3-dimethyl-3-silapiperidine **1**, and to investigate its structure and conformational behavior experimentally (gas-phase electron diffraction, low temperature NMR, IR and Raman spectroscopy) and theoretically (DFT, MP2, CCSD(T), NBO analysis). Synthetically, 3-silapiperidines (among other silaheterocycles) are a subject of long-standing interest.[25] However, in contrast to a variety of Si-functional 4-silapiperidines (that is, compounds with a labile Si−X bond, including Si−H, Si−OR, Si−Hal), there are only two examples of Si-functional 3-silapiperidines, namely, with the Si−F[26] and Si−OR bond.[24] No Si−H-containing 3-silapiperidines were known so far.

■ RESULTS AND DISCUSSION

Synthesis. The synthesis of the 1,3-dimethyl-3-silapiperidine **1** was accomplished using the sequence of reactions outlined in Scheme 1 and including the Pt-catalyzed hydrosilylation of allyl chloride, replacement of chlorine by OR group in adduct **3**, heterocyclization of silane **4** by the action of methylamine, and reduction of compound **5** to the target product **1** by lithium aluminum hydride.

In the first step, the reaction of hydrosilylation of allyl chloride is known to be accompanied by its reduction to propylene, which can evolve from the reaction mixture or enter the reaction of hydrosilylation itself,[27] thus contaminating the target product **3**. The advantage of the use of urea instead of tertiary amines as a scavenger of HCl in the second step is that the formed urea hydrochloride is easily separated from the substitution product **4**. Finally, because of a high lability of the Si−H bond, the target product in the last step was isolated without water workup, according to a modified procedure.[22] Because of formation of hardly separable byproducts, the intermediate products **3**, **4** were used in the next step without further purification. The structure of the products was proved by the ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy.

Gas-Phase Electron Diffraction and Quantum Chemical Study. The interconversion of the chair conformers of 1,3-dimethyl-3-silapiperidine **1** includes the ring and nitrogen inversion. However, since the NMe group in 1-methylpiperidine ($A = 3.85$ kcal/mol[28]) and 1,3-dimethylpiperidine ($A = 1.6$[12] or 2.40 kcal/mol[29]) strongly prefers the equatorial position (see also Table 2 below), fast N-inversion simplifies the conformational analysis of **1** to consideration of only two conformers, **1a** and **1e**, as shown in Scheme 2.

The combined gas-phase electron diffraction and mass spectrometric experiment, GED/MS[30−32] was carried out at

Scheme 1

Scheme 2

1a ⇌ **1e**
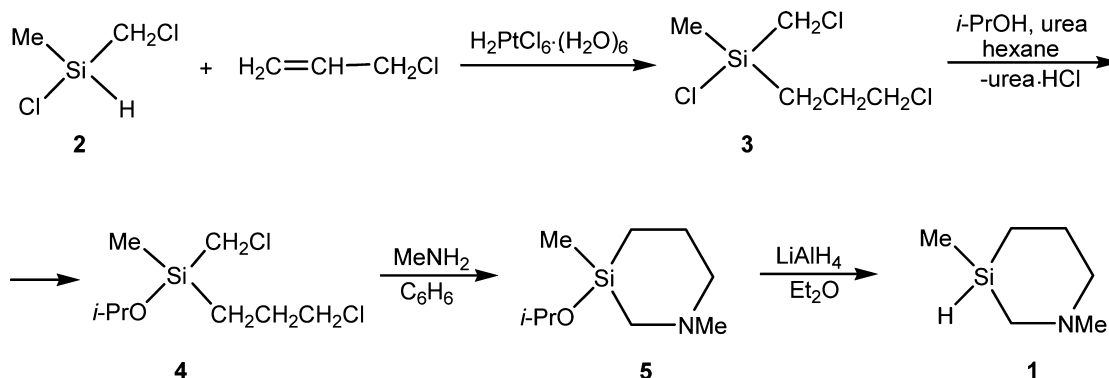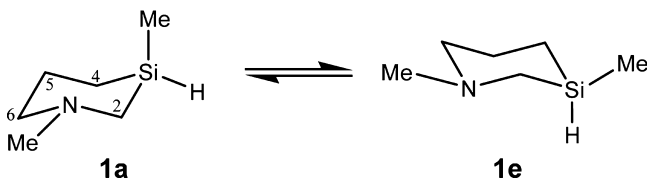
the effusion cell temperature 293(5) K. Mass spectra recorded at ionizing voltage U_i = 50 V showed a heaviest mass corresponding to the molecular ion and a set of lighter peaks, products of fragmentation under electron impact. Lowering the ionizing voltage down to ca. 12 V led to disappearing the peaks except the one of the molecular ion. This proves the absence of volatile impurities and decomposition products upon evaporating the sample. The dependence of the agreement factor on the conformational composition of compound **1** is shown in Figure 1, the experimental and theoretical $sM(s)$ curves along with
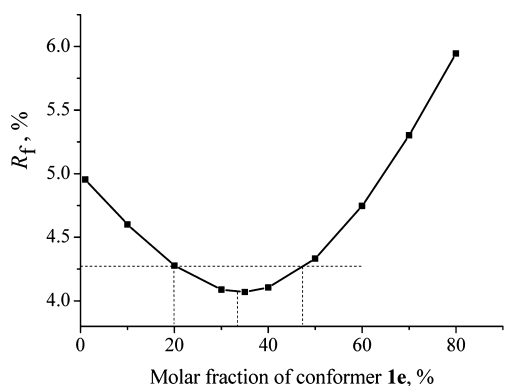

Figure 1. Agreement factor R_f as a function of molar fraction of **1e**. The horizontal line corresponds to the Hamilton criterion[33] at 0.05 significance level.

their differences $\Delta sM(s)$ are given in Figure 2, and the radial distribution curves $f(r)$ with the corresponding differences $\Delta f(r)$ are shown in Figure 3.
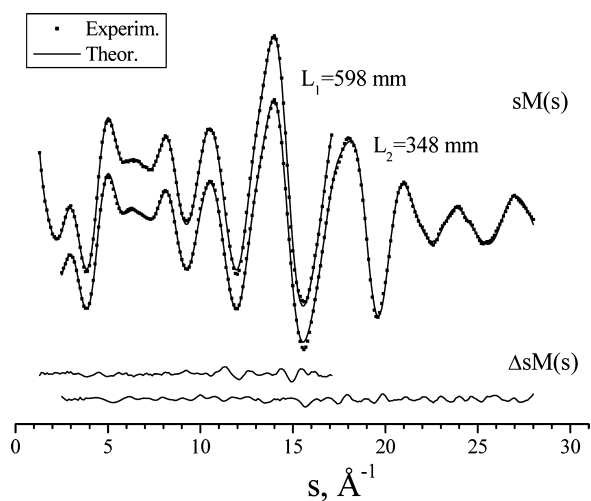

Figure 2. Experimental (dots) and theoretical (line) molecular scattering intensities. The difference curves "exp−theor" correspond to the optimized composition of the conformers.
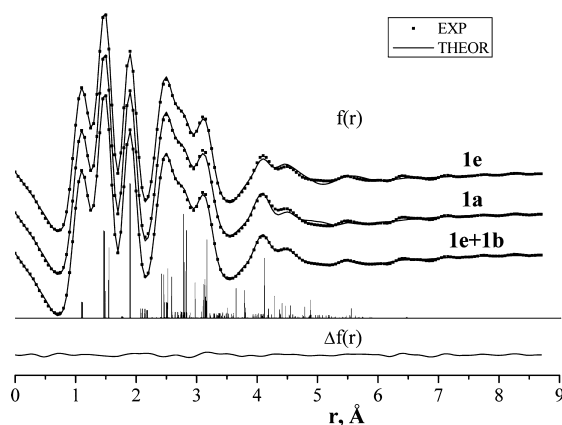

Figure 3. Radial distributions functions for conformers **1a**, **1e** and their mixture at refined composition 65(7)% **1a** and 35(7)% **1e**. All geometric and vibrational parameters were refined in all three cases. The difference curve $\Delta f(r)$ at the bottom is shown for the mixture.

From the plot in Figure 1, the contribution of conformer **1e** is between 20 and 47 mol %. Refinement of the conformers ratio along with the refinement of all geometric and vibrational parameters converged at 65(7)% **1a** and 35(7)% **1e**, where $3\sigma_{LS}$ is given in parentheses, R_f = 4.07%. The Gibbs free energy for the equilibrium **1a** ⇌ **1e** that corresponds to the GED results (65(7)% **1a** and 35(7)% **1e**) was estimated to be ΔG(293 K) = 0.36(18) kcal/mol.

The GED-determined and theoretically calculated geometries of compound **1a** are given in Table 1. The experimental geometrical parameters are very close to those of 1,3,3-trimethyl-3-silapiperidine[21] and are well reproduced by the methods employed.

Quantum chemical calculations of the conformers of compound **1** were performed at the DFT (B3LYP) and MP2 levels of theory with the cc-pVTZ basis set, at the G2 level, and as single-point CCSD(T) calculations with the MP2/cc-pVTZ optimized geometry using the Gaussian09 computational program.[34] No restrictions on the variation of geometric parameters were imposed during the optimization procedure. Vibrational calculations were performed in harmonic approximation at the B3LYP/cc-pVTZ level. The results are summarized in Table 2. It can be seen that, unlike DFT calculations, high level calculations (MP2, G2, CCSD(T)) give the SiMe$_{ax}$ conformer to be preferred in the gas phase in agreement with the GED experiment as well as with the results of IR and Raman spectroscopy (vide infra).

Molecular Spectroscopy. Along with GED and low temperature NMR, the IR and Raman spectroscopy and quantum chemical calculations are successfully used in conformational analysis of silacyclohexanes with the main focus made on the analysis of the ν(Si−C) bands.[35−40] Thus, 1-methyl-1-silacyclohexane, which is the most close to compound **1**, was shown by the temperature-dependent IR and Raman spectroscopy to exist as a mixture of two conformers in liquid, amorphous and plastic phases (with the equatorial conformer being predominant) and as the single equatorial conformer in the crystal.[39,40]

We have studied the conformational composition of compound **1** by FT-IR spectroscopy in the gas phase, in solution, in neat liquid, in the plastic phase (at 83 K) and by Raman spectroscopy. The assignment was based on DFT calculations of the conformers **1a** and **1e** at the B3LYP/cc-

Table 1. Selected Calculated and Experimental Geometrical Parameters[a] for 1,3-Dimethyl-3-silapiperidine 1 (cc-pVTZ Basis Set for DFT and MP2 Calculations)

1a	DFT	MP2	G2	1e	DFT	MP2	G2	exp(GED)[b]
				Bond distances				
Si−Me	1.885	1.877	1.890	Si−Me	1.886	1.879	1.890	1.881(4)
Si−H	1.492	1.487	1.484	Si−H	1.490	1.486	1.481	[1.490]
Si−C2	1.899	1.891	1.899	Si−C2	1.898	1.891	1.898	1.893(4)
N−C2	1.468	1.468	1.463	N−C2	1.467	1.465	1.461	1.472(4)
N−C6	1.463	1.461	1.456	N−C6	1.463	1.460	1.456	1.469(4)
C5−C6	1.531	1.525	1.531	C5−C6	1.531	1.525	1.531	1.534(8)
C4−C5	1.540	1.535	1.540	C4−C5	1.540	1.535	1.540	1.542(8)
Si−C4	1.890	1.882	1.889	Si−C4	1.887	1.880	1.888	1.882(4)
N−Me	1.455	1.455	1.448	N−Me	1.454	1.454	1.448	1.460(4)
				Bond angles				
Me−Si−H	109.2	110.3	109.0	Me−Si−H	109.3	109.9	109.0	112.5(17)
N−C2−Si	110.3	108.8	110.2	N−C2−Si	110.9	110.1	110.6	109.6(4)
C2−Si−C4	102.9	102.4	103.1	C2−Si−C4	103.2	102.7	103.4	103.1(7)
Si−C4−C5	110.2	109.2	110.0	Si−C4−C5	110.0	109.2	109.7	110.7(7)
C4−C5−C6	114.1	113.4	114.0	C4−C5−C6	114.0	113.3	114.0	114.8(11)
C5−C6−N	114.1	113.6	113.7	C5−C6−N	114.1	113.6	113.8	112.2(7)
C6−N−C2	113.1	111.6	113.3	C6−N−C2	113.4	111.8	113.5	114.4(14)
Σ(CNC)	335.7	330.8	335.9	Σ(CNC)	336.1	331.1	336.3	335.8(17)
				Dihedral angles				
N−C2−Si−C4	−46.1	−50.0	−45.6	N−C2−Si−C4	−45.0	−47.7	−44.8	−45.6(22)
C2−Si−C4−C5	41.5	44.7	41.1	C2−Si−C4−C5	41.4	43.4	41.0	41.1(21)
Si−C4−C5−C6	−51.8	−53.7	−51.9	Si−C4−C5−C6	−52.6	−54.1	−52.4	−51.7(25)
C4−C5−C6−N	65.2	66.7	65.9	C4−C5−C6−N	66.0	67.9	66.5	64.2(21)
C5−C6−N−C2	−70.5	−72.6	−71.3	C5−C6−N−C2	−69.7	−71.9	−70.8	−70.8(12)
C6−N−C2−Si	61.3	64.3	61.4	C6−N−C2−Si	59.7	62.2	60.2	62.4(18)

[a]Theoretical (r_e) and experimental (r_{h_1}) structure geometric parameters. [b]The calculated geometries of the two conformers are practically identical, except the dihedral angles, characterizing the axial or equatorial positions of the SiMe group. The calculated bond lengths differ, in most cases by maximum 0.003 Å and the bond angles by maximum 1.5 deg. (Table 1 and Table S1, Supporting Information). For this reason, the corresponding geometric parameters were taken to be equal in both conformers. The refined vibration amplitudes are in good agreement with those estimated on the base of the force fields adopted from B3LYP/cc-pVTZ calculations for each conformer individually. The values fixed in the least-squares refinement are given in square brackets. Full errors are given in parentheses.

Table 2. Relative Energies (ΔE, kcal/mol) and Free Energies (ΔG, 298.15 K, kcal/mol) of the Conformers of 1,3-Dimethyl-3-silapiperidine 1 vs. Experimental for the 1a $\leftrightharpoons$ 1e Equilibrium

	B3LYP/cc-pVTZ		MP2/cc-pVTZ		G2		CCSD(T)[a]	experiment	
conformer	ΔE	ΔG	ΔE	ΔG^b	ΔE	ΔG	ΔE	GED	NMR
SiMe$_{ax}$NMe$_{eq}$	0.02	0.11	0	0	0	0	0	1a:1e	1a:1e
SiMe$_{eq}$NMe$_{eq}$	0	0	0.47 (0.16)[c]	0.39 (0.08)[b,c]	0.30	0.25	0.40	= 65:35	= 31.5:69.5
SiMe$_{eq}$NMe$_{ax}$	3.86		4.37					ΔG(293 K)	ΔG(143 K)
SiMe$_{ax}$NMe$_{ax}$	4.50		4.74					= 0.36	= −0.22

[a]Single point CCSD(T)cc-pVTZ//MP2/cc-pVTZ calculations. [b]From the MP2 total energies and DFT vibrational calculations. [c]The values in brackets correspond to the PCM/MP2/cc-pVTZ calculations with CH_2Cl_2 as solvent.

pVTZ level of theory. In the gas phase at 295 K, the IR spectrum of 1,3-dimethyl-3-silapiperidine **1** shows a doublet ν(Si−H) band with the maxima at 2131 and 2137 cm^{-1} (Figure 4a). The calculated frequency difference $\Delta\nu$ is 9 cm^{-1} (Table 3).

According to calculations, the low frequency component belongs to the preferred axial conformer **1a** and the high frequency component to the equatorial conformer **1e**. Note, that the relative positions of the ν(Si−H) bands in conformers **1a** and **1e** are reversed from those in 1-X-1-silacyclohexanes (X = F,[36] Cl,[37] Me[40]), apparently, because of the presence of the ring nitrogen atom in compound **1**. From the peak height intensities obtained by graphical separation of the overlapped band, the ratio **1a:1e** was estimated to be 62(5):38(5), which

gives the ΔG value of 0.16(7) kcal/mol. This result is based on the assumption that the molar absorbances are similar for the two conformers. The excellent agreement between the FT-IR and GED results allowed us to use the same approach for determination of the conformer ratio **1a:1e** at low temperature in solution.

In heptane solution, a single ν(Si−H) band corresponding to the axial conformer **1a** is observed at 2128 cm^{-1}. The presence of **1e** is indicated by the asymmetry of its high-frequency wing in the FT-IR spectrum (Figure S8, Supporting Information). In the Raman spectrum of this solution, conformer **1e** appears as a shoulder on the 2128 cm^{-1} band (Figure 4b). Lowering the solution temperature to 163 K results in an increase of the fraction of **1e** and appearing a shoulder at 2137 cm^{-1} on the
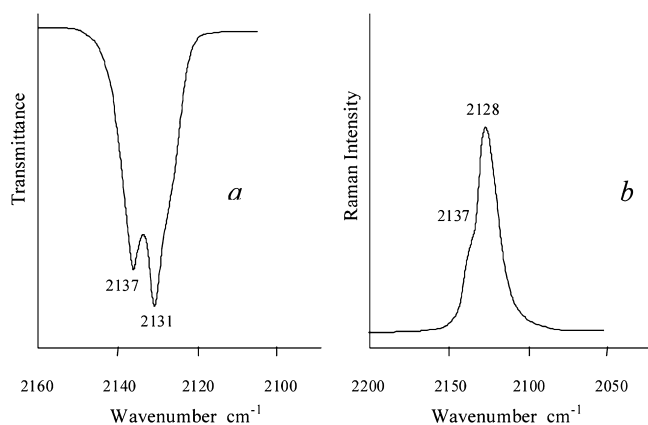
Figure 4. (a) FT-IR spectrum of **1** in the gas phase at 295 K in the range 2160−2100 cm^{-1}. (b) Raman spectrum of **1** in heptane solution at 295 K in the range 2200−2050 cm^{-1}.

Table 3. Experimental and Calculated (B3LYP/cc-pVTZ) FT-IR Frequencies (cm^{-1}) of 1,3-Dimethyl-3-silapiperidine 1 and Its Axial 1a and Equatorial 1e Conformers

FT-IR ν(Si−H)		calculated ν(Si−H)^a		FT-IR ν(Si−C)		calculated ν(Si−C)^a	
gas	heptane	1a	1e	gas	heptane	1a	1e
2131 s	2128 s	2175 (180)		608 w	614 w	607 (3)	
2137 m			2184 (137)	618 w	619 w		
				626 sh	626 w		612 (5)
				646 w	647 w	645 (10)	
				674 w	678 w	699 (2)	
				679 w			679 (10)
				684 sh			
				724 m	725 m	721 (22)	723 (71)
				777 sh	761 w	768 (11)	
					776 w		779 (3)

^{a}In parentheses, IR intensities in km/mol.

high-frequency wing of the ν(Si−H) band in the FT-IR spectrum (Figure S9, Supporting Information). The ratio **1a:1e** at 163 K becomes 56(12):44(12). At first glance, the fact that conformer **1e**, which is the minor component at 295 K, becomes more populated at 163 K seems to be in contradiction with the principles of thermodynamics. However, for equilibria, which are entropically unfavorable ($\Delta S < 0$) but energetically favorable ($\Delta H < 0$), the equilibrium constant must increase with lowering the temperature, whereas the sign of ΔG (that is, the predominance of this or that conformer) depends on the relative contribution of the entropy and enthalpy terms. Apparently, the studied equilibrium **1a** $\leftrightarrows$ **1e** falls in this category (see Solvent Effects, vide infra). It should be stressed that it is the FT-IR analysis that provided us with the information about the molar fractions of conformers **1a** and **1e** in the gas and their temperature variation in solution, thus making a bridge between the GED (gas) and NMR (solution) analyses.

The spectrum of neat liquid has a single symmetrical band ν(Si−H) at 2124 cm^{-1} that is retained upon lowering the temperature to 83 K, that is, after the transition to the plastic phase. In the Raman spectrum of liquid **1**, a slight asymmetry of the high-frequency wing of the ν(Si−H) band at 2125 cm^{-1} indicates the presence of a small fraction of the equatorial conformer **1e**.

The ν(Si−C) FT-IR bands in the range 600−800 cm^{-1} are weak in the gas phase and in heptane. The calculated ν^s(Si−C) bands at 607 (**1a**) and 612 cm^{-1} (**1e**) correspond to the doublet at 614, 619 cm^{-1} and singlet at 626 cm^{-1}. The intensity of the latter band increases with lowering the temperature of the heptane solution, that is, with the increase of the fraction of **1e**. In the Raman spectrum of liquid **1** and its heptane solution at 295 K, the ν(Si−C) of the conformers **1a** and **1e** appear as a band at 617 cm^{-1} and its high-frequency shoulder at 630 cm^{-1} (Figure S3, Supporting Information).

NMR Studies. Both ^{1}H and ^{13}C NMR spectra of 1,3-dimethyl-3-silapiperidine **1** were recorded in the freon solvent mixture CD$_2$Cl$_2$/CHFCl$_2$/CHF$_2$Cl (1:1:3); at 273 K the ring interconversion in Scheme 2 is still fast on the NMR time scale, and averaged signals for Si−Me, Si−H, and N−Me protons were obtained. The protons of the methylene groups are diastereotopic because of the presence of the Si-chiral center (Figure 5, Table 4). The assignment in Table 4 was made on the basis of H,H−COSY, HSQC and HMBC spectra and are in agreement with the known criteria.[21]

Upon cooling, both ^{1}H and ^{13}C NMR spectra of **1** show characteristic broadening and decoalescence (Figures S12 and S13, Supporting Information). The two sets of separated signals of the axial and equatorial conformers of different intensity were observed at 143 K (Table 4). The frozen ^{1}H and ^{13}C spectra of **1** at 143 K are shown in Figures 5b and 6b.

The low-temperature ^{1}H and ^{13}C NMR spectra of compound **1** were assigned through H,H−COSY and HSQC experiments and using the well-known general principles of ^{1}H/^{13}C NMR stereoanalysis: axial SiMe protons (carbon) resonate at lower (higher) field than the corresponding equatorial SiMe protons (carbon).[2,11,21,41] Applying these criteria to the frozen spectra in Figures 5b and 6b allowed us to conclude that the predominant conformer in solution is **1e**. The results from the ^{1}H and ^{13}C spectra are coherent to one another. The integration of the ^{1}H and ^{13}C signals of the SiMe group as well as the signals of all ^{13}C ring carbons below the coalescence temperature allows us to determine the **1a** to **1e** conformer ratio (33:67%, by ^{1}H; 30:70%, by ^{13}C, average 31.5:68.5) and the equilibrium constant $K_{av} = 2.13$, which corresponds to the free energy difference $\Delta G = -0.22$ kcal/mol. This value is significantly less than those for various C-methylated heterocycles (Chart 1) but very close to the values for the two known Si-methylated heterocycles: 1-methyl-1-silacyclohexane and 3-methyl-1,3-thiasilinane (Chart 2).

The rate constants and the barrier to ring inversion of heterocycle **1** were determined by complete line shape analysis of the SiMe group (both in ^{1}H and ^{13}C NMR spectroscopy) and of the other carbon atoms in ^{13}C NMR spectroscopy. The corresponding dynamic NMR parameters (k_c, $\Delta \nu$, $\Delta G^{\ddagger}$, population difference neglected) are given in Table 5. The barrier to ring inversions were estimated at T_c employing the usual approximations ($k_c = \pi \Delta \nu / \sqrt{2}$; $\Delta G^{\ddagger} = 19.14\ T_c\ (10.32 + \log\ T_c/k_c)$ and the dynamic NMR module of the Bruker TopSpin 3.0 software.[42] The barrier to ring inversion of **1** ($\Delta G^{\ddagger} = 8.9$−9.0 kcal/mol) is comparable to the formerly studied
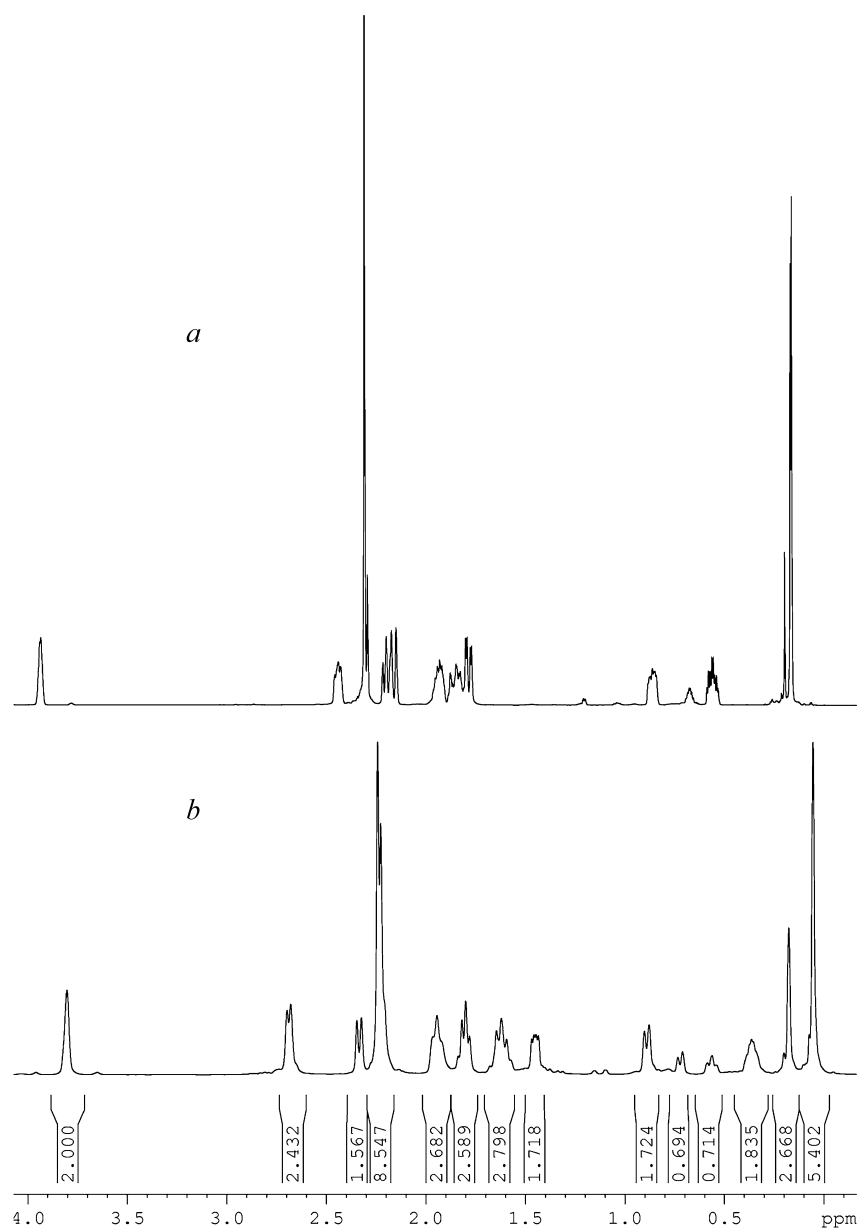
Figure 5. ^{1}H NMR spectra of 1,3-dimethyl-3-silapiperidine **1** at 273 K (a) and 143 K (b).

Table 4. ^{1}H and ^{13}C NMR Spectra of 1 at Various Temperatures in CD$_2$Cl$_2$/CHCl$_2$F/CHClF$_2$

T/K, conformer		MeSi	2-CH$_2$	4-CH$_2$	5-CH$_2$	6-CH$_2$	NCH$_3$	SiH
				δ(^{1}H), ppm				
273, **1**		0.17	2.16	0.86	2.22	2.40	2.29	3.91
			1.85	0.56	1.87	1.93		
143, **1a**, *minor*	ax	0.18	1.62	0.58	1.95	1.80		
	eq	−	2.24	0.72	1.62	2.69	2.23	3.80
143, **1e**, *major*	ax	−	1.46	0.36	1.95	1.80		
	eq	0.06	2.32	0.89	1.62	2.69	2.24	
				δ(^{13}C), ppm				
273, **1**		−6.6	47.0	9.5	25.8	60.4	52.3	
143, **1a**, *minor*	ax	−7.7	45.2	7.3	23.9	59.1	51.9	
143, **1e**, *major*	eq	−6.7	45.7	8.6	25.2	58.8	51.7	

analogues.[21−24] The values of other activation parameters are equal to $\Delta H^{\ddagger}$ = 9.6 kcal/mol, $\Delta S^{\ddagger}$ = 2.1 cal/(mol K).

Solvent Effects. Small energy difference between the axial and equatorial conformers **1a** and **1e** (Table 2) makes it difficult to rationalize the predominance of the former conformer in the gas phase and the latter one in solution. Nevertheless, we have tried to estimate the solvent effect on the conformational equilibrium using the PCM model at the MP2/
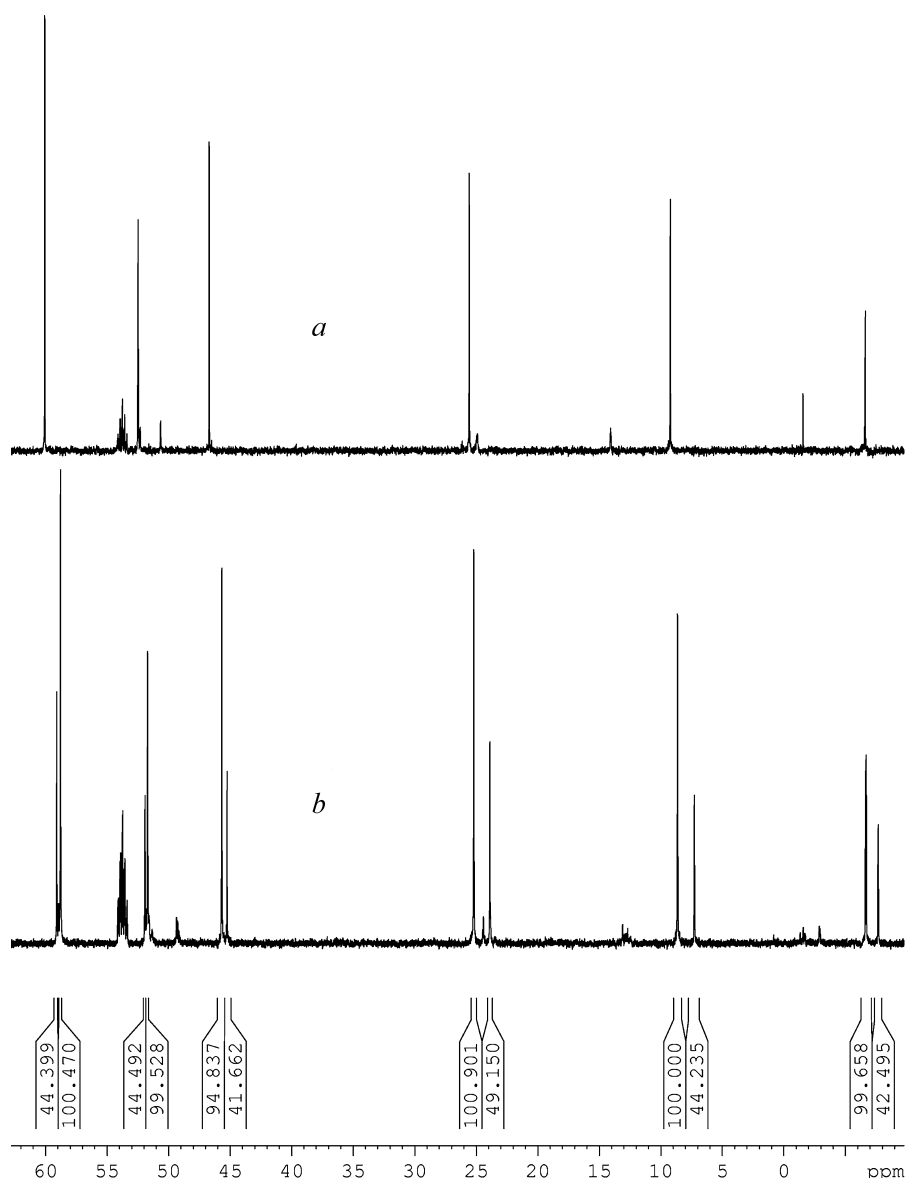
Figure 6. ^{13}C NMR spectrum of 1,3-dimethyl-3-silapiperidine **1** at 273 K (a) and at 143 K (b).

Table 5. Dynamic NMR Parameters of the Ring Inversion of 1,3-Dimethyl-3-silapiperidine 1

signal studied	T_c, K	$\Delta\nu$, Hz	k_c	$\Delta G^{\ddagger}$, kcal/mol
Si–C$\underline{H}_3$	190	72	159.9	9.0
Si-$\underline{C}H_3$	193	147	326.6	8.9
C-2	188	65	144.4	9.0
C-4	195	205	455.4	8.9
C-5	196	195	433.2	8.9
C-6	183	46	102.2	8.9
N–$\underline{C}H_3$	182	32	71.1	8.9

cc-pVTZ level of theory and dichloromethane as a solvent. The energy difference ΔE was reduced from 0.47 kcal/mol in the gas phase to 0.16 kcal/mol in CH$_2$Cl$_2$, and the free energy difference ΔG, from 0.39 to 0.08 kcal/mol; that is, in solution the proportion of the equatorial conformer **1e** increased. This result seems reasonable since conformer **1e** is more polar (μ 1.07 D in the gas and 1.55 D in solution) than conformer **1a** (μ 0.56 D in the gas and 0.72 D in solution).

■ CONCLUSIONS

The molecular structure of the first synthesized Si–H-containing azasilaheterocycle, 1,3-dimethyl-3-silapiperidine, is determined by gas-phase electron diffraction and is shown to be consistent with the calculated geometry (DFT, MP2, G2, CCSD(T)). The combined GED, IR, Raman, NMR and theoretical conformational analysis showed the compound to exist as a mixture of two conformers in the ratio depending on the aggregate state and temperature. In the gas phase at 295 K, the SiMe$_{ax}$ conformer **1a** predominates (**1a:1e** ~2:1). At low temperature in solution (143 K), the conformational preference is reversed, and the SiMe$_{eq}$ **1e** conformer becomes more stable (**1a:1e** ~1:2). The obtained results strongly complement the information on the conformational energies of substituents in silaheterocyclohexanes, which so far was available only for the methyl group in 1-methyl-1-silacyclohexane[15−17] and 3-methyl-3-silathiane[7] and for the phenyl group in 1-phenyl-1-silacyclohexane and 3-phenyl-3-silathiane.[43] MP2 calculations using the PCM solvation model indicate that in solution the

conformational equilibrium is shifted toward the equatorial conformer because of its higher polarity.

EXPERIMENTAL SECTION

General Methods. FT-IR spectra were registered in the range 295−83 K on a FT-IR 3100 spectrometer in a thermostated cell with KBr windows cooled with liquid nitrogen and 10 cm path cell for gas with KBr windows. The Raman spectra were recorded on FT-IR (RAM II) Spectrometer. The ratio of the conformers **1a** and **1e** was calculated from the peak intensities of the components of the ν(Si−H) band in the IR spectrum determined after its graphical separation, assuming equal extinction coefficients of the bands belonging to the axial and equatorial conformers. ^{1}H, ^{13}C and ^{29}Si NMR spectra were acquired on a 400 and 600 MHz spectrometers and are reported relative to TMS (δ 0.00). Low temperature NMR spectra were recorded on a 600 MHz spectrometer in a freon mixture of CD_2Cl_2/$CHFCl_2$/CHF_2Cl in a ratio of 1:1:3. Chemical shifts were determined relative to internal CD_2Cl_2 (^{13}C, δ 53.73). 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 ±2 K. The complete line shape analysis was processed by the DNMR routine in TOPSPIN; intensities, line widths, δ, J and signal populations are picked, the spectrum is iterated, and the rate constant k is determined for the certain temperatures. From the temperature dependence of k, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated from the Eyring equation. The HRMS ESI spectra were recorded using a Q-TOF$_{micro}$ mass spectrometer in positive electrospray mode. The capillary voltage was 3.2 kV, with a cone voltage between 20−25 V. Elemental compositions were determined by accurate mass measurement with standard deviation <5 ppm. H_3PO_4 was used as reference compound.

Ether was distilled from sodium metal and benzophenone. All other reagents were commercially available or purified and dried by standard procedures. TLC analysis was performed on 250 mm thick, 60 Å, aluminum backed, F254 silica plates, visualized by exposure to iodine vapors. Column chromatography was performed using silica gel (230−400 mesh).

Chloro(chloromethyl)(3-chloropropyl)(methyl)silane (3). Chloro-(chloromethyl)(methyl)silane **2**[44] (3.061 g, 23.6 mmol) was mixed with allyl chloride (1.807 g, 23.6 mmol). One fifth portion of this mixture was added to 0.1 N solution of hexachloroplatinic acid hexahydrate in isopropanol (0.03 mL) and heated to 30 °C, and then the temperature spontaneously raised to 55 °C, and the mixture turned black. The rest of the mixture of the reagents was then added dropwise, and after completion of addition, the mixture was heated to 90 °C. Vacuum distillation gave 3.263 g (60%) of compound **3** of ∼90% purity (from ^{1}H NMR): bp 85−91 °C (7 mm); ^{1}H NMR (CDCl$_3$) δ 0.57 (s, 3H, *Me*Si), 1.10−1.16 (m, 2H, SiC*H$_2$*C), 1.95 (quint, 2H, J = 7.5 Hz, CC*H$_2$*C), 2.99 (s, 2H, SiC*H$_2$*Cl), 3.57 (t, 2H, J = 6.5 Hz, CC*H$_2$*Cl); ^{13}C NMR (CDCl$_3$) δ −1.54 (*Me*Si), 13.25 (SiC*H$_2$*C), 26.20 (CC*H$_2$*C), 29.28 (SiC*H$_2$*Cl), 47.03 (CC*H$_2$*Cl); ^{29}Si NMR (CDCl$_3$) δ 23.6.

(Chloromethyl)(3-chloropropyl)(isopropoxy)(methyl)silane (4). The mixture of adduct **3** (3.823 g, 18.6 mmol), isopropanol (2.355 g, 39.2 mmol), urea (1.422 g, 23.7 mmol) in hexane (20 mL) was stirred for 8 h at reflux and cooled, the upper liquid layer was decanted from the lower oily layer of urea hydrochloride, volatiles were removed under a vacuum, and vacuum distillation of the residue gave 3.447 g (80%) of compound **4** of ∼85% purity (from ^{1}H NMR): bp 110−112 °C (7 mm); ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 3H, *Me*Si), 0.82−0.88 (m, 2H, SiC*H$_2$*C), 1.18 (d, 6H, J = 6.0 Hz, C*H$_3$*C), 1.82−1.92 (m, 2H, CC*H$_2$*C), 2.82 (s, 2H, SiC*H$_2$*Cl), 3.54 (t, 2H, J = 6.8 Hz, CC*H$_2$*Cl), 4.09 (sept, J = 6.0 Hz, 1H, OC*H*). ^{13}C NMR (CDCl$_3$) δ −4.57 (*Me*Si), 11.74 (SiC*H$_2$*C), 25.83 (C*H$_3$*C), 26.69 (CC*H$_2$*C), 28.90 (SiC*H$_2$*Cl), 47.66 (CC*H$_2$*Cl), 66.06 (OC*H*C); C*H$_3$*C and CC*H$_2$*C signals were assigned from the *j*-mod spectrum; ^{29}Si NMR (CDCl$_3$) δ 6.24 ppm.

1,3-Dimethyl-3-isopropoxy-3-silapiperidine (5). The mixture of compound **4** (3.4 g, 14.8 mmol), methylamine (2.415 g, 77.8 mmol),

benzene (5 mL) was heated in a sealed tube for 10 h at 100 °C. After cooling, the precipitate was filtered off and washed with benzene (5 mL) and pentane (10 mL), and the solvents were distilled off at atmospheric pressure on a Vigreux column. Vacuum distillation of the residue gave 1.690 g (61%) of compound **5**: bp 87 °C (28 mm). The NMR spectra of **5** were described by us recently.[24]

1,3-Dimethyl-3-silapiperidine (1). To a suspension of LiAlH$_4$ (0.223 g, 5.9 mmol) in Et$_2$O (4 mL), a solution of heterocycle **5** (1.650 g, 8.8 mmol) in Et$_2$O (3 mL) was added dropwise at room temperature, the reaction mixture was refluxed for 2 h and then allowed to cool to ambient temperature, and the formed precipitate was allowed to settle. The upper layer was decanted, and the precipitate was washed with pentane (5 mL). ^{1}H NMR spectrum of the combined solution showed that the reduction was practically completed. Volatile components were evaporated in a vacuum (170 mm) and condensed into a cold trap at −196 °C to give pure compound **1** (0.103 g, 0.8 mmol) and a fraction (0.197 g) containing the product contaminated with solvents. After careful evaporation of solvents at atmospheric pressure, pure product **1** (0.138 g, 1.1 mmol) was isolated. Because of high volatility, the total yield was 0.241 g (21%): bp 100 °C; HRMS calcd for C$_6$H$_{14}$NSi (M − H)$^+$ 128.0895, found 128.890.

ASSOCIATED CONTENT

Supporting Information

Calculated and experimental geometric parameters, IR and Raman spectra, 2D and variable-temperature ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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