Received: 29 April 2010,

Revised: 23 May 2010,

Published online 21 July 2010 in Wiley Online Library: 2011

(wileyonlinelibrary.com) DOI 10.1002/poc.1758

Conformational Analysis of 3-Methyl-3-Silathiane and 3-Fluoro-3-Methyl-3-Silathiane

Svetlana V. Kirpichenko^a*, Erich Kleinpeter^b, Igor A. Ushakov^a and Bagrat A. Shainyan^a

The conformational equilibria of 3-methyl-3-silathiane 5, 3-fluoro-3-methyl-3-silathiane 6 and 1-fluoro-1-methyl-1-silacyclohexane 7 have been studied using low temperature ¹³C NMR spectroscopy and theoretical calculations. The conformer ratio at 103 K was measured to be about $5_{ax}:5_{eq} = 15:85$, $6_{ax}:6_{eq} = 50:50$ and $7_{ax}:7_{eq} = 25:75$. The equatorial preference of the methyl group in 5 (0.35 kcal mol⁻¹) is much less than in 3-methylthiane 9 (1.40 kcal mol⁻¹) but somewhat greater than in 1-methyl-1-silacyclohexane 1 (0.23 kcal mol⁻¹). Compounds 5-7 have low barriers to ring inversion: 5.65 (ax \rightarrow eq) and 6.0 kcal mol⁻¹ (eq \rightarrow ax) (5), 4.6 kcal mol⁻¹ (6), 5.1 kcal mol⁻¹ (Me_{ax} \rightarrow Me_{eq}), and 5.4 kcal mol⁻¹ (Me_{eq} \rightarrow Me_{ax}) (7). Steric effects cannot explain the observed conformational preferences, like equal population of the two conformers of 6, or different conformer ratio for 5 and 7. Actually, by employing the NBO analysis, in particular, considering the second order perturbation energies, vicinal stereoelectronic interactions between the Si-X and adjacent C-H, C-S, and C-C bonds proved responsible. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: conformational analysis; low-temperature NMR spectroscopy; NBO analysis; quantum chemical calculations; 3-silathianes

INTRODUCTION

The conformational behavior of diheterocyclohexanes having the sulfur atom and a second heteroatom in the 1,3-position of the ring systems (1,3-dithianes, 1,3-oxathianes) was the subject of intensive experimental and theoretical studies.^[1-6] However, only limited data have been reported on the conformational properties of the related heterocycles having the endocyclic silicon atom, in particular, 1,3-thiasilacyclohexanes (3-silathianes). Over many years there has been a considerable interest in the chemistry of these heterocycles most significant results of which are given in a recent review.^[7] Due to the presence of two heteroatoms of different nature, 3-silathianes exhibit the peculiar and complementary reactivity. However, much less is known about the conformational behavior of these compounds as compared to the related monoheterocycles containing only the sulfur or silicon atom. In the last few years Arnason et al. intensively investigated the conformational equilibria, steric effects of substituents and stereoelectronic interactions in 1-X-1-silacyclohexanes (X = H^[8], Me^[9,10], $F^{[11,12]}_{,,}$, CF^[13], SiH^[14], cf. Scheme 1) by various physico-chemical methods such as gas-phase electron diffraction, dynamic nuclear magnetic resonance, microwave spectroscopy, temperature-dependent Raman spectroscopy and guantum chemical calculations.

It was shown that the conformational behavior of silacyclohexanes differs significantly from that of the related cyclohexanes. The equatorial preference of the substituents drastically diminishes (for 1) or even inverts (for 2–4) on going from monosubstituted cyclohexanes to the corresponding silacyclohexanes. The increasing population of the axial conformer and the decrease in the ring inversion barriers in silacyclohexanes relative to the corresponding cyclohexanes (5–6 kcal mol⁻¹ vs. 10–11 kcal mol⁻¹) was explained originally by the longer endocyclic Si–C bond (1.904 Å) compared to the C–C bond (1.534 Å)^[9,15] although stereoelectronic effects were also suggested to play an important role.^[16–19]

As to silathianes, some years ago the route of the chair-to-chair inversion of the unsubstituted 3-silathiane was calculated. According to these calculations, the free energy of activation was found to be 5.5 kcal mol⁻¹.^[20] Recently, we reported the results of experimental and computational investigation of the conformational behavior of 2-X-3,3-dimethyl-3-silathiane (X = H, Me, SiMe₃) by low-temperature ¹³C NMR spectroscopy.^[21] In continuation of these studies, we present here the first data on the effect of the substituent at the silicon atom and the joint effect of the two ring heteroatoms on the conformational properties of these compounds.

- S. V. Kirpichenko, I. A. Ushakov, B. A. Shainyan
 A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian
 Academy of Sciences, 1 Favorsky Street, Irkutsk 664033, Russia
- b E. Kleinpeter Department of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam(Golm), Germany

^{*} Correspondence to: S. V. Kirpichenko, A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky Street, Irkutsk 664033, Russia. E-mail: svk@irioch.irk.ru



Scheme 1. Conformational equilibrium in 1-X-1-silacyclohexanes.

RESULTS AND DISCUSSION

The changes observed in the 13 C NMR spectra of 3-methyl-3-silathiane **5** and 3-fluoro-3-methyl-3-silathiane **6** upon lowering the temperature down to 103 K reveal the ring interchange process (Scheme 2).

The room-temperature ¹³C NMR parameters for **5**, **6** and (for comparison purposes) 1-fluoro-1-methyl-1-silacyclohexane **7** are listed in Table 1 as are the low-temperature spectral data for the axial and equatorial conformers at 103 K as far as possible (e.g. **5**_{ax} and **5**_{eq} in Scheme 2). The well-defined changes in the ¹³C NMR spectra for **5** with temperature are shown in Fig. 1.

On lowering the temperature down to 103 K the ¹³C NMR spectrum of **5** reveals line broadening and following splitting (excluding the C-6 signal) into a set of main (at lower field) and smaller (at higher field) signals, that indicate a mixture of a major and a minor conformer. Because of the small discrepancy



Scheme 2. Conformational equilibrium in 3-X-3-Me-3-silathianes.

between the ¹³C chemical shifts for C-2 and C-4 in the ¹³C NMR spectra and slightly different low-temperature high field shifts, the splitting of these two signals at 103 K cannot be examined with respect to the conformational equilibrium; the ¹³C signal of the Si–Me and C-5 are residual and were examined. The signal set at high field in the ¹³C NMR spectra was assigned to the **5**_{ax} conformer by analogy with those for 1-methyl-1-silacyclohexane^[9] and in line with known criteria for methylcyclohexane.^[22–24] The axial–equatorial conformer ratio of 15:85 determined from area measurements of the Si–Me and C-5 signals in the spectrum of **5** gave a *K* value of 5.67 corresponding to a free energy difference (*A* value) of 0.35 kcal mol⁻¹ in favor of the **5**_{eq} conformer at 103 K (cf. Scheme 2).

The low-temperature ¹³C NMR spectrum of **6** (Fig. 2) shows broad but already separated signals for C-5 and the Si-methyl carbon atoms of the axial and equatorial conformers at 103K; integration is difficult because the decoalesced signals are still very broad but a conformer ratio of **6**_{ax}:**6**_{eq} ca. 1:1 can be unequivocally concluded (cf. Fig. 2).

To compare the conformational characteristic of **6** with those of related silacyclohexane, we prepared 1-fluoro-1-methyl-1silacyclohexane **7** and studied its conformational behavior. The low-temperature ¹³C NMR spectra of **7** are shown in Fig. 3 and the spectral data are given in Table 1. Determination of a **7**_{ax}:**7**_{eq} ratio at low temperature was only possible from integration of the Me-Si signals (Fig. 3) that led to a value of ca. 75% for the **7**_{eq} conformer in the equilibrium at 103 K (considering the impurity doublet at the **7**_{eq} signal).^[25] This gives an A value of 0.28 kcal mol⁻¹ in favor of **7**_{eq} at this temperature.

The decoalescence of signals of the axial and equatorial conformers of **5–7** was clearly observed and the corresponding coalescences temperatures T_c for all compounds are well-defined within a range of about 10 K. The following Gibbs free energies of activation ΔG^{\ddagger} for the ring inversion were determined by the method of Shanan-Atidi and Bar-Eli^[26] from the coalescence temperatures considering the different population of participating conformers: 5.65 kcal mol⁻¹ (ax \rightarrow eq) and 6.0 kcal mol⁻¹ (eq \rightarrow ax) (123 K) for **5**; ca. 4.6 kcal mol⁻¹ (106 K) for **6**; 5.1 kcal mol⁻¹ (Me_{ax} \rightarrow Me_{eq}) and 5.4 kcal mol⁻¹ (Me_{eq} \rightarrow Me_{ax}) (112 K) for **7**. These ring inversion barriers are lower than that in 3,3-dimethyl-3-silathiane (6.3 kcal mol⁻¹).^[21]

	Chemical shifts δ , ppm (J, Hz)										
Compound	T (K)	C-2	C-4	C-5	C-6	MeSi					
5	298	11.97	11.35	27.17	32.21	-5.59					
5 _{ax}	103	107.04		25.4	31.0	-4.62					
5 ea	103	10.7,	9.4	28.0		8.87					
6	298	14.54 d (14.78)	14.07 d (12.20)	28.79 d (2.15)	32.15	-3.93 d (14.86)					
6 _{ax}	103	ca. 12.9	ca. 12.9	ca. 26.8	31.1	ca5.8					
6 _{eq}	103			ca. 28.9		ca3.3					
7	298	14.60 d (14.74)	29.54	24.04 d ^a (12.53)	14.60 d (14.74)	-2.55 d (14.86)					
7 _{ax}	103	13.5	28.8	23.5		са. —4.6					
7 _{eq}	103	Not identified	Not identified	Not identified	Not identified	ca2.5					
^a C-5 and C-3.											

Table 1. ¹³C NMR parameters for compounds **5-7** in CDCl₃ solution at 298 K and in the mixture CD₂Cl₂/CHFCl₂/CHF₂Cl (1:1:3) at low temperatures



Figure 1. Low-temperature ¹³C NMR spectra of 3-methyl-3-silathiane 5.

The room-temperature NMR spectra of compounds **5** and **6** are time-averaged due to the fast ring inversion (Scheme 2). Still, the diastereotopic protons of the 2-CH₂ and 6-CH₂ methylene groups give separate signals, that rises the question of their assignment to the protons *cis* or *trans* to the SiMe group. Such an assignment was made by using the 2D HSQC and HMBC techniques. The H-2 protons in **5** appear as two doublets at 1.67 and 1.86 ppm with ²J 14.6 Hz and have equal ¹J_{CH} of 129.6 Hz. The upfield signal is further split by long-range H–H couplings. The H-4 protons appear as two multiplets at 0.66 and 0.88 ppm with ²J 15.0 Hz and have ¹J_{CH} constants of 118.8 and 119.8 Hz, respectively.

The 2D-HMBC spectra of **5** show cross peaks of the SiMe carbon only with the downfield signals of the H-2/4 protons suggesting that these signals belong to protons *trans* to the SiMe group. The same conclusion follows from analysis of the ${}^{3}J_{\rm HH}$ couplings with the SiH proton.

To calculate the weight-averaged room-temperature coupling constants, one should take into account that from the equation $\Delta G^{\circ} = -RT \ln K$, the ratio $\mathbf{5}_{ax}:\mathbf{5}_{eq} = 15:85$ at 103 K becomes 35:65 at room temperature. The so calculated weight-averaged *trans* coupling constants are equal to 4.2 Hz, and the corresponding *cis* coupling constants are 1.4 Hz, in excellent coincidence with the experimental values of ${}^{3}J_{\text{H-2-SiH}}$ (4.1 and 2.0 Hz) and ${}^{3}J_{\text{H-4-SiH}}$ (4.3 and 2.4 Hz).

The H-2 protons in **6** appear as two doublets at 1.75 and 2.00 ppm with ${}^{2}J$ 14.9 Hz. The upfield signal is further split by coupling with the fluorine atom and long-range H–H couplings. The ${}^{1}H{-}^{19}F$ coupling of the upfield signal disappears in the fluoro decoupled ${}^{1}H$ NMR spectrum. Since only the ax,ax coupling is large enough to be found in usual 2D NMR spectra the signal at 1.75 ppm must belong to the proton *trans* to fluorine. The ${}^{19}F$ signal in the ${}^{1}H$ coupled ${}^{19}F$ NMR spectrum is a sextet (due to



Figure 2. Low temperature ¹³C NMR spectra of 3-fluoro-3-methyl-3-silathiane 6.



Figure 3. Low-temperature ¹³C NMR spectra of 1-fluoro-1-methyl-1-silacyclohexane 7.

similar ¹H,¹⁹F coupling constants to two vicinal axial and three geminal methyl protons).

The 2D-HMBC spectra of **6** show a strong cross peak of the signal at 2.00 ppm with the SiMe carbon, whereas the signal at 1.75 ppm gives weak cross peaks with the C-4/6 ring carbon atoms and no cross peak with the SiMe carbon. This agrees well with the calculated J_{HC} coupling constants. The calculated averaged *trans* coupling constant ${}^{3}J_{H-2-SiMe}$ is 1.25 Hz, and the *cis* coupling constant ${}^{3}J_{H-2-SiMe}$ is only 0.17 Hz, that proves their correct assignment made above.

The presence of cross peaks of the SiMe group protons with both protons of the SiCH₂S methylene group in the NOESY spectrum agrees well with about the equal population of the two conformers proved by low-temperature NMR.

The ${}^{1}J_{CH}$ couplings for the SiCH₂S group in **6** are different and equal to 128.5 Hz for the signal at 1.75 ppm and 131.2 Hz for that at 2.00 ppm. The calculated values for **6**-ax are ${}^{1}J_{CHax} = 133.6$, ${}^{1}J_{CHeq} = 129.4$ Hz, and for **6**-eq ${}^{1}J_{CHax} = 129.9$, ${}^{1}J_{CHeq} = 128.5$ Hz. When averaged, they give ${}^{1}J_{CH} = 131.0$ Hz for the proton *cis* to fluorine, and ${}^{1}J_{CH} = 129.6$ Hz for that *trans* to the fluorine. As distinct of that, the experimental values of ${}^{1}J_{CH}$ for the two SiCH₂S protons in **5** are equal, 129.6 Hz. Calculations give ${}^{1}J_{CHax} = 132.2$, ${}^{1}J_{CHeq} = 128.7$ Hz for **5**_{ax}, and ${}^{1}J_{CHax} = 131.1$, ${}^{1}J_{CHeq} = 128.8$ Hz for **5**_{eq}. After weight-averaging they give the same ${}^{1}J_{CH}$ of 130.0 and 130.2 Hz for the protons *trans* and *cis* to Me, in excellent agreement with their experimental coincidence. Note, that SiCH₂S group in both conformers of **5** and **6** shows the reverse Perlin effect, ${}^{1}J_{CHax} = {}^{1}J_{CHeq}$.

The experimental and calculated characteristics of conformational equilibria for compounds **5–7** are given in Table 2. A series of reference molecules, 3-fluoro-3-silathiane **8**, 3-methylthiane **9**, 3-fluorothiane **10**, 3-fluoro-3-methylthiane **11**, 1-methylcyclohexane **12**, 1-fluorocyclohexane **13**, 1-fluoro-1-methylcyclohexane **14** was also calculated for direct comparison (Table 2).

It is well known that the replacement of a CH₂ group in cyclohexane derivatives by heteroatom results in changes in some structural parameters and affects the conformational characteristics of the heterocycles.^[1-6] In monosubstituted

cyclohexanes, the equatorial position of a substituent is usually favored.^[34] It was explained by 1,3-diaxial repulsion effects destabilizing the axial conformers. In compliance with this classical postulate the longer S–C (1.82 Å) bond compared to the C–C bond (1.54 Å) would decrease steric hindrance of the axial forms in thianes with respect to the corresponding cyclohexanes. Indeed, the equatorial preference for the methyl group in 3-methylthiane **9** is smaller than that in methylcyclohexane **12**. Further decrease in the *A* value on going from 3-methylthiane **9** to 3-methyl-3-silathiane **5** (Table 2) can be due to the longer C–Si bond (1.90 Å).

As for monosubstituted halocyclohexanes, all halogen atoms prefer the equatorial position. However, the conformational free energy of the fluorine atom (0.28 kcal mol⁻¹) is much smaller than for other halogen atoms.^[29,35–37] In 3-X-halothianes (X = Cl, Br), the equatorial isomers are 1.8 kcal mol⁻¹ favored over the axial isomers.^[38] Although there are no data about 3-fluorothiane **10**, the calculations show a significant preference $(1.38 \text{ kcal mol}^{-1})$ of its equatorial conformer, which is $0.46 \text{ kcal mol}^{-1}$ smaller than that of 3-methylthiane 9. The increase of the calculated ratio in favor of the axial conformer of 3-fluoro-3-silathiane 8 (16:84) as compared to that of 3-fluorothiane 10 (9:91) is reasonable because of the longer C-Si bond. However, in 3-fluoro-3methylthiane 11, the conformational energies of Me and F having the same sign are subtracted in a nonadditive manner, as if the smaller effect of F in 10 outweighs the larger effect of Me in 9 and the **11**-Me_{ax}F_{eq} conformer becomes energetically more favorable. This is indicative of other than steric effects operating in the systems containing both fluorine and sulfur atoms. Indeed, in the absence of the sulfur atom in the ring, the conformational equilibrium of the geminal 1-Me-1-X-cyclohexanes (X = CI, Br) is dictated by the methyl group having the A value much greater than that of the halogen atoms.^[37] The experimental ΔG° values for both halogen compounds show only minor deviations from the values calculated with the assumption of additivity.[37] According to the data of Table 2, both 1-fluoro-1-methylcyclohexane 14 and 1-fluoro-1-methyl-1-silacyclohexane 7 also show a significant preference for the Me-equatorial conformers **Table 2.** B3LYP/6-311G(d,p) calculated and experimental characteristics for conformational equilibria of compounds **1**, **2**, **5–14** ($\Delta E = E_{ax} - E_{eqr}$, $A = G_{ax} - G_{eqr}$, kcal mol⁻¹) (MP2 values are given in parentheses)

Molecule	<i>E</i> (Me _{ax}), au	<i>E</i> (Me _{eq}), au	ΔE	А _{298 К}	(ax:eq) _{calc}	(ax:eq) _{exp}	$A_{\rm exp}$ (K)	References
1	-526.684783	-526.685474	0.43	0.66	25:75	32:68	0.45 (293)	[4]
						26:74	0.23 (110)	
2 ^a	-586.684583	-586.684256	-0.20	-0.24	60:40	63:37	-0.31 (293)	[7]
5	-885.575584	-885.575701	0.07	0.19	42:58	15:85	0.35 (103)	This work
	(-883.859490)	(-883.859244)	(-0.15)	(-0.04)				
6	-984.917954	-984.916553	-0.88	-0.78	79:21	50:50	0 (103)	This work
	(-983.013448)	(-983.011509)	(-1.22)	(-1.22)				
7 ^b	-626.027407	-626.028144	0.46	0.72	23:77	25:75	0.28 (103)	This work
8 ^a	-945.572620	-945.574447	1.15	0.98	16:84	n.a.		
9	-634.155530	-634.158292	1.73	1.84	4:96	2:98	1.40 (190)	[21]
10 ^a	-694.096433	-694.098861	1.52	1.38	9:91	n.a.		
11	-733.426986	-733.426340	-0.41	-0.13	55:45	n.a.		
12	-275.266440	-275.269792	2.10	2.46	1.5:98.5	0.3:99.7	1.76 (157)	[22]
13 ^{a,c}	-335.211564	-335.211342	-0.14	-0.11	45:55	37:63	0.24 (218)	[23]
	(-334.244228)	(-334.243845)	-0.24	-0.21				
14	-374.539487	-374.541931	1.53	1.66	6:94	n.a.		

^a For compounds **2**, **8**, **10**, **13**, having no Me group, the first column of energy refers to the F_{ax} conformers.

^b When our manuscript was under preparation, Arnason and al. reported conformational analysis of compound **7** by low-temperature ¹⁹F NMR.^[18] Our data on the low-temperature ¹³C NMR are in good agreement with his data.

^c The calculated conformational energies *A* of the fluorine atom in fluorocyclohexane are small negative, -0.1 to -0.2 kcal mol⁻¹, as distinct from small positive experimental *A* value.^[30]

– calculated for the reference compound **14** and both measured and calculated for compound **7**.

On going from 1-fluoro-1-methylcyclohexane **14** to 3-fluoro-3-methylthiane **11** and then to 3-fluoro-3-methyl-3-silathiane **6**, the preference of the Me_{ax} conformers increases in the order 1.66 > -0.41 > -0.78 kcal mol⁻¹ being inverted when the sulfur atom appears in the ring. The alternative sequence $14 \rightarrow 7 \rightarrow 6$ gives the order 1.66 > 0.72 > -0.78 kcal mol⁻¹, also inverting the sign with appearing the sulfur atom in the ring.

Some other conclusions from analysis of the calculated data of Table 2 can be summarized as follows. In 1-fluoro-1-methylcyclohexane **14** the equatorial preference of the Me group (1.66 kcal mol⁻¹) is considerably reduced relative to 1-methylcyclohexane **12** (2.46 kcal mol⁻¹) in spite of the close to zero *A* value for the fluorine atom in **13**. This is indicative of nonadditivity of the effects of the two substituents. In 1-fluoro-1-methyl-1silacyclohexane **7**, these effects are summed up since the Me group and F atom at silicon have the *A* values of the opposite sign (cf. with **1** and **2**). The appearing of the sulfur atom in the ring results in a moderate increase of the equatorial predominance of the Si–Me group (cf. **5** and **1**), whereas the calculated equatorial preference of the Si–F substituent increases drastically (cf. **8** and **2**). Accordingly, the relative stability of **6**_{ax} with respect to **7**_{ax} increases.

Therefore, because of the dependence of the *A* values on the presence, nature, and relative position of heteroatoms, the situation is not as simple as if it were determined only by the conformational energies of the substituents at the silicon atom. First, the value of *A* for fluorine atom attached to Si is negative (ca. $-0.3 \text{ kcal mol}^{-1}$).^[12] Second, the value of *A* for the Me group attached to Si remains positive although much less than in carbon analogs (ca. $0.4 \text{ kcal mol}^{-1}$).^[9] Third, the 1,3-diaxial F···H

interactions cannot play an important role since even in 1-Fcyclohexane and 3-F-thiane the corresponding calculated F...H distance (\sim 2.7 Å) exceeds the sum of the vdW radii to say nothing of 3-F-3-silathiane and compound **6**, where it is larger than 3 Å. If the mentioned influences on the A values were the only factors determining the relative stability of the conformers of the compounds under consideration, the equilibrium in Scheme 2 would be similar for 6 and 7, and more shifted to the right for 6 than for 5 since the axial fluorine should impart an additional stability to the 6-eq conformer. As can be seen from Table 2, this is not the case for 3-silathianes: the 5_{ax}:5_{eq} ratio is 15:85, whereas the $\mathbf{6}_{ax}$: $\mathbf{6}_{eq}$ ratio is ca. 1:1 and $\mathbf{7}_{ax}$: $\mathbf{7}_{eq}$ ratio is 25:75. Therefore, the question is what are the factors stabilizing or destabilizing the axial and equatorial conformers of 5-7. In order to rationalize the observed differences we have performed the NBO analysis of these conformers and compared the second order perturbation energies E(2) for the donor-acceptor interaction between the pertinent vicinal bonds. In $\mathbf{6}_{axt}$ the interaction of the σ (C2–S) and σ (C4–C5) orbitals with σ^* (Si–F) orbital (2.06 kcal mol⁻¹) is 0.5 kcal mol⁻¹ stronger than the doubled σ (C2–C3) $\rightarrow \sigma^{*}$ (Si–F) interaction in $\mathbf{7}_{ax}$, while the sum of the two $\sigma(C-H_{ax}) \rightarrow \sigma^*(Si-F)$ interactions in $\mathbf{6}_{eq}$ (3.74 kcal mol⁻¹) is 0.36 kcal mol⁻¹ weaker than in $\mathbf{7}_{eq}$. This suggests that $\mathbf{6}_{ax}$ is less unfavorable with respect to $\mathbf{6}_{eq}$ as compared to $\mathbf{7}_{ax}$ versus $\mathbf{7}_{eq\prime}$ and accounts for the difference between the $\mathbf{6}_{ax}$: $\mathbf{6}_{eq}$ ratio of ca. 50:50 and the $\mathbf{7}_{ax}$: $\mathbf{7}_{eq}$ ratio of 25:75. Similarly, the E(2) value for all orbital interactions between the antiperiplanar Si-H and C-H_{ax} bonds in **5**_{eq} $(5.24 \text{ kcal mol}^{-1})$ is $1.5 \text{ kcal mol}^{-1}$ stronger than in $\mathbf{6}_{eq}$, whereas the $\sigma(C2-S) \rightarrow \sigma^*(Si-H)$ interaction in $\mathbf{6}_{ax}$ (0.97 kcal mol⁻¹) is weaker than the $\sigma(C2-S) \rightarrow \sigma^*(Si-F)$ interaction (1.52 kcal mol⁻¹). This is responsible for the difference between the **6**_{ax}:**6**_{eq} ratio of ca. 50:50 and the one of $\mathbf{5}_{ax}$: $\mathbf{5}_{eq}$ equal to 15:85.

CONCLUSIONS

The conformational equilibria of 3-methyl-3-silathiane 5 and 3-fluoro-3-methyl-3-silathiane 6, and, for comparison, of 1-fluoro-1-methyl-1-silacyclohexane 7, were studied using low-temperature ¹³C NMR spectroscopy down to 103 K and by theoretical calculations. The conformational behavior of 3-silathianes significantly differs both from that of the related thianes and from that of the related silacyclohexanes: the experimental ratio $\mathbf{5}_{ax}:\mathbf{5}_{eq}$ at 103 K is close to the 26:74 ratio measured for 1-methyl-1-silacyclohexane but drastically differs from the 2:98 ratio for 3-methy-Ithiane. At the same time, the experimental ratio $\mathbf{6}_{ax}\!:\!\mathbf{6}_{eq}$ of ca. 50:50 differs from the experimental ratio $\mathbf{7}_{ax}$: $\mathbf{7}_{eq} = 25:75$; although there are no experimental data for 3-fluoro-3-methy-Ithiane, the calculations predict small predominance of the $Me_{ax}F_{eq}$ conformer. Simple steric reasoning can neither predict nor even explain the observed conformational preferences, like equal population of the two conformers of 6, or different ratio of the conformers for 5 and 7. This was made possible by using the NBO analysis, namely, considering the vicinal orbital interactions between the Si-X and the adjacent C-H, C-S and C-C bonds.

EXPERIMENTAL

General

All starting materials and solvents were commercially available and were dried and purified by conventional procedures prior to use. Synthesis and room-temperature NMR spectra of 3-methyl-3-silathiane **5** and 3-fluoro-3-methyl-3-silathiane **6** were described in Ref.^[39] 1-Methyl-1-phenyl-1-silacyclohexane was synthesized from methylphenyldichlorosilane similar to the earlier described procedure.^[40]

1-Methyl-1-phenyl-1-silacyclohexane (15)

A solution of methylphenyldichlorosilane (7.6 g, 0.04 mol) in diethyl ether (100 ml) was added dropwise to the di-Grignard reagent prepared from 1,5-dibromopentane (9.2 g, 0.04 mol) and magnesium powder (3.6 g, 0.15 mol) in diethyl ether (250 ml) at room temperature. The reaction mixture was refluxed for 6 h, cooled and a saturated aqueous NH₄Cl solution was then added. The layers were separated and the aqueous layer was extracted with Et₂O. The combined organic phase was dried (CaCl₂), filtered and diethyl ether removed. The residue was purified by vacuum distillation to give 15 (2.69 g, 35% yield) as a colorless liquid, b.p. 96–97°C/ 2 mmHg. ¹H NMR (CDCl₃): $\delta = 0.28$ (s, 3H, MeSi), 0.80–0.86 (m, 2H, CH^A-2/6), 0.92–0.99 (m, 2H, CH^B-2/6), 1.40–1.47 (m, 1H, CH^A-4), 1.52–1.59 (m, 1H, CH^B-4), 1.68–1.75 (m, 2H, CH^A-3/5), 1.78–1.84 (m, 2H, CH^B-3/5), 7.36–7.38 (m, 3H, H_{m+p}), 7.55–7.57 (m, 2H, H_o). ¹³C NMR (CD₂Cl₂/CHCl₂F/CHCl₂): $\delta = -3.8$ (Si–*Me*), 13.8 (C-2/6), 25.6 (C-3/ 5), 31.2 (C-4), 130.0 (C_p), 128.9 (C_m), 134.8 (C_o), 140.6 (C_i). The ¹H and ¹³C NMR data coincide with the published data.^[41]

1-Fluoro-1-methyl-1-silacyclohexane (7)

BF₃.2CH₃COOH (1.59 ml, 11.6 mmol) was added to a stirred solution of 1-methyl-1-phenyl-1-silacyclohexane (2.00 g, 10.5 mmol) in CH_2Cl_2 (5 ml). The reaction mixture was refluxed for 5 h, cooled to room temperature, diluted with *n*-pentane (5 ml), and neutralized with a saturated solution of Na_2CO_3 (0.4 ml). The mixture was extracted with *n*-pentane, the combined organic extracts were

dried (MgSO₄), filtered and the solvents removed. Compound **7** was obtained a colorless liquid in 66% yield (0.88 g) by fast vacuum distillation with a heat gun (140–160°C). ¹H NMR (CDCI₃): δ = 0.26 (d, 3H, *Me*Si, ³J_{H-F} = 7.3 Hz), 0.61–0.71 (m, 2H, CH-2/6), 0.87–0.94 (m, 2H, CH-2/6), 1.34–1.43 (m, 1H, CH-4), 1.53–1.59 (m, 1H, CH-4), 1.73–1.78 (m, 4H, CH-3/5). ¹³C NMR (Table 1). ¹⁹F NMR (CDCI₃): δ = -138.18 (sext, J_{H-F} = 6.0 Hz). ²⁹Si NMR (CDCI₃): δ = 27.66 (d, J_{Si-F} = 286.2 Hz). The ¹H, ¹³C, ²⁹Si NMR data are consistent with the reported data.^[18]

NMR experiments

The ¹H, ¹³C, ¹⁹F, ²⁹Si NMR spectra were recorded on a Bruker DPX-400 spectrometer (¹H, 400.1 MHz; ¹³C, 100.6 MHz; ¹⁹F, 376.3 MHz; ²⁹Si, 79.5 MHz) and the low temperature ¹³C NMR spectra on a Bruker AV-600 (at 150.95 MHz). Chemical shifts were determined relative to residual CHCl₃ (¹H, δ 7.27), internal CDCl₃ (¹³C, δ 77.0), internal CD₂Cl₂ (¹³C, δ 53.73) and are given in ppm downfield to TMS (for ¹H, ¹³C, ²⁹Si) or CFCl₃ (for ¹⁹F). Analysis and assignment of the ¹H NMR data were supported by homonuclear (COSY) and heteronuclear (HSQC ¹³C-¹H, HMBC ¹³C-¹H) 2D correlation experiments. ¹J_{C-H} coupling constants were measured by using coupled 2D HMBC or 2D HSQC experiments. ¹³C NMR spectra were recorded with broad-band proton decoupling and were assigned by using DEPT experiments. The ${}^{1}J_{CH}$ coupling constants were obtained from cross sections of the $2D{^{1}H-^{13}C}$ HSQC spectra^[42] recorded without wide band decoupling from ¹³C by GARP pulse sequence.

From the 2D HSQC spectrum of 3-fluoro-3-methyl-3-silathiane **6** the values of ${}^{3}J_{FH} = -1.2$ Hz for the proton signal at 2.00 ppm and ${}^{3}J_{FH} = +3.2$ Hz for that at 1.75 ppm were determined. The theoretically calculated averaged (1:1) *trans* and *cis* values are +5.15 and -0.61 Hz, respectively.

A solvent mixture of CD₂Cl₂, CHFCl₂, and CHF₂Cl in a ratio of 1:1:3 was used for the low temperature measurements. 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 chemical shifts difference Δv_{cr} Hz was determined by extrapolation to the coalescence temperature T_c and used to calculate k_c and the ring inversion barriers by the Eyring equation at T_c in the usual way for compound **6**,^[43] and employing the method of Shanan-Atidi and Bar-Eli^[26] for compounds **5** and **7**, due to population differences of the conformers.

Computational methods

The geometry optimization and the energy calculations were carried out at the DFT/B3LYP/6-311G(d,p) level of theory for the axial and equatorial conformers of compounds 1, 2, 5-14. Vibrational frequencies and thermodynamic parameters were computed at the same level of theory at 298.15 K and 1 atm of pressure using the unscaled zero point vibrational energies (ZPE). For silathianes 5, 6 and fluorocyclohexane 13 the MP2/ 6-311G(d,p) calculations were also performed; thermodynamic parameters were calculated using the MP2 energies and the results of B3LYP vibrational calculations. All calculations were performed with full optimization of all variables using the Gaussian 03 package.^[44] The chemical shieldings and coupling constants were calculated using the GIAO^[45,46] method at the B3LYP/6-311G(d,p) level of theory. The NBO analysis $^{\left[47,48\right] }$ as implemented in the Gaussian 03 package, was performed for the axial and equatorial conformers of 5-7.

Acknowledgements

The financial support of this work by the Russian Foundation for Basic Research and Deutsche Forschungsgemeinschaft (Grant RFBR-DFG No. 08-03-91954) is gratefully acknowledged. Recording of the low-temperature spectra by Dr. Matthias Heydenreich and Dipl.-Ing (FA) Angela Krtitschka (University of Potsdam) is greatly acknowledged.

REFERENCES

- [1] E. L. Eliel, Acc. Chem. Res. 1970, 3, 1-8.
- [2] J. B. Lambert, Acc. Chem. Res. 1971, 4, 87-94.
- [3] N. S. Zefirov, I. V. Kazimirchik, Russ. Chem. Rev. 1974, 43, 252-265.
- [4] E. Juaristi, Acc. Chem. Res. 1989, 22, 357-364.
- [5] E. Kleinpeter, in Conformational Behavior of Six-Membered Rings. Analysis, Dynamics, and Stereoelectronic Effect (Ed.: E. Juaristi), Wiley-VCH, New York, **1995**, pp. 201–243.
- [6] E. Kleinpeter, Advances in Heterocyclic Chemistry, Elsevier Academic Press, Amsterdam, 2004, 86, pp. 41–127.
- [7] G. Rousseau, L. Blanco, Tetrahedron 2006, 62, 7951–7993.
- [8] I. Arnason, G. K. Thorarinsson, E. Matern, Z. Anorg. Allg. Chem. 2000, 626, 853–862.
- [9] I. Arnason, A. Kvaran, S. Jonsdottir, P. I. Gudnason, H. Oberhammer, J. Org. Chem. 2002, 67, 3827–3831.
- [10] L. B. Favero, B. Velino, W. Caminati, I. Árnason, Á. Kvaran, Organometallics 2006, 25, 3813–3816.
- [11] L. B. Favero, B. Velino, W. Caminati, I. Arnason, A. Kvaran, J. Phys. Chem. A 2006, 110, 9995–9999.
- [12] A. Bodi, Á. Kvaran, S. Jonsdottir, E. Antonsson, S. Ó. Wallevik, I. Arnason, A. V. Belyakov, A. A. Baskakov, M. Hölbling, H. Oberhammer, Organometallics 2007, 26, 6544–6550.
- [13] G. V. Girichev, N. I. Giricheva, A. Bodi, P. I. Gudnason, S. Jonsdottir, A. Kvaran, I. Arnason, H. Oberhammer, *Chem. Eur. J.* 2007, 13, 1776–1783.
- [14] S. Ó. Wallevik, R. Bjornsson, A. Kvaran, S. Jonsdottir, I. Arnason, A. V. Belyakov, A. A. Baskakov, K. Hassler, H. Oberhammer, J. Phys. Chem. A 2010, 114, 2127–2135.
- [15] C. H. Bushweller, J. W. O'Neil, H. S. Bilofsky, *Tetrahedron* 1971, 27, 3065–3068.
- [16] A. J. Weldon, G. S. Tschumper, Int. J. Quant. Chem. 2007, 107, 2261–2265.
- [17] R. Bjornsson, I. Arnason, Phys. Chem. Chem. Phys. 2009, 11, 8689–8697.
- [18] S. Ó. Wallevik, R. Bjornsson, Á. Kvaran, S. Jonsdottir, G. V. Girichev, N. I. Giricheva, K. Hassler, I. Arnason, J. Mol. Struct. 2010, in press, 10.1016/j.molstruc.2010.02.059.
- [19] A. Bodi, R. Bjornsson, I. I. Arnason, J. Mol. Struct. 2010, in press, 10.1016/j.molstruc.2009.12.002.
- [20] F. Freeman, C. Cha, C. Fang, A. C. Huang, J. H. Hwang, P. L. Louie, B. A. Shainyan, J. Phys. Org. Chem. 2005, 18, 35–48.
- [21] S. V. Kirpichenko, E. Kleinpeter, B. A. Shainyan, J. Phys. Org. Chem. 2010, 48, in press, 10.1002/poc.1677.
- [22] D. K. Dalling, D. M. Grant, J. Am. Chem. Soc. 1967, 89, 6612–6622.
- [23] F. A. L. Anet, C. H. Bradley, G. W. Buchanan, J. Am. Chem. Soc. 1971, 93, 258–259.
- [24] A. E. Aliev, K. D. M. Harris, J. Am. Chem. Soc. 1993, 115, 6369-6377.
- [25] Due to the impurity signal exactly on the methyl 7_{eq} signal (at 103 K), this line appears less broad than the methyl 7_{ax} signal at higher field; however, following the line shape variations along the whole low temperature measurements (cf. Figure 3) this equivocality proves obvious.

- [26] H. Shanan-Atidi, K. H. Bar-Eli, J. Phys. Chem. 1970, 74, 961–963.
- [27] R. L. Willer, E. L. Eliel, J. Am. Chem. Soc. 1977, 99, 1925-1936.
- [28] K. B. Wiberg, J. D. Hammer, H. Castejon, W. F. Bailey, E. L. DeLeon, R. M. Jarret, J. Org. Chem. 1999, 64, 2085–2095.
- [29] F. A. Bovey, E. W. Anderson, F. P. Hood, R. L. Kornegay, J. Chem. Phys. 1964, 40, 3099–3109.
- [30] In the literature, calculations of fluorocyclohexane give inconsistent results varying from -0.6 to 0.3 depending on the method and the basis set used;^{17,31-33} variation of the results for fluorocyclohexane with the level of theory was specially mentioned.³² Still, since the values obtained at good levels of theory are close to zero irrespective of the sign, the position of the equilibrium in Scheme 2 and of similar equilibria for the model compounds having only one of the two heteroatoms, as said above, is expected to be governed by the A value of the methyl group, that is, shifted toward the Me-equatorial conformers.
- [31] K. B. Wiberg, J. Org. Chem. 1999, 64, 6387-6393.
- [32] A. J. Weldon, T. L. Vickrey, G. S. Tschumper, J. Phys. Chem. A 2005, 109, 11073–11079.
- [33] W. S. Ohlinger, P. E. Klunzinger, B. J. Deppmeier, W. J. Hehre, J. Phys. Chem. A 2009, 113, 2165–2175.
- [34] C. H. Bushweller, in Conformational Behavior of Six-Membered Rings. Analysis, Dynamics, and Stereoelectronic Effects, (Ed.: E. Juaristi,). Wiley-VCH, New York, **1995**, pp. 25–58.
- [35] E. L. Eliel, R. J. L. Martin, J. Am. Chem. Soc. 1968, 90, 689-697.
- [36] F. R. Jensen, C. H. Bushweller, B. H. Beck, J. Am. Chem. Soc. 1969, 91, 344–351.
- [37] H.-J. Schneider, N. M. Hoppen, J. Org. Chem. 1978, 43, 3866-3873.
- [38] R. Borsdorf, P. F. Matzen, H. Remane, A. Z. Zschunke, Z. Chem. 1971, 11, 21–22.
- [39] S. V. Kirpichenko, A. I. Albanov, J. Organomet. Chem. 2010, 695, 663–666.
- [40] H. Sakurai, T. Hirose, A. Hosomi, J. Organomet. Chem. 1975, 86, 197–203.
- [41] R. Q. Wiedenhoefer, B. Krzyzanowska, Webb-Wood, Organometallics 1998, 17, 5124–5127.
- [42] A. Bax, S. Subramanian, J. Magn. Reson. 1986, 67, 565-569.
- [43] K. Pihlaja, E. Kleinpeter, "Carbon-13 NMR Chemical Shifts in Structural and Stereochemical Analysis", Methods in Stereochemical Analysis, VCH, New York, 1994.
- [44] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.03, Gaussian, Inc., Pittsburgh PA, 2003.
- [45] J. R. Ditchfield, Mol. Phys. 1974, 27, 789-807.
- [46] J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, J. Chem. Phys. 1996, 104, 5497–5509.
- [47] F. Weinhold, C. R. Landis, Valency and Bonding: A Natural Bond Orbital Donor–Acceptor Perspective, Cambridge University Press, Cambridge, 2005.
- [48] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO Version 3.1, Gaussian, Pittsburgh, PA, CT, 2003.