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Conformational preferences of Si–Ph,H and Si–Ph,Me silacyclohexanes and 1,3-thiasilacyclohexanes. Additivity of conformational energies in 1,1-disubstituted heterocyclohexanes

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ABSTRACT

The conformational equilibria of 1-phenyl-1-silacyclohexane **1**, 3-phenyl-1,3-thiasilacyclohexane 2, 1-methyl-1-phenyl-1-silacyclohexane **3**, and 3-methyl-3-phenyl-1,3-thiasilacyclohexane **4** have been studied for the first time by low temperature ^{13}C NMR spectroscopy at 103 K. Predominance of the equatorial conformer of compound **1** (Ph_{eq}/Ph_{ax}=78%:22%) is much less than in its carbon analog, phenylcyclohexane (nearly 100% of Ph_{eq}). And in contrast to 1-methyl-1-phenylcyclohexane, the conformers with the equatorial Ph group are predominant for compounds **3** and **4**: at 103 K, Ph_{eq}/Ph_{ax} ratios are 63%:37% (**3**) and 68%:32% (**4**). As the Si–C bonds are elongated with respect to C–C bonds, the barriers to ring inversion are only between 5.2–6.0 (ax→eq) and 5.4–6.0 (eq→ax) kcal mol^{-1}. Parallel calculations at the DFT and MP2 level of theory (as well as the G2 calculations for compound **1**) show qualitative agreement with the experiment. The additivity/nonadditivity of conformational energies of substituents on cyclohexane and silacyclohexane derivatives is analyzed. The geminally disubstituted cyclohexanes containing a phenyl group show large deviations from additivity, whereas in 1-methyl-1-phenyl-1-silacyclohexane and 3-methyl-3-phenyl-1,3-thiasilacyclohexane the effects of the methyl and phenyl groups are almost additive. The reasons for the different conformational preferences in carbocyclic and heterocyclic compounds are analyzed using the homodesmotic reactions approach.

1. Introduction

There has been a considerable interest in medium-sized silicon–carbon heterocycles over many years from a theoretical and synthetic point of view, and especially for stereochemical and mechanistic studies of the reactions at silicon.[1,2] Therefore, structural studies of silacyclohexanes remain a state-of-the-art problem of conformational analysis. In the last few years Arnason et al. intensively investigated the conformational equilibria, steric effects, and stereoelectronic interactions in 1-X-1-silacyclohexanes (X=Me,[3,4] F,[5,6] CF_3,[7,8] SiH_3[9]) by various physico-chemical methods such as gas-phase electron diffraction, dynamic nuclear magnetic resonance, microwave spectroscopy, temperature-dependent Raman spectroscopy, and theoretical calculations. Replacement of carbon with silicon in the monosubstituted six-membered cycles drastically alters the conformational energies of the substituents. Thus, the conformational free energy (*A* value) for the methyl group decreases from 1.78 to 0.23 kcal mol^{-1} on going from methylcyclohexane[10] to 1-methyl-1-silacyclohexane.[3] Moreover, the conformational preferences may even invert. Thus, in contrast to fluorocyclohexane[11] and trifluoromethylcyclohexane,[12] the axial conformers are predominant for 1-fluoro-1-silacyclohexane[6] and 1-trifluoromethyl-1-silacyclohexane.[7,8] The increase of the relative axial preference of substituents at silicon in silacyclohexanes with respect to cyclohexanes is favored by the longer C–Si (1.892 Å) as compared to the C–C bond (1.540 Å).

However, the influence of stereoelectronic effects cannot be ruled out either.[13–15] The latter become even more important upon introduction of a second heteroatom into the heterocyclic system. For example, the population of the axial conformer is increased from fluorocyclohexane to 1-fluoro-1-silacyclohexane but is substantially decreased with the further inclusion of ring heteroatoms, e.g., by introduction of the sulfur atom, that is, in 3-fluoro-3-sila-1-thiacyclohexane.[16]

The substituents at the silicon atom, for which the conformational preferences were studied experimentally, are confined to the above mentioned groups (Me, F, CF_3, SiH_3). Besides, the conformational preferences for a large number of substituents in 1-X-1-

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silacyclohexanes were calculated theoretically.[14,15] The studied compounds, however, did not include Si–Ph-substituted silacyclohexanes in spite of a wide application of the Si–Ph-substituted silanes in synthetic organic and organosilicon chemistry.[17–21] For example, the electrophilic cleavage of Si–Ar bonds is an effective method for the preparation of a variety of Si-functionalized acyclic and cyclic compounds.[19,20] Recently, the Si–X-derivatives of 1,3-thiasilacyclohexanes (X=H, F, OR), and 1-Me-1-F-1-silacyclohexane have been synthesized in this way.[16] So far, no conformational studies were reported for these Si-phenyl substituted silacyclohexanes or other heterosilacyclohexanes, or even for any heterocyclohexanes with a phenyl–heteroatom bond except for a computational study of the P–Ph-substituted phosphorinane *P*-oxides.[22] Apart from never being conformationally studied, these compounds are of special interest because they are qualitatively different from the methyl- or halogen-substituted analogs[16] since the phenyl group is an asymmetric rotor and its rotation about the Si–Ph bond may (and does) cause notable variations of nonbonded intramolecular interactions, as was shown by molecular mechanics[23–25] and quantum chemical[26] calculations of phenylcyclohexane. Another feature of the phenyl group is its ability to act as a conformational anchor without notable distortion of the cyclohexane ring (as is the case, e.g., for the *tert*-butyl group).[12,27]

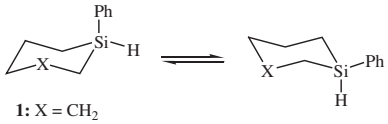
In the case of geminally disubstituted cyclohexanes or heterocyclohexanes the problem of additivity of their conformational free energies arises. This problem, which until recently was confined to cyclohexane derivatives, can be traced back to the 60s of the last century[28] but is still the subject of research including new objects and methods.[29–31] For cyclohexanes, the lack of additivity was concluded to be the rule.[32] The most vivid example of non-additivity is 1-methyl-1-phenylcyclohexane, investigated both experimentally[33] and theoretically.[23–26] The principal conclusion was that the predominance of the axial phenyl conformer over the equatorial in spite of a larger conformational free energy for the phenyl group (2.87 kcal mol^{-1})[33,12] than for the methyl group (1.78 kcal mol^{-1})[10] is due to destabilizing nonvalent interactions of the phenyl ring with the 2,6-H_{eq} and Me protons in the Ph-equatorial conformer.[26] Still, in the similarly substituted cyclohexanes the additivity can be fulfilled for a limited range of the substituents.[32] Recently, based on the CCSD(T)/CBS calculations of the monosubstituted silacyclohexanes with substituents F, CH_3, CF_3, and mono- and disubstituted cyclohexanes with the same substituents, it was concluded that for the equally disubstituted rings the addition model 'works only moderately well for the cyclohexanes' and 'remarkably well for the silacyclohexanes within the limited selection of substituents'.[34]

The conformational analysis of silathiacyclohexanes (silathianes) and their derivatives is our continuing interest.[16,35–41] The subject of the present study is to examine the conformational preferences of the phenyl group in the mono- and disubstituted silacyclohexanes and 1,3-thiasilacyclohexanes using the methods of low temperature NMR spectroscopy and quantum chemical calculations, and to compare them with those in the carbocyclic analogs. As a result of this dynamic NMR study the general problem of the applicability of the concept of additivity of conformational effects of geminal substituents to the cyclohexane and silaheterocyclohexane series is discussed. As the objects for the experimental study we chose 1-phenyl-1-silacyclohexane **1**, 3-phenyl-1,3-thiasilacyclohexane **2**, 1-methyl-1-phenyl-1-silacyclohexane **3**, and 3-methyl-3-phenyl-1,3-thiasilacyclohexane **4**. Phenylcyclohexane **5** and 1-methyl-1-phenylcyclohexane **6** were used as the reference carbocyclic compounds, and 3-phenylthiane **7** and 3-methyl-3-phenylthiane **8** were calculated theoretically as additional reference molecules for the silathianes **3** and **4**, respectively.

2. Results and discussion

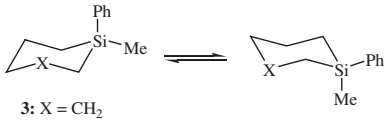
2.1. Dynamic NMR measurements

As follows from the low temperature ^{13}C NMR study, heterocycles **1**–**4** are conformationally flexible. On lowering the temperature down to 103 K, their ^{13}C NMR spectra show changes typical of dynamic exchange processes, namely, broadening, decoalescence, and splitting of the ^{13}C signals. The conformational equilibria are depicted in Schemes 1 and 2.



1: X = CH_2
2: X = S

Scheme 1. Conformational equilibrium of compounds **1** and **2**.



3: X = CH_2
4: X = S

Scheme 2. Conformational equilibrium of compounds **3** and **4**.

The spectral data at room temperature and at the lowest reached temperature of 103 K are given in Table 1. Variable temperature spectra for compounds **2** and **3** are given in Figs. 2 and 4, and the frozen spectra are shown in Figs. 1, 3, 5, and 6. As follows from Table 1, upon lowering the temperature, the aliphatic signals from the room temperature ^{13}C NMR spectrum of 1-phenyl-1-silacyclohexane **1** are shifted upfield and at ~115 K the former two signals decoalesce as shown in the spectrum at 103 K (Fig. 1).

The assignment of the closely spaced ^{13}C resonances of C-2 and C-4 in 3-phenyl-1,3-thiasilacyclohexane **2** was proved by the HMQC spectrum, which shows the correlations of the ^{13}C signal at 10.48 ppm with the two diastereotopic $SiCH_2C$ protons, and the signal at 11.18 ppm with the two diastereotopic $SiCH_2S$ protons (see Fig. SI-1 in Supplementary data). Lowering of the temperature causes continuous upfield shifts, finally broadening of all four signals (Fig. 2) and at the lowest reached temperature (103 K) small signals of the second conformer at ca. 7.3 and 25.5 ppm appear (Fig. 3).

Room temperature NMR spectra of 1-methyl-1-phenyl-1-silacyclohexane **3** were described in our previous paper;[16] at low temperatures the signals of carbons attached to silicon decoalesce (Fig. 4) and the ratio of the conformers was determined from the frozen spectrum (Fig. 5).

For 3-methyl-3-phenyl-1,3-thiasilacyclohexane **4**[42] the assignment of the closely resonating C-2 and C-4 was made from HMBC as in case of **2**. Both SiMe and C-2/C-4 signals decoalesce below 110 K, however only the SiMe signal could be resiliently evaluated with respect to free energy differences; the frozen spectrum at 103 K is given in Fig. 6.

Note that the decoalescence is most pronounced for carbon atoms directly attached to silicon. This seems reasonable since it is the silicon atom, which bears two different substituents (H, Ph in **1**, **2** or Me, Ph in **3**, **4**) changing their positions upon the ring inversion (Schemes 1 and 2).

The principal question for determination of the ratio of the conformers is the assignment of the decoalesced signals of the axial and equatorial conformers of **1**–**4**. For the Si–Me,Ph-substituted compounds **3** and **4**, the more intense high-field Si–Me signals in

Table 1
^{13}C chemical shifts for compounds **1**–**4** at 298 K ($CDCl_3$) and 103 K ($CD_2Cl_2/CHFCl_2/CHF_2Cl$ 1:1:3)

No.	*T*, °K	MeSi	C-2/6	C-3/5	C-4	No.	*T*, °K	MeSi	C-2	C-4	C-5	C-6
1	298		10.67	24.89	29.86	**2**	298		11.18	10.48	27.58	32.28
1-Ph_{ax}	103		8.39	23.52	29.11	**2**-Ph_{ax}	103		7.4	7.3	25.4	25.5
1-Ph_{eq}	103		10.44	24.95	29.11	**2**-Ph_{eq}	103		10.2	9.33	27.85	31.05
3[a]	298	−3.8	13.8	25.6	31.2	**4**	298	−4.86	13.40	12.69	26.99	32.30
3-Ph_{ax}	103	−1.84	11.00	23.99	29.35	**4**-Ph_{ax}	103	−1.74	12.61	11.44	26.72	31.44
3-Ph_{eq}	103	−7.59	12.06	23.99	29.35	**4**-Ph_{eq}	103	−8.10	[b]	10.50	26.72	31.44

[a] In the mixture $CD_2Cl_2/CHFCl_2/CHF_2Cl$ (1:1:3).
[b] Overlaps with the signal at 11.44 or 10.50 ppm.

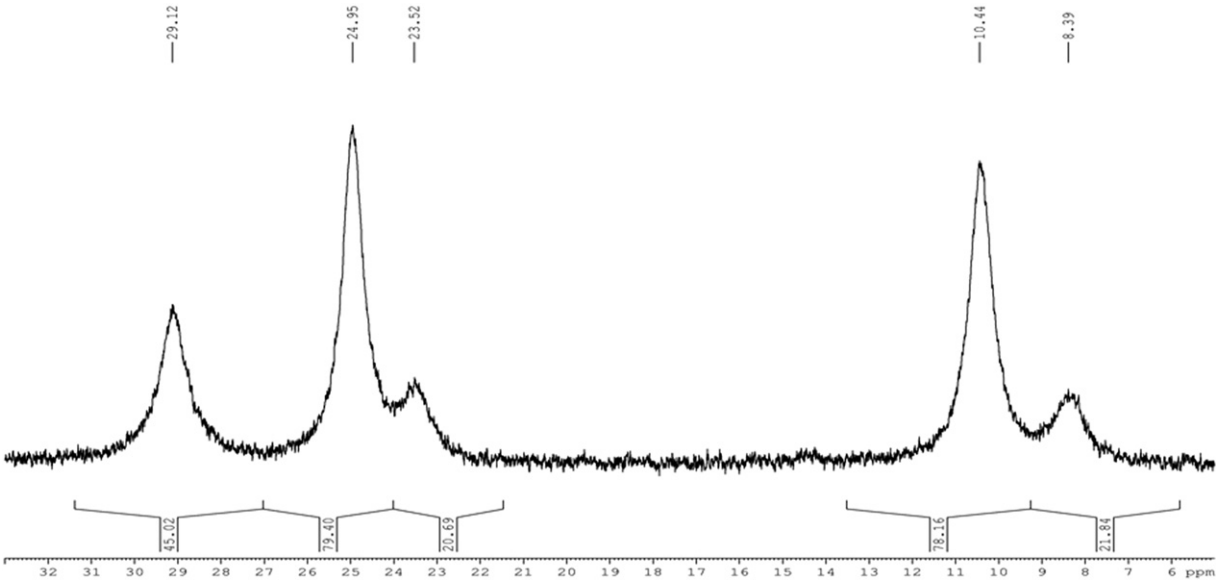


Fig. 1. ^{13}C NMR spectrum of the frozen conformational equilibrium of 1-phenyl-1-silacyclohexane **1** at 103 K.

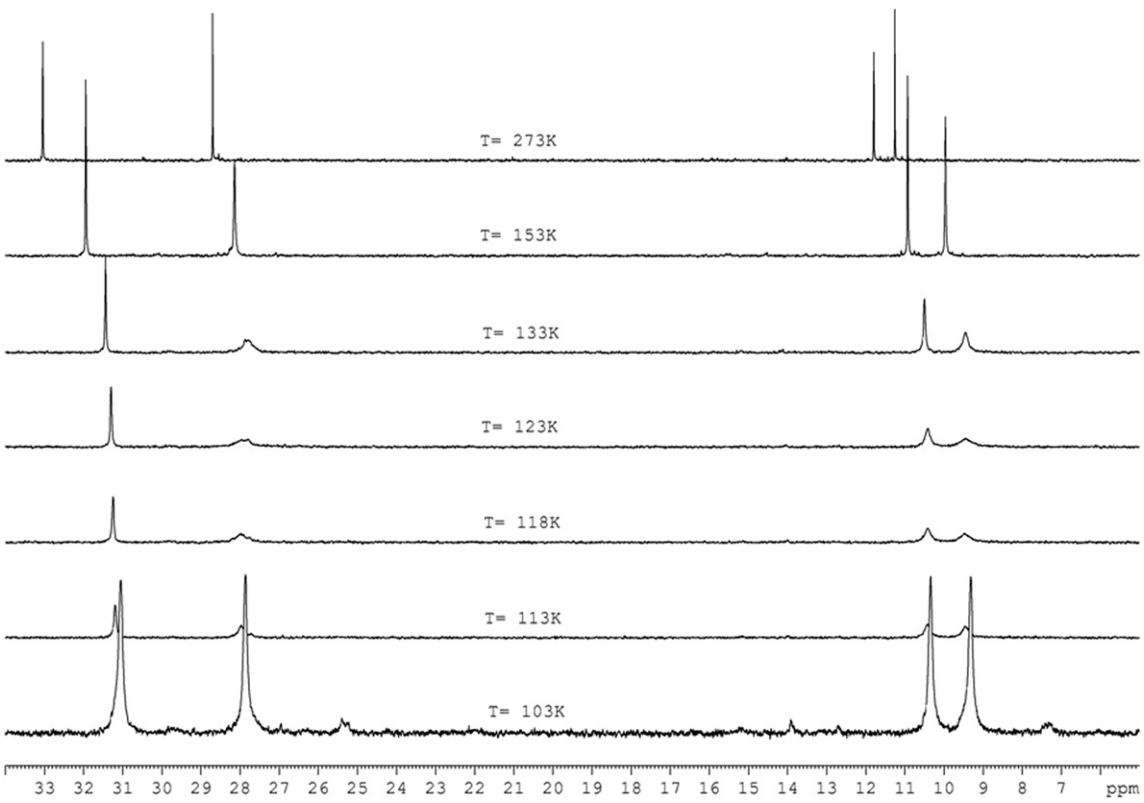


Fig. 2. Variable temperature ^{13}C NMR spectra of 3-phenyl-1,3-thiasilacyclohexane **2**.

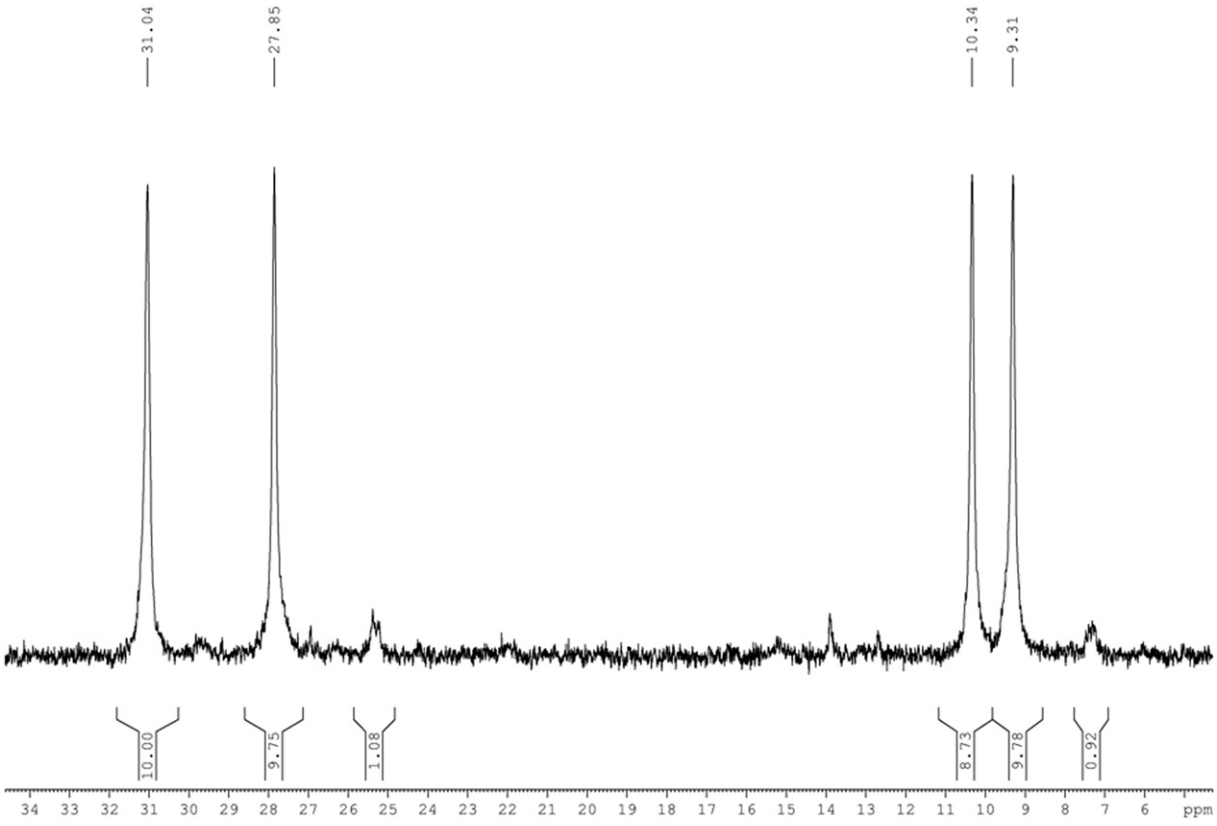


Fig. 3. ^{13}C NMR spectrum of the frozen conformational equilibrium of 3-phenyl-1,3-thiasilacyclohexane **2** at 103 K.

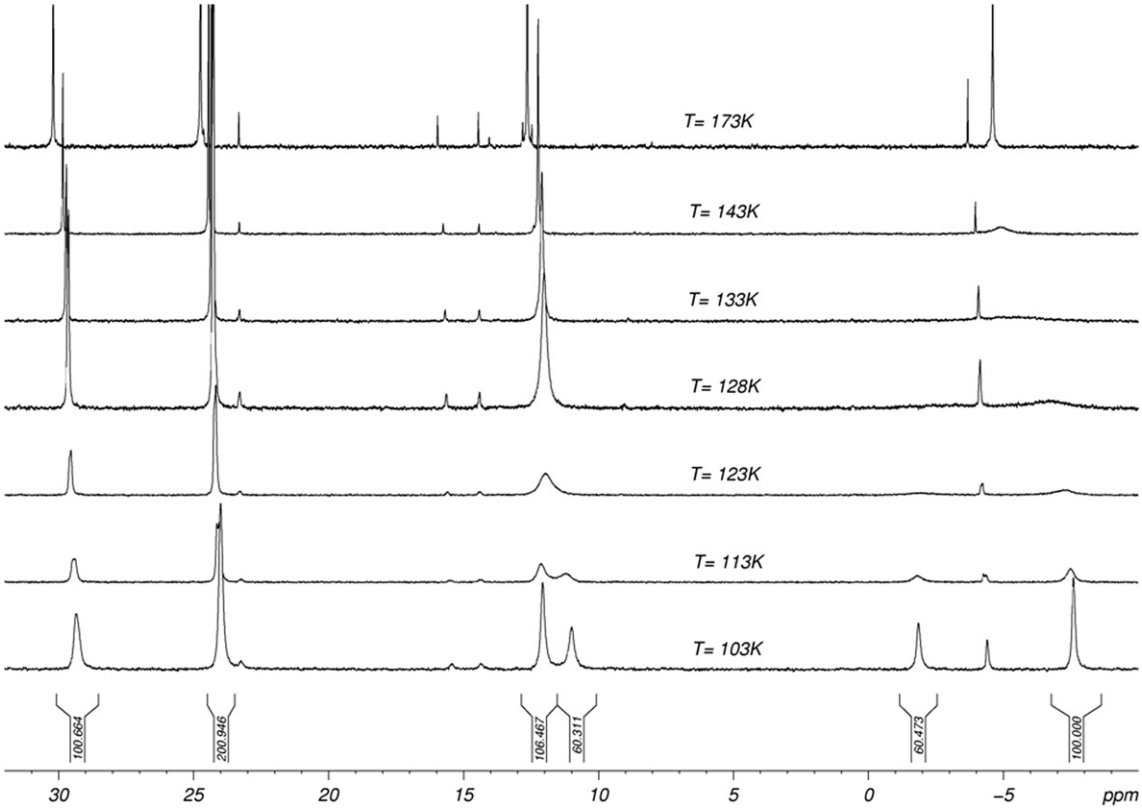


Fig. 4. Variable temperature ^{13}C NMR spectra of 1-methyl-1-phenyl-1-silacyclohexane **3**.

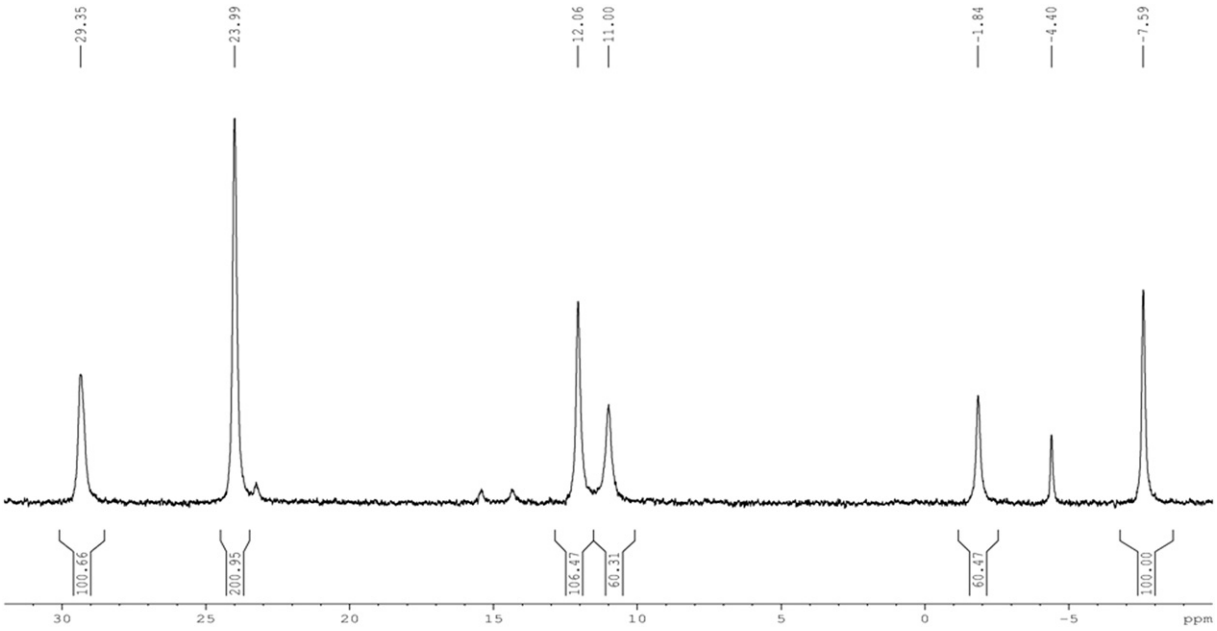


Fig. 5. ^{13}C NMR spectrum of the frozen conformational equilibrium of 1-methyl-1-phenyl-1-silacyclohexane **3** at 103 K.

the low temperature spectra (Figs. 5 and 6) were assigned to the axial methyl groups by analogy with the assignment made for 1-methyl-1-phenylcyclohexane,[33] 1-methyl-1-silacyclohexane derivatives[3] and are in accordance with general rules of cyclohexane stereochemistry.[43] For 1-phenyl-1-silacyclohexane **1**, the assignment of the signals to the axial or equatorial conformer (Fig. 1) was made by analogy with that for its Si–Me analog **3** since the positions of the C-2,6 and C-3,5 signals in compounds **1** and **3** are very similar, and is consistent with that for 1-phenyl-1-cyclohexane[44] and its derivatives.[33] The same spectral pattern observed for 3-phenyl-1,3-thiasilacyclohexane 2 (Fig. 3) allowed us to assign the appearing signals at 7.3 and 25.5 ppm to the minor axial conformer.

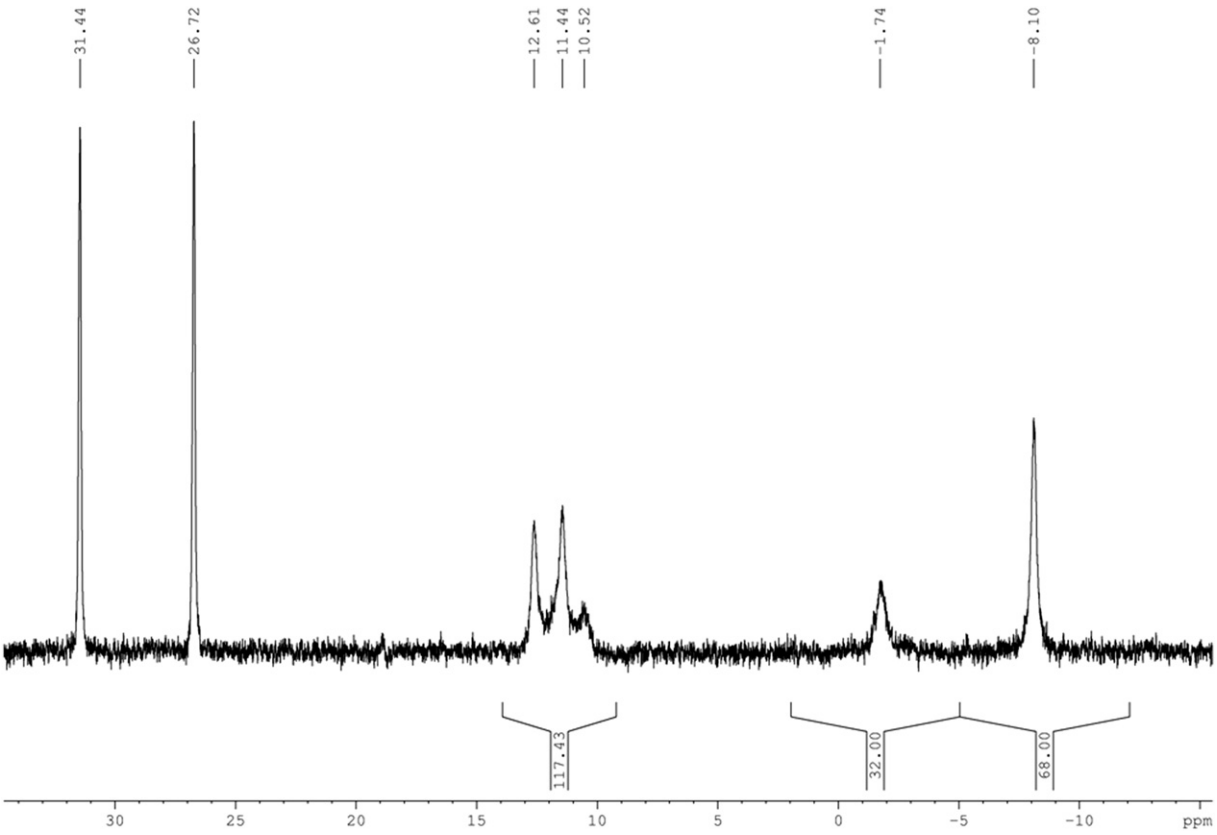


Fig. 6. ^{13}C NMR spectrum of the frozen conformational equilibrium of 3-methyl-3-phenyl-3-sila-1-thiacyclohexane **4** at 103 K.

Therefore, compounds **1**–**4** exist predominantly as Ph_{eq}-conformers. The ratio of the conformers and other conformational characteristics are given in Table 2 together with phenylcyclohexane **5** and 3-phenylthiane **7**, which were shown to be conformationally homogeneous and existing as single Ph_{eq}-conformers.

Table 2
Conformational characteristics of 1-phenyl-1-silacyclohexane **1**, 3-phenyl-1,3-thiasilacyclohexane **2**, 1-methyl-1-phenyl-1-silacyclohexane **3**, 3-methyl-3-phenyl-1,3-thiasilacyclohexane **4**, and reference compounds phenylcyclohexane **5** and 3-phenylthiane **7**

Compound	Ph_{eq}/Ph_{ax}, %	K	$A=G_{ax}-G_{eq}$, kcal mol^{-1}	T_c, K (pairs of signals)	$\Delta G^{\neq}$, (eq→ax)/(ax→eq), kcal mol^{-1}
1	78:22	3.35	0.25	118 (C-2/6)	5.39/5.71
	79:21	3.00	0.22	113 (C-3/5)	5.17/5.42
2	95:5	19.0	0.60 (at 103 K)	115–125	—
	75:25	3.0	0.64 (at 296 K)		
3	62:38	1.78	0.12	130 (SiMe)	5.96/6.01
	64:36	1.63	0.10	120 (C-2/6)	5.50/5.63
4	68:32	2.12	0.15	120 (SiMe)	5.47/5.67
5	~100:0	—	2.87[a]	—	—
7	~100:0	—	3.30[b]	—	—

[a] Ref. 34.
[b] ΔG_{298K} calculated at the B3LYP/6-311G** level of theory.

Because the conformational equilibrium of 3-phenyl-1,3-thiasilacyclohexane **2** is so highly biased at 103 K we also simulated the room temperature ^{1}H NMR spectrum of this compound. The comparison of experimental and simulated spectra is given in Fig. 7 (spread parts, for emphasizing the excellent agreement, and chemical shifts/H,H-coupling constants thus obtained are given in Supplementary data).

the 2-equatorial conformation. Employing the corresponding values ($^3J_{4ax,5ax}$=13.15, $^3J_{4ax,5eq}$=4.8, $^3J_{4eq,5ax}$=3.25, $^3J_{4eq,5eq}$=5.2, $^3J_{5ax,6ax}$=11.9, $^3J_{5ax,6eq}$=2.85, $^3J_{5eq,6ax}$=2.3, $^3J_{5eq,6eq}$=4.85 Hz) as references[16] and adopting $^3J_{4,5trans}$=10.4, $^3J_{4,5cis}$=6.75, $^3J_{5,6trans}$=11.0, $^3J_{5,6cis}$=7.1 Hz for **2** as experimental values (all data δ and J of **2** are given in Supplementary data) from the spectrum simulation after $K=[^3J_{ax,ax}-^3J_{trans}]/[^3J_{ax,ax}-^3J_{eq,eq}]$ and $K=[^3J_{ax,ax}-^3J_{cis}]/[^3J_{ax,ax}-^3J_{eq,eq}]$, respectively, the following mean results were obtained: K=0.25 for the minor (25%) and 0.75 for the major conformer (75%). This gives the conformational equilibrium constant K=3.0 (Scheme 1), and $(G_{ax}-G_{eq})$=0.64 kcal mol^{-1} at room temperature very similar to that at 103 K (0.60 kcal mol^{-1}) obtained from the low temperature study (Table 2). These simulation results at room

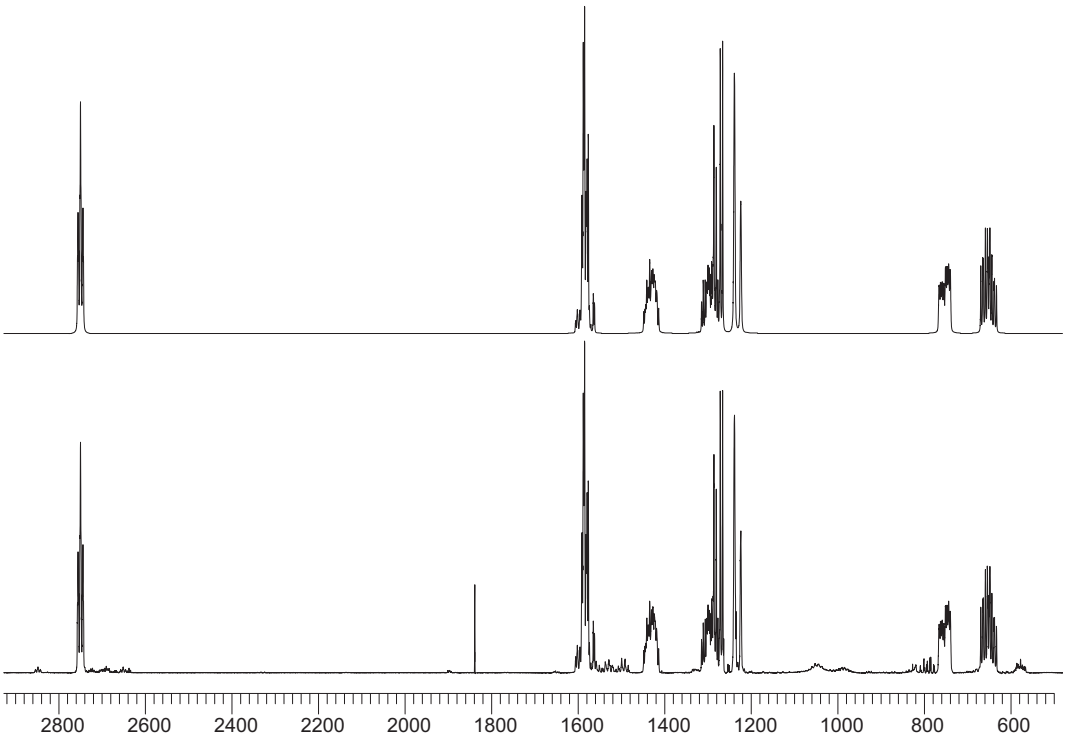


Fig. 7. Simulated (above) and experimental (below) ^{1}H NMR spectrum of 3-phenyl-1,3-thiasilacyclohexane **2**.

In order to detect the room temperature conformational equilibrium of **2** we used the vicinal H,H-coupling constants of the protons at C-4 to C-6 and compared them to those in 2-Me_3Si-3,3-dimethyl-3-silathiane,[16] which was proved to exist exclusively in

temperature are really significant because it proves (i) the preferred conformer of **2** to be the conformer with the equatorial phenyl substituent at silicon in **2** (from the $^3J_{3ax,4ax}$=5.8 Hz compared with $^3J_{3ax,4eq}$=1.3 Hz) and (ii) that the high-field signals at 103 K in the

^{13}C NMR spectrum (at 7.3 and 25.5 ppm) are really generated by the second, the minor conformer with the axial phenyl substituent at silicon.

For further discussion, it was important to obtain the so far unknown conformational free energy for the phenyl group attached to silicon. The value of ΔG^{o} measured by us from the low temperature ^{13}C NMR spectra of 1-phenylsilacyclohexane **1**, is 0.22–0.25 kcal mol^{-1} (Table 2), which is one order of magnitude lower than the conformational energy of the Ph group in phenylcyclohexane (2.87 kcal mol^{-1}). Note, however, that conformational preferences of the Ph group depend not only on the nature of heteroatom it is attached to but also on the presence (and, apparently, the nature) of another heteroatoms in the ring, as clearly demonstrated by larger predominance of the Ph$_{eq}$-conformer of compound **2** versus compound **1** (Table 2).

2.2. Theoretical calculations

To get a deeper insight into the effect of heteroatoms (Si and S) on the conformational equilibrium of heterocyclohexanes we have performed DFT and MP2 calculations of the conformers of the monophenyl compounds **5**, **1**, **2**, and the Me,Ph-geminally disubstituted compounds **6**, **3**, **4**. For 1-phenyl-1-silacyclohexane **1** the G2 calculations were also performed. The results are summarized in Table 3.

$$\mathbf{1}-\mathrm{ax}: E(2)[\sigma(\mathrm{Si{-}H})\rightarrow \mathrm{all}\sigma^{*}] + E(2)[\sigma(\mathrm{Si{-}C_{Ph}})\rightarrow \mathrm{all}\sigma^{*}] = 10.39 + 18.89 = 29.28\ \mathrm{kcal\,mol^{-1}}$$

$$\mathbf{1}-\mathrm{eq}: E(2)[\sigma(\mathrm{Si{-}H})\rightarrow \mathrm{all}\sigma^{*}] + E(2)[\sigma(\mathrm{Si{-}C_{Ph}})\rightarrow \mathrm{all}\sigma^{*}] = 10.58 + 17.64 = 28.22\ \mathrm{kcal\,mol^{-1}}$$

$$\mathbf{2}-\mathrm{ax}: E(2)[\sigma(\mathrm{Si{-}H})\rightarrow \mathrm{all}\sigma^{*}] + E(2)[\sigma(\mathrm{Si{-}C_{Ph}})\rightarrow \mathrm{all}\sigma^{*}] = 11.11 + 18.71 = 29.82\ \mathrm{kcal\,mol^{-1}}$$

$$\mathbf{2}-\mathrm{eq}: E(2)[\sigma(\mathrm{Si{-}H})\rightarrow \mathrm{all}\sigma^{*}] + E(2)[\sigma(\mathrm{Si{-}C_{Ph}})\rightarrow \mathrm{all}\sigma^{*}] = 10.72 + 19.02 = 29.74\ \mathrm{kcal\,mol^{-1}}$$

These results allow one to conclude that (i) interaction with the heterocycle of higher acceptor activity **2** is expectedly larger than with **1**; (ii) this effect is small for the axial conformer (0.54 kcal mol^{-1}) but substantially larger for the equatorial conformer (1.52 kcal mol^{-1}). Therefore, on going from **1** to **2**, the conformational equilibrium should shift in favor of the equatorial conformer, which is the case (Table 2).

Table 3
MP2/6-311G(d,p), B3LYP/6-311G(d,p) (*in italics*) and G2 (**in bold**) calculated total energies (E, hartrees) and thermodynamic parameters (ΔE=E(Ph$_{ax}$)−E(Ph$_{eq}$), ZPE, ΔH^{o}_{298}, ΔG^{o}_{298}, kcal mol^{-1}, S^{o}, cal mol^{-1} K^{-1}) for the conformational equilibria in compounds **1**–**6**

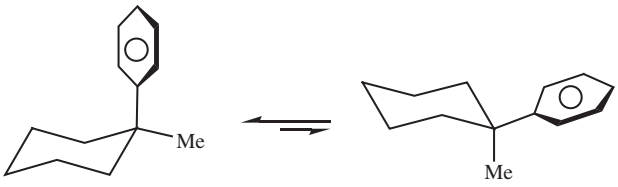
No.	Ph$_{ax}$			Ph$_{eq}$			ΔE	$-\Delta H^{o}_{298}$	$-\Delta G^{o}_{298}$
	E	ZPE	S^{o}	E	ZPE	S^{o}			
5[a]	−465.570121	158.39	101.14	−465.576233	158.03	100.52	3.84	4.14	3.95
	−467.040766	*157.42*	*100.62*	*−467.047692*	*157.16*	*99.49*	*4.35*	*4.58*	*4.25*
1	−716.596008	151.56	108.79	−716.596885	151.36	109.72	0.55	0.67	0.95
	−718.459153	*150.59*	*108.62*	*−718.460616*	*150.53*	*109.44*	*0.92*	*0.92*	*1.17*
	−717.986477			**−717.987632**			**0.72**	**0.72**	**0.68**
2	−1075.065105	134.31	110.71	−1075.065057	134.12	111.90	−0.03	0.08	0.43
	−1077.350025	*133.48*	*111.16*	*−1077.350913*	*133.39*	*110.96*	*0.92*	*0.97*	*1.16*
6[a]	−504.774572	175.81	108.58	−504.771484	175.95	104.04	−1.94	−2.00	−3.35
	−506.365209	*174.60*	*105.58*	*−506.364306*	*174.61*	*104.14*	*−0.57*[b]	*−0.59*	*−1.02*
3	−755.809324	169.58	117.67	−755.808109	169.45	117.18	−0.76	−0.67	−0.82
	−757.798740	*168.44*	*109.59*	*−757.798801*	*168.32*	*116.81*	*0.04*	*−0.46*	*1.69*
4	−1114.276815	152.32	119.73	−1114.277252	152.18	119.70	0.27	0.38	0.37
	−1116.688918	*151.38*	*118.10*	*−1116.689815*	*151.21*	*119.79*	*0.56*	*0.67*	*1.17*

[a] A detailed theoretical conformational analysis of compounds **5** and **6** was reported in the literature.[26] The results for these compounds in Table 2 are given for uniformity of comparison.
[b] Experimental value determined from low temperature ^{13}C NMR spectra is −0.32 kcal mol^{-1}.[33]

For the monophenyl substituted species **1**, **2**, **5** the conformational equilibrium is shifted to the Ph$_{eq}$-conformers, being maximum for phenylcyclohexane **5**, in full agreement with the experiment. The appearance of more than 20% of the axial conformer for 1-phenyl-1-silacyclohexane **1** (Table 2) is reasonably rationalized considering the ring enlargement due to the longer C–Si versus C–C bonds (vide supra). However, this effect cannot account for a reverse shift of the conformational equilibrium toward the equatorial conformer by further enlargement of the ring size by introduction of the sulfur atom, that is, on going from **1** to **2** (Table 2). A tentative explanation can be suggested based on the recent hypothesis of partitioning the total energy of substituted cyclohexanoids into ring and substituent contributions.[45] For this, we have performed the NBO analysis of the conformers of **1** and **2** and compared the second order perturbation energies of the donor orbitals σ(Si–H) and σ(Si–C$_{Ph}$) with the proper orbitals of the heterocycle:

In contrast to 1-methyl-1-phenylcyclohexane **6**, the experimentally determined preferable conformation for the geminally disubstituted heterocycles **3** and **4** is the one with the equatorial phenyl and axial methyl group. For the Si,S-heterocycle **4** this is proved at both DFT and MP2 levels of theory, whereas for the Si-heterocycle **3** only DFT calculations predict strong predominance of the Ph$_{eq}$ conformer.

As concluded by Wiberg et al.,[26] the main reason for the unfavorable **6**-Ph$_{eq}$ conformation is the presence of the axial geminal methyl group, which does not allow the equatorial phenyl group to adopt the conformation minimizing steric repulsive interactions with the H-2,6$_{eq}$ atoms, that is, when the plane of the phenyl ring bisects the C2–C1–C6 angle (Scheme 3).



Scheme 3. Conformational equilibrium of 1-methyl-1-phenylcyclohexane **6**.

As a result, depending on the method of calculation, the **6**-Ph_{ax} conformer is 0.52–1.85 kcal mol^{-1} more stable than the **1**-Ph_{eq} conformer (see Ref. 26 and our data in Table 3). Evidently, the longer Si–C (1.904 Å) and S–C (1.82 Å) bonds compared to the C–C bond (1.534 Å) should attenuate such a destabilizing effect of the geminal methyl group. Indeed, the H···H distances between the phenyl *ortho* hydrogens (H_o) and the methyl and methylene hydrogens in the axial and equatorial conformers of compounds **3** and **4** are larger than the sum of the van der Waals (vdW) radii of hydrogen atoms (2.4 Å). Note, that the calculated structure of **3**-Ph_{ax} excellently coincides with the X-ray structure of *trans*-1-(*p*-bromophenyl)-4-*tert*-butyl-1-methyl-1-silacyclohexane.[46]

As was shown in Introduction, the additivity of the conformational energies of the substituents is rather an exception in the cyclohexane series, but a rule in the silacyclohexane series. To make more valid conclusions on additivity or nonadditivity, we have analyzed the up to now available data on the conformational equilibria for the geminally disubstituted compounds of the two series. The following *A* values from the most recent compilation of Bushweller[47] were used: Me (1.74), CF_3 (2.50), Ph (2.87), F (0.36), Cl (0.54), Br (0.48), Me_2N (1.53), OH (1.01). The results are summarized in Table 4.

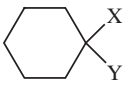
Even a brief inspection of Table 4 reveals that, in general, deviations from additivity are much larger for the cyclohexane than for the silacyclohexane series. This might seem to be fully consistent with the conclusion made by Arnason et al.,[34] unless there was a good deal of evidence of additivity even in the cyclohexane series, for example, in 1-halo-1-methylcyclohexanes,[11,52] 1-vinyl- and 1-ethynyl-1-cyclohexanols, or 1-acetoxy-1-methylcyclohexanes[11] omitted from Table 4 for brevity. Therefore, the lack of additivity in cyclohexanes cannot be considered as a general rule although the trend when comparing with silacyclohexanes is evident. The next important issue is the aforementioned specific behavior of substituents, which are asymmetric rotors, like Ph, whose rotation about the C–Ph or Si–Ph bond is affected by the second geminal substituent leading to substantial variations in energy, as proved by the largest deviations from additivity (Table 4, $\Delta\Delta G^o$=1.36–1.84). It may even reverse the positions of the two substituents in the preferable conformer relative to the predicted from their conformational energies, like in 1-methyl-1-phenylcyclohexane, 1-methyl-1-phenylcyclohexanol, or 1-(dimethylamino)-1-phenylcyclohexane. Note also that the presence of a heteroatom in a position remote from the endocyclic carbon atom bearing two substituents practically does not alter the situation observed for cyclohexanes: deviations for 3-methyl-3-phenylthiane and 3-methyl-3-fluorothiane are large, being maximum for the former (Table 4).

To gain a better insight into the origin of these differences and to estimate the energetic consequences of the nonbonded interactions, we have calculated the homodesmotic reactions[53,54] of the conformers of 3-methyl-3-phenyl-1,3-thiasilacyclohexane **4** with its unsubstituted analog, 1,3-thiasilacyclohexane, with retention of the positions of the substituents, as depicted in Eqs. 1 and 2, and the corresponding reactions of the conformers of 1-methyl-1-phenyl-1-silacyclohexane **3** (Eqs. 3 and 4) and 3-methyl-3-phenylthiane **8** with their unsubstituted analogs (Eqs. 5 and 6).

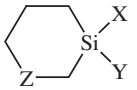
Reactions 1 and 2 are only slightly exothermic, the values of ΔE, ΔH^o_{298} and ΔG^o_{298} being −0.43, −0.36 and −0.38 kcal mol^{-1} for reaction 1, and −0.51, −0.52 and −1.19 kcal mol^{-1} for reaction 2. Noteworthy, the similar reactions of the conformers of 1-methyl-1-phenylcyclohexane **6** with cyclohexane calculated in Ref. 26 have different signs of the thermal effect: the reaction of **6**-Ph_{eq} is also exothermic by −2.0 kcal mol^{-1}, whereas that of **6**-Ph_{ax} is endothermic by 0.8 kcal mol^{-1}.

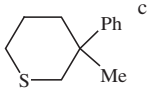
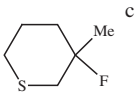
The values of ΔE, ΔH^o_{298} and ΔG^o_{298} are equal to −0.35, −0.21, and −0.50 kcal mol^{-1} for reaction 3, and 0.09, 0.08, and −0.14 kcal mol^{-1} for reaction (4), and are rather close to those for 1-methyl-1-phenylcyclohexane **6**. For reactions 5 and 6 the

Table 4
Additivity of substituent effects in the geminally disubstituted cyclohexanes and heterocyclohexanes, kcal mol^{-1} (ΔG^o_{add} is the algebraic sum of ΔG^o for the corresponding monosubstituted species)



X	Y	ΔG^o_{ax-eq} [a]	ΔG^o_{add}	$\Delta\Delta G^o$	Ref.
Me	F[b]	0.86	1.60	0.74	34
		0.86	1.38	0.52	
Me	CF_3[b]	0.53	1.31	0.78	34
		0.53	0.76	0.23	
Me	Ph	0.32	−1.13	1.45	23,26
Me	NMe_2	−0.4	0.21	0.61	48
Ph	NMe_2	−0.5	1.34	1.84	49
Me	OH	0.31	0.73	0.42	50,51
Ph	OH	0.5	1.86	1.36	32

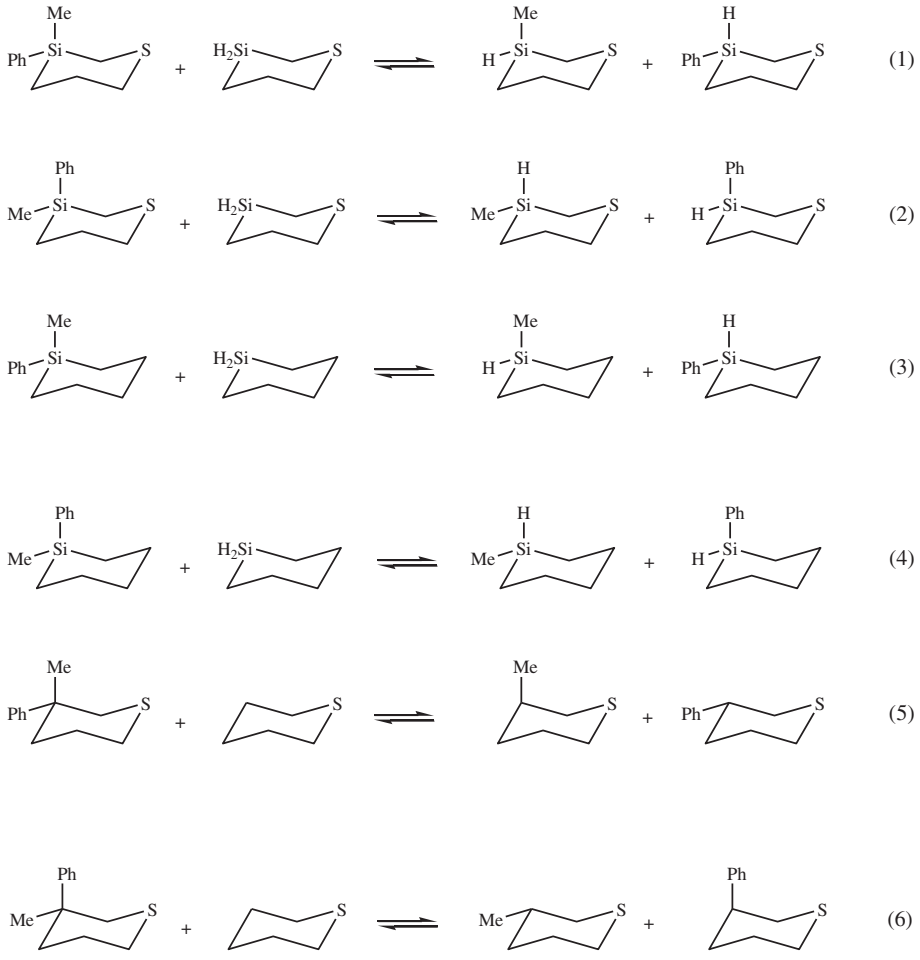


Z	X	Y	ΔG^o_{ax-eq} [a]	ΔG^o_{add}	$\Delta\Delta G^o$	Ref.
CH_2	Me	F	0.26	0.36	0.10	34
			0.28	0.52	0.24	16
CH_2	Me	CF_3	0.39	0.63	0.24	34
CH_2	Me	Ph	−0.11	0.02	0.09	This work
S	Me	Ph	0.15	0.25	0.10	This work
S	Me	F[c]	−0.78	−0.79	0.01	16
			0.10	1.46	1.36	This work
			−0.13	0.46	0.59	16

[c]

[c]

[a] 'ax' refers to conformers with $X_{ax}Y_{eq}$, 'eq'—with $X_{eq}Y_{ax}$.
[b] CCSD(T)/CBS calculated ΔE values are given.
[c] B3LYP/6-311G** calculated ΔG values are given.



values of ΔE, ΔH^{o}_{298} and ΔG^{o}_{298} are much larger: −3.74, −3.63, and −4.39 kcal mol^{-1} for reaction 5, and −2.28, −2.12, and −3.02 kcal mol^{-1} for reaction 6.

In the case of additivity, the homodesmotic reactions similar to those above occurring with retention of the positions of the substituents must be close to thermoneutral, and so they are for reactions 1–4. At the same time, reactions 5 and 6 of the conformers of 3-methyl-3-phenylthiane **8** are exothermic. The degree of exothermicity is a measure of internal strain created by the two geminal substituents in the molecule. Careful analysis of the geometry of the conformers, in particular, of the dihedral angle α between the plane of the phenyl ring and the plane bisecting the CSiC [in Eqs. 1–4] or C-2–C-3–C-4 [in Eqs. 5 and 6] angle revealed that α is close to 90° for the Ph-eq conformers of compounds **1**–**4** and **7**, and α is close to 0° for the Ph-ax conformers of compounds **1** and **2**. That means that in reactions 1, 3, and 4 the nonbonded interactions of the phenyl group with the heterocyclohexane ring are very similar and the reactions must be almost thermoneutral, which is just the case. The rotation of the phenyl group caused by the geminal methyl group and defined as $\Delta\alpha = \alpha(\text{Ph,Me}) - \alpha(\text{Ph,H})$ amounts to 2.5, 9.0, 5.0, 1.0, 57.0, 38.0° for the corresponding (Ph,Me) and (Ph,H) substituted pairs of compounds in reactions 1–6. That means that the deviations from thermoneutrality (characterizing the changes of the nonbonded interactions) should increase in the order:

$$\mathbf{3}-\text{Ph}_{ax} < \mathbf{4}-\text{Ph}_{eq} < \mathbf{3}-\text{Ph}_{eq} < \mathbf{4}-\text{Ph}_{ax} < \mathbf{8}-\text{Ph}_{ax} < \mathbf{8}-\text{Ph}_{eq}$$

and, indeed, the $\Delta\alpha$ values excellently correlate with the DFT calculated values of ΔG^{o}_{298} for reactions 1–6:

$$\Delta G^{o}_{298} = (0.22 \pm 0.10) + (0.074 \pm 0.003)\Delta\alpha \quad r = 0.996, n = 6, s_o = 0.2.$$

3. Experimental

3.1. Synthesis

Synthetic manipulations were carried out using standard inert atmosphere techniques. Solvents were dried and purified by standard procedures. Thin layer chromatography was performed on 20 mm precoated Merck silica gel plates (60 F-254) and visualized by iodine vapors. Column chromatography was carried out using silica gel 60 (0.063–0.200 mm, ICN Biomedical Inc.).

Synthesis of 1-methyl-1-phenyl-1-silacyclohexane **3** and 3-methyl-3-phenyl-1-thia-3-silacyclohexane **4** was described earlier.[16,42]

*3.1.1. 1-Phenyl-1-silacyclohexane (**1**).* 1-Phenyl-1-silacyclohexane (**1**) was prepared by a modified procedure of West.[55] A di-Grignard ethereal solution (350 mL) prepared from 1,5-dibromopentane (14.81 g, 0.064 mol) and magnesium powder (4.2 g, 0.175 g-a) was added dropwise to a stirred solution of $PhSiCl_3$ (14.81 g, 0.07 mol) in diethyl ether (70 mL) at room temperature, stirred at reflux for 6 h, cooled to room temperature, *n*-hexane (125 mL) was added, and the mixture was stored for 2 days at room temperature. The precipitate was separated by decantation and the solution concentrated in vacuo to a volume of ca. 100 mL. Addition of *n*-hexane and evaporation of the solvent was repeated

twice until a solid precipitated almost quantitatively. This solid was filtered off, the solvent removed under reduced pressure, and the residue distilled in vacuo to give crude 1-chloro-1-phenyl-1-silacyclohexane **9** as colorless liquid (4.26 g, 0.02 mol, 29% yield, bp 99–104 °C/1 mmHg). δ_H ($CDCl_3$): 1.12 (ddd, 2H, C*H*^{A}-2/6, J=15.0, 10.9, 4.8 Hz), 1.23 (m, 2H, C*H*^{B}-2/6), 1.38 (m, 1H, C*H*^{A}-4), 1.75 (m, 3H, C*H*^{B}-4), 1.90 (m, 2H, C*H*-3/5), 7.45 (m, 3H, H_{m+p}), 7.66 (dd, 2H, J 7.3, 1.2 Hz). δ_C NMR ($CDCl_3$): 15.52 (C-2/6), 23.47 (C-3/5), 29.16 (C-4), 127.97 (C_p), 130.32 (C_m), 133.27 (C_o), 134.73 (C_i). δ_{Si} ($CDCl_3$): 15.71. This crude product was dissolved in diethyl ether (4 mL) and added to a stirred suspension of $LiAlH_4$ (0.51 g, 13 mmol) in diethyl ether (10 mL). The resulting mixture was refluxed for 3 h, cooled to room temperature, and *n*-pentane (20 mL) and a saturated aqueous NH_4Cl solution were added. The organic layer was separated, the aqueous phase extracted with *n*-pentane, and the combined organic extracts dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue distilled in vacuo to give (**1**) in 60% yield (2.10 g, 11.9 mmol) as a colorless liquid, bp 99–103 °C/6 mmHg. δ_H ($CDCl_3$): 0.90 (ddd, 2H, C*H*^{A}-2/6, J=19.5, 10.1, 4.9 Hz), 1.08 (m, 2H, C*H*^{B}-2/6), 1.40 (m, 1H, C*H*^{A}-4), 1.67 (m, 3H, C*H*^{B}-4, C*H*^{A}-3/5), 1.91 (m, 2H, C*H*^{B}-3/5), 4.37 (t, 1H, Si–*H*, J 4.9 Hz), 7.39 (m, 3H, H_{m+p}), 7.58 (m, 2H, H_o). δ_C ($CDCl_3$): 10.67 (C-2/6), 24.89 (C-3/5), 29.86 (C-4), 127.96 (C_m), 129.37 (C_p), 134.49 (C_o), 136.09 (C_i). δ_{Si} ($CDCl_3$): −18.37. The ^{13}C NMR data of (**9**) and (**1**) are consistent with the reported data.[56]

*3.1.2. 3-Phenyl-1-thia-3-silacyclohexane (**2**).* To a suspension of $LiAlH_4$ (0.153 g, 4.0 mmol) in Et_2O (3 mL) was added 3-[(chloromethyl)phenylsilyl]propylthioacetate **10** (1.10 g, 4.0 mmol) in Et_2O/*n*-pentane (12 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h at this temperature. Then it was added to a stirred mixture of hydrochloric acid (10%, 10 mL) and ether (5 mL) at 0 °C, the aqueous layer separated and extracted with *n*-pentane. The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Chromatography of the residue (0.795 g) (SiO_2, *n*-pentane/Et_2O, gradient) yielded 3-phenyl-1-thia-3-silacyclohexane **2** (0.355 g, 90% purity by ^1H NMR spectroscopy, 41%) and 3-(methylphenylsilyl) propanethiol **11** (0.5 mmol, 0.090 g, 11%) arising from the simultaneous reduction of the thioacetate and CH_2Cl groups.

Analytically pure product **2** was obtained by column chromatography (hexane/Et_2O, 100/1) as a colorless oil. ν_{max} (liquid film) 3066, 3048, 3007, 2903, 2846, 2125, 1427, 1148, 962, 857, 834, 810, 724, 699 cm^{-1}; δ_H (400 MHz; $CDCl_3$; Me_4Si): 1.01 (1H, ddt, ^2J=14.8 Hz, ^3J=10.2 and 5.0 Hz, C*H*^{A}-4), 1.20 (1H, ddd, ^2J=14.8 Hz, ^3J=7.2 and 3.8 Hz, C*H*^{B}-4), 2.06 (2H, m, CH_2-2), 2.13 (m, 1H, C*H*^{A}-5), 2.31 (1H, m, C*H*^{B}-5), 2.58 (1H, ddd, ^2J=14.1 Hz, ^3J=9.2 and 2.7 Hz, C*H*^{A}-6), 2.62 (1H, ddd, ^2J=14.1 Hz, ^3J=10.1 and 3.9 Hz, C*H*^{B}-6), 4.55 (1H, tt, $^2J_{Si-H}$=197.5 Hz, ^3J=5.2 Hz and $^3J_{H-Si-H'}$=1.6 Hz, *H*Si), 7.42 (3H, m, H_{m+p}), 7.62 (2H, m, H_o). δ_C (100 MHz; $CDCl_3$; Me_4Si): 10.48 (*C*-4), 11.18 (*C*-2), 27.58 (*C*-5), 32.28 (*C*-6), 128.01 (C_m), 129.79 (C_p), 134.36 (C_o), 134.94 (C_i). δ_{Si} (100 MHz; CD_2Cl_2; Me_4Si): −26.29. HRMS: M^+, 194.0598. $C_{10}H_{14}SSi$ requires M^+, 194.0586.

Compound **11**: δ_H (400 MHz; $CDCl_3$; Me_4Si): 0.38 (3H, d, ^3J=3.4 Hz, *Me*Si), 0.97 (2H, m, SiCH_2C), 1.35 (1H, t, ^3J=7.8 Hz, S*H*), 1.71 (2H, quint, ^3J=7.8 Hz, CCH_2C), 2.53 (2H, dd, ^3J=7.4 Hz, CCH_2S), 4.39 (1H, q, ^3J=3.2 Hz, *H*Si), 7.40 (3H, m, H_{m+p}), 7.56 (2H, d, H_o). δ_C (100 MHz; $CDCl_3$; Me_4Si): −5.66 (*Me*Si), 12.67 (SiCH_2C), 29.21 (CCH_2C), 32.24 (CCH_2S). δ_{Si} (100 MHz; $CDCl_3$; Me_4Si): −13.59. Found: C, 61.24; H 8.05; Si 14.06%. $C_{10}H_{16}SiS$ requires C, 61.16; H, 8.21; Si, 14.30%.

*3.1.3. 3-[(Chloromethyl)phenylsilyl]propylthioacetate (**10**).* Freshly distilled thioacetic acid (0.586 g, 7.7 mmol) was added dropwise to (chloromethyl)allylphenylsilane **12** (1.377 g, 7.0 mmol) and irradiated with a DRT-400 mercury lamp for 3 h at 40 °C. Excess of thioacetic acid was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, hexane/Et_2O, increasing polarity from 50:1 to 1:1) to afford **10** (1.207 g, 4.4 mmol, 63%). δ_H (400 MHz; $CDCl_3$; Me_4Si): 1.14 (2H, m, SiCH_2C), 1.74 (2H, m, CCH_2C), 2.33 (3H, s, CH_3CO), 2.93 (2H, t, ^3J=7.3 Hz, CCH_2S), 3.07 (1H, dd, ^2J=13.8 Hz, ^3J=2.9 Hz, Si*H*^{A}Cl), 3.11 (1H, dd, Si*H*^{B}Cl), 4.49 (1H, quint, ^3J=3.1 Hz, *H*Si), 7.42 (3H, m, H_{m+p}), 7.58 (2H, d, H_o). δ_C (100 MHz; $CDCl_3$; Me_4Si): 9.90 (SiCH_2C), 24.50 (CCH_2C), 26.79 (*C*H_2Cl), 30.70 (*C*H_3CO), 32.07 (CCH_2S), 128.24 (C_m), 130.34 (C_p), 134.83 (C_o), 134.47 (C_i), 195.80 (*C*O). δ_{Si} (100 MHz; $CDCl_3$; Me_4Si): −12.47. Found: C 52.90; H 6.36; Si 10.33%. $C_{12}H_{17}SiOSCl$ requires C, 52.82; H, 6.28; Si, 10.29%.

*3.1.4. (Chloromethyl)allylphenylsilane (**12**).* (Chloromethyl)allylphenylsilane (**12**) was prepared from phenyl(chloromethyl)chlorosilane (3.162 g, 16.5 mmol) in 43% yield (90% purity by ^1H NMR spectroscopy) by a procedure described for (chloromethyl)methylallylphenylsilane[42] and used without further purification. δ_H (400 MHz; $CDCl_3$; Me_4Si): 2.07 (2H, m, SiCH_2C), 3.12 (2H, m, SiCH_2Cl), 4.51 (1H, quint, ^3J=2.9 Hz, *H*Si), 4.99 (1H, dd, ^3J=10.1 Hz, C=CH_2), 5.05 (1H, dd, ^3J=17.1 Hz, C=CH_2), 5.86 (1H, ddt, ^3J=17.0 and 8.1 Hz, C*H*=C), 7.43 (3H, m, H_{m+p}), 7.62 (2H, m, H_o). δ_C (100 MHz; $CDCl_3$; Me_4Si): 17.73 (SiCH_2C), 26.37 (SiCH_2Cl), 115.51 (=*C*H_2), 128.28 (C_m), 130.49 (C_p), 132.89 (*C*H=), 134.50 (C_i), 134.89 (C_o). δ_{Si} (100 MHz; $CDCl_3$; Me_4Si): −12.29.

3.2. NMR measurements

^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies 400 (^1H), 100 (^{13}C), and 79 (^{29}Si) MHz and the low temperature ^{13}C NMR spectra on a Bruker AV-600 (at 150.95 MHz). Chemical shifts were determined relative to residual $CHCl_3$ (^1H, δ 7.27), internal $CDCl_3$ (^{13}C, δ 77.0), and internal CD_2Cl_2 (^{13}C, δ 53.73) and are given in parts per million downfield to TMS (for ^1H, ^{13}C). Analysis and assignment of the ^1H 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 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 equilibrium constants (K) were determined by integration of the separated signals in the frozen spectra at 103 K, and the free energy differences were calculated as $\Delta G^o = -RT \ln K$. The chemical shifts difference $\Delta\nu_c$ [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; due to population differences of the conformers, the method of Shanan-Atidi and Bar-Eli was employed.[57] A complete line shape analysis was not performed because of very few k/T pairs at low temperatures required for the Eyring correlation. Moreover, $\Delta G^{\neq}$ is strongly preferred as a kinetic parameter as compared with $\Delta H^{\neq}$ and $\Delta S^{\neq}$ since the latter values are less reliable for discussing the kinetics of the studied dynamic processes.[58,59]

3.3. Theoretical calculations

All calculations were performed with full optimization of all variables at the DFT level of theory with the Becke's three-parameter hybrid method using the Lee, Yang, and Parr correlational functional and the triple split valence basis set 6-311G(d,p), or at the MP2 level (Møller–Plesset second order perturbation theory) with the same basis set as implemented into the Gaussian 03 package.[60] Vibrational frequencies were computed on the geometry optimized structures at the same level of theory at 298.15 K and

1 atm of pressure. Unscaled zero point vibrational energies (ZPVE) were used for the calculation of thermodynamic parameters.

4. Conclusions

The conformational equilibria of 1-phenyl-1-silacyclohexane **1**, 3-phenyl-1,3-thiasila-cyclohexane **2**, 1-methyl-1-phenyl-1-silacyclohexane **3**, and 3-methyl-3-phenyl-1,3-thiasilacyclohexane **4** were studied by low temperature ^{13}C NMR spectroscopy down to 103 K and theoretical computations. The predominant conformers of the Me,Ph–Si disubstituted compounds **3** and **4** are those with the equatorial phenyl group, as distinct from 1-methyl-1-phenylcyclohexane **6**. This occurs due to the longer Si–C bonds that allows rotation of the equatorial phenyl group about the Si–C_i bond to minimize its repulsive interactions with all Si–CH_α hydrogen atoms, which is impossible in phenylcyclohexane **6** because of H_o···Me repulsive interactions. The equilibrium constants for compounds **1**, **2**, **3**, and **4** are 3.00–3.35, 19, 1.63–1.78 and 2.12, respectively. The barriers to direct ring inversion (from the less populated to the more populated conformer) are 5.2–6.0 and the reverse barriers 5.4–6.0 kcal mol^{-1}. The ring inversion barrier of 1-phenyl-1-silacyclohexane **1** (5.4–5.7 kcal mol^{-1}) is much lower than that of phenylcyclohexane (8.8 kcal mol^{-1}).[44]

The analysis of the problem of additivity of conformational energies in the geminally substituted silacyclohexanes versus cyclohexanes has shown that, in general, the conformational effects in silacyclohexanes are much closer to additivity than in their carbocyclic analogs. In both series, maximum deviation from additivity is observed for the Ph-substituted species, since rotation of the phenyl group, as an asymmetric rotor, leads to substantial variations of nonbonded interactions in the molecule. The homodesmotic reactions approach proved that the deviations from thermoneutrality (or additivity of conformational effects) increase linearly with the dihedral angle α characterizing the rotation of the phenyl ring about the C–Ph or Si–Ph bond.

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Supplementary data

HMQC NMR spectrum of **1**, simulated ^1H NMR spectra of **2**, results of calculations of compounds **1**–**8**. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2011.10.082.

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