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Silacyclohexanes and silaheterocyclohexanes—why are they so different from other heterocyclohexanes?

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ABSTRACT

Stereochemical studies on silaheterocyclohexanes is a ‘hot topic’ as evidenced by the growing number of publications. During last 10 years a substantial number of substituted silacyclohexanes and heterocyclohexanes containing sulfur, oxygen or nitrogen as the second (or third) heteroatom have been synthesized and studied by variable temperature dynamic NMR spectroscopy, gas-phase electron diffraction, variable temperature IR, Raman, microwave spectroscopy with respect to thermodynamic (frozen conformational equilibria) and kinetic (barrier to ring inversion) information. As the stereochemistry of cyclohexane and its *N*-, *O*-, *P*-, *S*-hetero analogues is one of keystones of modern theoretical and synthetic organic and heterocyclic chemistry, the stereochemistry of silacyclohexane and its hetero analogs is an important element of theoretical and synthetic organosilicon chemistry. The various classes of saturated six-membered rings were critically compared and studied in detail with respect to differences in their stereochemistry and dynamic behavior.

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1. Introduction

In a contribution to Advances in Heterocyclic Chemistry in 2004[1] the conformational analysis of silacyclohexanes was reviewed. At that time not very many of them had been studied: silacyclohexane, 1,4-disilacylohexanes, and 1,3,5-tris-silacylohexanes both non-substituted as well as Si-alkyl substituted.[2,3] The conformational analysis of the silacylohexanes studied that time established these compounds to occur as chair conformers with the substituents at silicon to prefer equatorial conformations.[3] So even with the elongated Si–C bond length and reduced C–Si–C bond angles compared with the carbon analogues the principal stereochemical properties could be considered as similar to those of their carbon predecessors, cyclohexanes. The barriers to the chair-to-chair interconversion in silacyclohexanes, however, due to the chair conformer being more flattened than the cyclohexane analogues, are much lower, and their measurement requires special solvents (liquid at very low temperatures and still dissolving the sample) and special NMR hardware (to calibrate probe temperatures at these low temperatures). Meanwhile the ring interconversion barriers can be measured now in special freon mixtures and peculiar probe heads, which can be calibrated down to 100 K; hereby barrier down to 4–5 kcal/mol get attainable.

From the synthetic point of view, along the same period, many new silacyclohexanes and silaheterocyclohexanes have been synthesized and were studied by dynamic NMR spectroscopy, GED, IR, Raman, MW spectroscopy. The conformational equilibria could be frozen and barriers of chair-to-chair interconversion could be determined. In addition to silacyclohexane and polysilacyclohexanes, various Si-mono- and di-substituted derivatives were published and the effect of the Si-substituents on the conformational equilibria (ΔG°) and the barriers to ring inversion ($\Delta G^{\neq}$) could be established. In addition to silicon, other heteroatoms, such as nitrogen, oxygen and sulfur, were introduced into the saturated six-membered ring system and again both ΔG° and $\Delta G^{\neq}$ were determined and the dynamic NMR results obtained were examined with respect to the Perlin effect, the anomeric effect, and inherent substituent/heteroatom interactions/influences on both ΔG° and $\Delta G^{\neq}$ in the light of parallel computational, Natural Bond Orbital (NBO), and Natural Chemical Shielding (NCS) studies. When comparing both substituent and heteroatom influences on the dynamic NMR parameters of the silacyclohexane derivates, a new quality of conception of conformational properties of substituted and heterosilacyclohexanes can be pursued. This is one aim and one object of the present paper.

The basic question in the conformational analysis of the silicon-containing heterocycles is if there is a principal difference in the conformational behavior of silaheterocyclohexanes and their carbon analogues. It is easy to show that such a difference does exist and can even lead to the reversal of conformational preferences. For

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example, 1-phenylcyclohexane exists exclusively as the equatorial conformer,[4] whereas for 1-phenylsilacyclohexane 22% of the axial conformer are observed.[5] Introduction of the sulfur atom into the β-position to the silicon atom shifts the conformational equilibrium of 1-phenylsilacyclohexane from eq/ax=78%:22% to 95%:5% in 3-phenyl-3-silathiane.[5] Opposite conformational preferences are observed also in the geminally disubstituted cyclohexanes and silaheterocyclohexanes; thus, the $Ph_{ax}Me_{eq}$ conformer of 1-methyl-1-phenylcyclohexane is more favorable (72:28),[6] whereas the $Ph_{eq}Me_{ax}$ conformer predominates (63:37) in 1-methyl-1-phenylsilacyclohexane.[5]

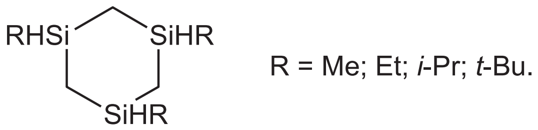
It is the second major object of this paper to investigate the effect of additional nitrogen, oxygen or sulfur heteroatoms in the cyclohexane analogues on both axial/equatorial conformation of substituents at silicon, nitrogen, and carbon atoms and the barrier to ring inversion of the saturated six-membered heterocyclic ring. Moreover, for geminally disubstituted cyclohexanes and silaheterocyclohexanes another question arises: are conformational effects of substituents additive or not in the various series of compounds? This topic deserves special consideration and will be studied as well.

2. Results and discussion

2.1. Silacyclohexanes

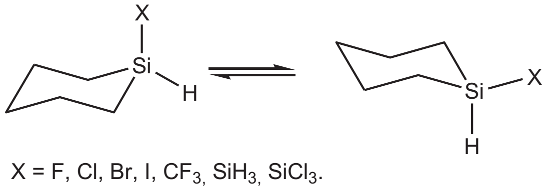
Silacyclohexane itself was first studied theoretically in 2000 and the barrier to the chair-to-chair interconversion was found to be 5–6 kcal/mol dependent on the level of theory employed.[7] In addition to the chair conformer, two different twist conformers were identified, which are ~3 kcal/mol less stable; the mechanism of the ring inversion was suggested[8] although debated after additional calculations.[9] 1,2-, 1,3-, and 1,4-Disilacyclohexanes were studied by gas-phase electron diffraction (GED) and at the MP2 and DFT levels of theory.[10] Chair and twist forms were found to be minima and the boat conformations to be the transition states for the ring inversion process. The barriers to inversion of approximately 5 kcal/mol rank in the order 1,4->1,2->1,3-disilacyclohexane. Experimental (GED) and theoretical studies of 1,3,5-trisilacyclohexane, the intermediate between cyclohexane and cyclohexasilane, showed it to be closer to the latter from the viewpoint of the energy difference between the chair and a twist boat conformations equal to 2.2, 6.5, and 1.9 kcal/mol for $C_3Si_3H_{12}$, C_6H_{12}, and Si_6H_{12}, respectively.[11,12]

Symmetrically trissubstituted Si-alkylated analogues of 1,3,5-trisilacyclohexane were studied theoretically and showed the equatorial preference of the alkyl groups, although much less pronounced for non-branched substituents than in the cyclohexane series: ΔE(ax−eq)=0.3−0.4 (Me), 0.4−0.5 (Et), ~0.6 (*i*-Pr), 2.2−2.5 (*t*-Bu).[3]



The simplest *Si*-substituted silacyclohexane, 1-methylsilacyclohexane was studied by microwave MW,[13] temperature-dependent Raman spectroscopy,[14,15] GED, and low-temperature ^{13}C NMR spectroscopy[2] and showed a slight preference (0.23 kcal/mol from ^{13}C NMR) for the equatorial conformation; the barrier to the ring inversion proved to be 5.8–5.9 kcal/mol.

1-Monosubstituted silacyclohexanes with various substituents (X=F,[16,17] Cl,[18] Br,[19] I,[20] CF_3,[21] SiH_3,[15a] $SiCl_3$,[15] Scheme 1) were studied theoretically and experimentally using MW and temperature-dependent Raman spectroscopy (X=F, CF_3), GED (X=F, Cl, Br, I, CF_3), and ^{19}F NMR spectroscopy (X=F, CF_3).[15–21]



Scheme 1.

For 1-silylsilacyclohexane, GED, ^{13}C NMR, and Raman spectroscopy showed the ratio of the axial to equatorial conformers close to unity.[15a] On going to 1-X-silacyclohexanes with electronegative substituents X, for 1-fluorosilacyclohexane, MW spectroscopy shows a slight axial preference of 42 cm^{-1} (or −0.12 kcal/mol).[16] Raman spectroscopy gives the value of $\Delta H=-0.25\pm0.03$ kcal/mol (depending on the medium).[17] The conformational energy of the fluorine atom in 1-fluorosilacyclohexane was found to be −0.31±0.2 kcal/mol (GED).[17] This is directly opposite to the equatorial preference of the fluorine atom in fluorocyclohexane (~0.3 kcal/mol).[22] An even larger difference is observed for the chlorine analogue. The GED-measured value of A ($A=\Delta G^\circ=-RT\ln K$) for the chlorine atom in 1-chlorosilacyclohexane is −0.43±0.18 kcal/mol,[18] whereas in 1-chlorocyclohexane it is 0.53±0.02 kcal/mol (in various solvents).[22] Variable temperature IR and Raman study showed the 69:31% predominance of the axial conformer at room temperature.[18a] Similarly, in 1-bromo- and 1-iodosilacyclohexane the GED-measured values of A are −0.82±0.32[19] and −0.59±0.22 kcal/mol,[20] respectively, whereas in 1-bromo- and 1-iodocyclohexane they are 0.48 and 0.49 kcal/mol,[22] respectively. Thus, the axial preference of the halogen atoms in the series of 1-halosilacyclohexanes as compared to the corresponding halocyclohexanes increases from F (0.4–0.6 kcal/mol) to Cl (0.96 kcal/mol), I (1.08 kcal/mol), and Br (1.3 kcal/mol). This characteristic difference in energy was attributed to electrostatic and hyperconjugation effects of the Si–Hal bond.[18–20]

The most striking effect is observed for the trifluoromethyl-substituted compounds. Whereas in trifluoromethylcyclohexane the A value of the CF_3 group is 2.5 kcal/mol,[22] in 1-trifluoromethylsilacyclohexane it is as low as 0.4±0.1 kcal/mol in solution (^{19}F NMR, 17% axial) and becomes even negative in the gas phase: −0.19±0.29 kcal/mol (GED, 58% axial).[21a] Thus, the difference of conformational energies of the CF_3 group as determined by NMR is 2.1 kcal/mol. Later on, the same authors reported that the assignment was erroneous and the correct value of A is −0.4 rather than +0.4 kcal/mol.[21b] In our context, however, this means only that the difference of conformational energies of the CF_3 group becomes even larger, 2.9 kcal/mol.

A strong electrostatic effects in silacyclohexanes stemming from strongly electropositive silicon atom was clearly demonstrated by comparing the lengths of the $Si-CH_2$ and $Si-CF_3$ bonds in trifluoromethylsilacyclohexane.[21] The latter bond is 0.078 Å longer than the former due to repulsive interactions between the silicon atom and the partly positive charge of the trifluoromethyl carbon and attractive interactions between the silicon atom and the partly negative charge of the methylene carbon.[21] Practically the same conclusion follows from comparison of the Si–Me bond length in methylsilacyclohexane (1.862(4) Å) and $Si-CF_3$ bond in trifluoromethylsilacyclohexane (1.934(10) Å) with the difference of 0.072(11) Å.

In a recent conformational study of 1-phenylsilacyclohexane by low temperature ^{13}C NMR spectroscopy a substantial fraction

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