



Substituent effects in silacyclohexanes: Theory vs. experiment

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Introduction

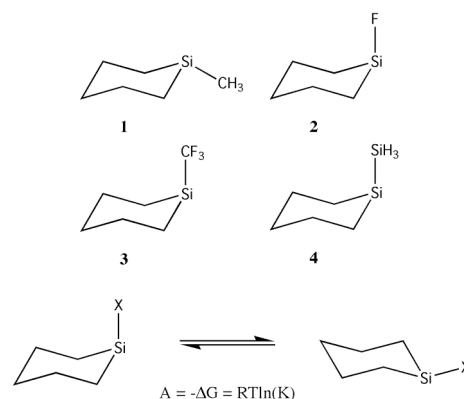
The conformational behavior of monosubstituted saturated six-membered ring systems plays an important role in organic stereochemistry. For monosubstituted cyclohexane derivatives the equatorial conformer is almost always lower in energy which means that it has a positive A value (see Scheme 1 for definition of A value). Bulkier and heavier substituents generally result in higher A values. The rare cases of mercury bonded substituents, where the A value is close to zero or even negative, are exceptions to this rule.

In monosubstituted silacyclohexanes, this trend may be turned upside down as we have previously shown in studies of **1** and **3** [1,2].

The unexpected conformational properties of **3** has prompted us to continue our investigation on monosubstituted silacyclohexanes using various experimental and theoretical methods.

The conformational properties of the following monosubstituted silacyclohexanes have been studied by gas electron diffraction, dynamic NMR, microwave spectroscopy, Raman spectroscopy, and quantum chemical calculations.

A values and other energy values are given in kcal/mol.



Scheme 1

Results

| | GED (A / mol % axial) | QC (A / mol % axial) ^a | MW (ΔE) ^b | QC (ΔE) ^a | NMR (A / mol % axial) ^c | QC with solvent effects ^d | Raman (ΔH) ^e | QC (ΔH) ^a |
|------------------------|--|--|--------------------------------|--------------------------------|---|--|-----------------------------------|--------------------------------|
| CH₃ | 0.45(14) / 32 (7) % [1] T = 298 K | B3LYP: 0.66 / 25 % MP2: 0.35 / 36 % | 0.0 (2) [3] | B3LYP: 0.52 MP2: 0.21 | 0.23 (2) / 26(1) % [1] T = 110 K | B3LYP: 0.38 to 0.39 MP2: 0.08 to 0.09 | | |
| CF₃ | -0.19(29) / 58 (12) % [2] T = 293 K | B3LYP: 0.13 / 45 % MP2: -0.28 / 63 % | | | 0.4 (1) / 17(2) % at 113 K [2] T = 113 K | B3LYP: 0.78 to 0.91 MP2: 0.37 – 0.50 | -0.51 (pentane) [6] | B3LYP: -0.12 MP2: -0.52 |
| F | -0.31(20) / 63 (8) % [4] T = 293 K | B3LYP: -0.24 / 60 % MP2: -0.15 / 56 % | -0.12(7) [5] | B3LYP: -0.31 MP2: -0.23 | -0.13 (2) / 64(2) % [4] T = 112 K | B3LYP: -0.69 to -0.61 MP2: -0.61 to -0.53 | -0.25 (neat) [4] | B3LYP: -0.32 MP2: -0.23 |
| SiH₃ | -0.17(15) / 57(7) % [6] T = 321 K | B3LYP: 0.52 / 29 % MP2: 0.20 / 42 % | | | | | | |

^a Geometries and thermal and ZPE corrections calculated at the B3LYP/6-311+G** level of theory in all cases. B3LYP: Electronic energies at the 6-311+G** level; MP2: Electronic energies at the MP2/aug-cc-pvtz level.

^b Microwave analysis was carried out at room temperature.

^c Low temperature NMR measurements were done in a 1:1:3 solvent mixture of CD₂Cl₂, CH₂Cl₂, and CHF₂Cl.

^d Solvation effects were calculated by geometry optimization in the solution with the PCM model and then single point energy calculations were carried out with the IPCM model at the B3LYP/6-311G** level of theory. The effects of the NMR solvent were approximated by the effects of CHCl₃ and CH₂Cl₂ because they are believed to represent a lower and upper limit respectively of the solvation effects in the freon mixture [2]. Free energies of solution at the NMR temperatures were then added to the MP2 and B3LYP electronic energies.

^e Raman measurements were carried out at variable temperatures and the van't Hoff relation used.

Discussion

- The methyl derivative **1** has a positive A value according to GED and NMR experiments albeit a much lower one than methylcyclohexane ($A = 1.8 - 2.05$ kcal/mol). This is well predicted by QC calculations.
- The trifluoromethyl derivative **3** has a negative A value in the gas phase, which is surprising compared to the large positive A value of trifluoromethylcyclohexane ($A = 2.5$ kcal/mol). Interestingly in a polar solution at low temperatures the conformational equilibrium of **3** changes and the A value becomes positive.
- Fluorosilacyclohexane **2** has a negative A value both in the gas phase and in the polar NMR solution.
- The silyl derivative **4** has a negative A value in the gas phase according to the GED experiment.

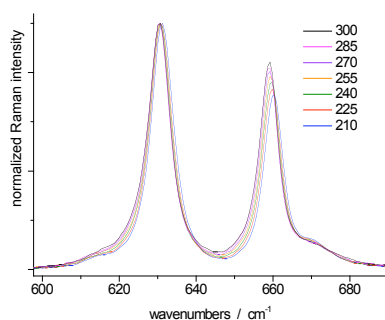


Figure 1. Raman band pair 630/658 cm⁻¹ of pure fluorosilacyclohexane **2** at decreasing temperatures

GED vs. QC calculations

The A values from the GED experiments are predicted similarly well by MP2 and B3LYP in the case of CH₃ and F substituents. The A value of the CF₃ derivative is predicted well only by MP2. The A value of the SiH₃ derivative is predicted wrong in sign by both methods, MP2 is doing better, however.

FT-MW vs. GED and QC calculations

Only two compounds, **2** and **3** have been analyzed by microwave spectroscopy. These gas phase results are similar to those from GED. The ΔE values from MW are better predicted by MP2 than B3LYP calculations.

NMR vs. QC calculations with solvent effects

Silacyclohexanes have activation energies of about 5.5 to 6.0 kcal/mol. Therefore NMR analyses have to be carried out at very low temperatures causing experimental difficulties. A limited number of solvents is available. Valuable thermodynamic data can be obtained, however. QC calculations of solvent effects are difficult; a good agreement may be a lucky case.

Raman vs. NMR and QC calculations

Variable temperature Raman spectroscopy has recently been applied in conformational analysis for **2** and **3**. This method can be applied to neat liquids and solutions in a wide temperature range. The results are in the form of ΔH and less thermodynamic data are obtained than in the case of NMR. Problems arising from solvent effects may be expected when the results are compared with QC calculations.

References

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