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Conformational properties of 1-fluoro-1-methyl-1-silacyclohexane. Are *A* values additive?

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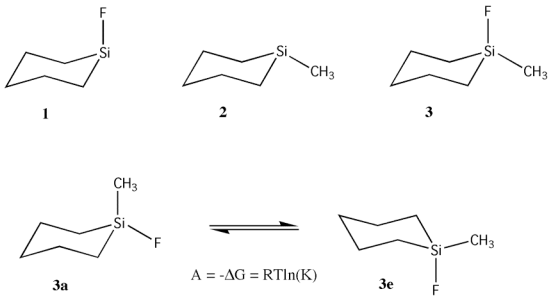
Introduction

The conformational properties of cyclohexanes are well know. Considerably less data is available on the conformational properties of silacyclohexanes but some representative monosubstituted derivatives have been investigated in recent years. In some cases their conformational properties are different, or even opposite, to what is known from cyclohexane analogues, where equatorial preference for a substituent is the "normal" behavior.

Results for 1-fluoro-1-silacyclohexane **1** [1,2] and 1-methyl-1-silacyclohexane **2** [3] are given in Table 2.
We have now synthesized the new compound 1-fluoro-1-methyl-1-silacyclohexane **3**.
The conformational properties of **3** have been investigated by GED and NMR experiments as well as quantum chemical calculations. The results are compared to those for **1** and **2**.



Gas Electron Diffraction

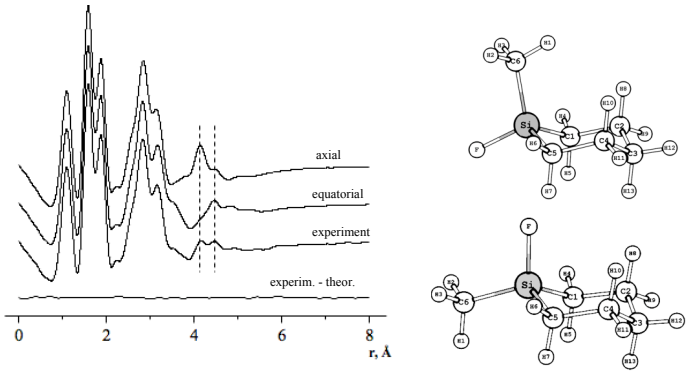


Figure 1. Radial distribution functions of **3** (left) and molecular models of the axial and equatorial conformers (right)

Table 1. Skeletal experimental and calculated geometric parameters [a,b] for the axial conformer of **3**

	GED	MP2/6-31G**	B3LYP/6-31G**
Si-C1	1.878(1)	1.873	1.881
Si-C6	1.876	1.872	1.878
Si-F	1.630(6)	1.637	1.632
C1-Si-F	108.9(6)	110.0	109.4
C1-Si-C5	107.3(6)	104.9	105.1
Si-C1-C2	110.7(3)	110.1	110.9
C1-C2-C3	115.3	113.5	113.9
C2-C3-C4	112.0	114.2	114.6
C1-Si-C6	112.4 (6)	112.2	112.9
Si-C6-H1	109.5 (15)	110.9	111.2
ϕ (C5-Si-C1-C2)	–37.8(25)	–45.7	–43.7
ϕ (C1-C2-C3-C4)	–66.6	–65.6	–64.4
ϕ (Si-C1-C2-C3)	52.9	56.0	54.5
ϕ (C5-Si-C1-C2)	-36.2(22)	-43.8	-41.7

[a] Values in Å and degrees
[b] Uncertainties are 3σ values

Low temperature ^{19}F NMR spectra

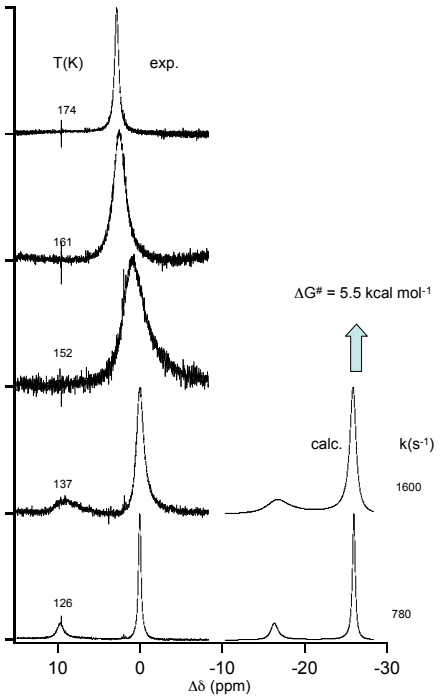


Figure 2. Experimental ^{19}F NMR spectra on the left and simulated spectra on the right.

Results

Table 2. Conformational properties of **3** vs. **1** and **2**. Theory vs. experiment

	Method	A (kcal/mol)	% mol axial
	GED (293 K)	-0.31 (20)	63 (8) %
1	NMR (^{19}F at 112 K)	-0.13 (2)	64 (2) %
	QC (MP2/aug-cc-pvtz) [a,b]	-0.15	56 %
	GED (298 K)	0.45 (14)	32 (7) %
2	NMR (^{13}C at 110 K)	0.23 (2)	26 (1) %
	QC (MP2/aug-cc-pvtz) [a,b]	0.35	36 %
	GED (282 K)	0.11 (13)	45 (6) %
3	NMR (^{19}F at 126 K)	0.26 (7)	25 (5) %
	QC:[a]		
	B3LYP/aug-cc-pvtz	0.56	28 %
	MP2/6-311+G**	0.26	39 %
	MP2/aug-cc-pvtz [c]	0.20	42 %
	MP2/aug-cc-pvtz at 118 K + solv. corr. [c,d]	0.72	4 %

[a] B3LYP/aug-cc-pvtz thermal corrections used for all QC methods
[b] Optimized geometry at B3LYP/6-311+G**
[c] Optimized geometry at MP2/6-311+G**
[d] Calculated with solvent effects for both a CH_2Cl_2 and a $CHCl_3$ solution with the IPCM/PCM solvation model (B3LYP/6-311+G**)

Discussion

The methyl group has a moderate preference for the equatorial position in silacyclohexane, whereas the fluorine prefers the axial position. If their effects were additive in compound **3**, then **3e** conformer would have over 90% population.
According to the GED experiment, **3e** is only slightly favored over **3a**, so this simple model does not apply. DFT calculations do not reproduce the GED results well, only high level MP2 calculations give satisfying results.
According to the ^{19}F NMR experiment at low temperatures in a freon mixture, the abundance of **3e** is 75(5)%. So far, we have not been able to reproduce this experiment in a satisfying way by QC calculations.

References

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