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CONFORMATIONAL PROPERTIES AND MOLECULAR STRUCTURE OF 1-PHENYL-1-METHOXY-SILACYCLOHEXANE

The molecular structure and conformational behavior of a large number of 1-monosubstituted-silacyclohexanes has been investigated by various methods including NMR, electron diffraction, microwave, infrared, Raman spectroscopy and theoretical calculations. The conformational equilibrium of 1-phenylsilacyclohexane was found to be $\text{Ph}_{\text{eq}}:\text{Ph}_{\text{ax}} = 78:22\%$ by ^{13}C NMR at 103K [1] and 62(10):38(10)% from gas-phase electron diffraction (GED) at 293K [2]. For 1-methoxysilacyclohexane the low temperature Raman analysis gives $\Delta H_{\text{e} \rightarrow \text{a}} = -0.11$ kcal/mol [3], the quantum chemical (QC) calculations show that the axial conformer is energetically more stable by $\Delta E = 0.15$ kcal/mol [4] and, from GED data, $\text{Ax}:\text{Eq} = 59(12):41(12)\%$ [5]. In this work, the conformational behavior of 1-phenyl-1-methoxy-silacyclohexane **1** was studied by QC calculations.

The geometry and vibrational calculations were performed using DFT (with B3LYP-GD3 and M062X functionals) and MP2 methods with 6-311G** and cc-pVTZ basic sets. According to the QC calculations, compound **1** may exist in five forms: $g\text{-Ph}_{\text{eq}}$ **I**, $g\text{-Ph}_{\text{ax-out}}$ **II**, $tr\text{-Ph}_{\text{eq}}$ **III**, $tr\text{-Ph}_{\text{ax-out}}$ **IV** and $tr\text{-Ph}_{\text{ax-in}}$ **V**, see Fig. 1. The relative total electron energies and free Gibbs energies are given in Table 1.

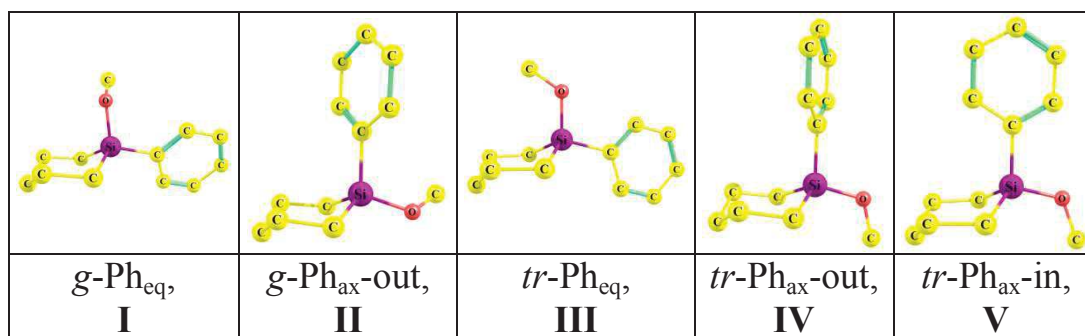


Fig. 1. Conformers of compound **1** (hydrogen atoms not indicated)

Table 1: Relative total electron energy and free Gibbs energy (kcal/mol) of conformers of 1

Method/basis set	ΔE					$\Delta G^\circ(298K)$				
	I	II	III	IV	V	I	II	III	IV	V
B3LYP-GD3/6-311G**	0	-0.06	0.86	1.02	0.83	0	-0.06	-0.01	0.82	0.97
B3LYP-GD3/cc-pVTZ	0	0.13	0.90	1.15	0.96	0	0.21	0.16	0.81	1.00
M062X/6-311G**	0	-0.04	1.21	1.20	1.36	0	0.06	1.26	1.14	1.19
M062X/cc-pVTZ	0	0.15	1.29	1.31	1.54	0	0.33	1.38	1.20	1.42
MP2(FC)/6-311G**	0	-0.50	1.52	0.68	1.33	0	0.04	1.72	0.64	1.00

The B3LYP-GD3 calculations predict the conformer **III** as the most stable with ΔG° value of -0.01 to 0.16 kcal/mol relative to **I**, though the lowest vibrational frequency of this conformer is $10\text{--}12\text{ cm}^{-1}$ for the methoxy group rotation around the Si–O bond which may predict incorrect ΔG° values in harmonic approximation. From the M06-2X calculations, the conformers **I** and **II** are most stable, and electron energies and Gibbs energies of other conformers (**III**, **IV** and **V**) are by $1.20\text{--}1.54$ and $1.14\text{--}1.42$ kcal/mol, respectively. In the case of MP2 level, the conformers **I**, **II** and **III** are most stable. It should be noted that sophistication of the basis set increases the ΔE and ΔG° values.

It has to be pointed out, that when starting from the conformer **V**, the rotation of the methoxy group by more than 90° leads to immediate structure conversion to the Ph_{ax}-out, whereas starting from the latter keeps the twist orientation of the phenyl group. The energy barrier for **II**→**IV** conversion was found to be *ca.* 2.33 kcal/mol (M062X/6-311G**).

In the case of the equatorial conformers, the methoxy group rotation influences on rotation of the phenyl group. The energy barriers for the conversions **I**→**III** and between the **I'**→**I''** enantiomers are 1.50 and 1.66 kcal/mol, respectively (M062X/6-311G**). On the other hand, the phenyl group rotation does not noticeably affect the methoxy group orientation.

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