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Molecular structure and conformational behavior of 1-methyl-1-phenylsilacyclohexane studied by gas electron diffraction, IR spectroscopy and quantum chemical calculations

Tran Dinh Phien [a], Sergey A. Shlykov [a, *], Bagrat A. Shainyan [b]

[a] Ivanovo State University of Chemistry and Technology, Research Institute for Thermodynamics and Kinetics of Chemical Processes, Department of Physical and Colloidal Chemistry, Sheremetev Ave, 7, 153000, Ivanovo, Russian Federation
[b] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of Russian Academy of Science, Favorsky Street, 1, 664033, Irkutsk, Russian Federation

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ABSTRACT

Conformational properties and molecular structure of 1-methyl-1-phenylsilacyclohexane **1** were studied by quantum chemical (QC) calculations, combined gas electron diffraction/mass spectrometry (GED/MS) and IR spectroscopy. Molecule **1** may exist in four forms that differ by axial or equatorial positions of the substituents and by relative orientation of the two rings. Two of these conformers were found to dominate in the gas phase: **1**-Ph_{eq}-orth conformer with the phenyl ring plane bisecting the CSiC endocyclic angle, and **1**-Ph_{ax}-twist with the phenyl ring and the CSiC exocyclic angle oriented nearly perpendicularly to each other. From the GED data, the summarized molar fractions of the conformers were found to be Ph_{eq}:Ph_{ax} = 42(15):58(15)% which corresponds to $\Delta G = G_{eq} - G_{ax} = 0.19(37)$ kcal/mol. Experimental and calculated IR spectra provides an evidence of existence of both conformers in the liquid phase. The QC calculations yielded the $\Delta G = G(Ph_{eq}\text{–orth}) - G(Ph_{ax}\text{–twist})$ values of 0.18–0.36 DFT and 0.82 MP2 kcal/mol.

1. Introduction

Compounds having a saturated six-membered heterocyclic ring can be found in various fields of chemistry, e.g., natural products, drugs and polymers. Determinations of equatorial-axial equilibrium in derivatives of saturated six-membered heterocycles have provided valuable information regarding the nature of steric and electronic interactions in organic molecules. The conformational properties of saturated six-membered heterocyclic rings were reviewed by Kleinpeter.[1] Of special interest to our research are silacyclohexanes and their derivatives, which show drastic differences from both cyclohexanes and six-membered heterocycles having N, O, or S heteroatoms. Over the last two decades the molecular structure and conformational behavior of a large number of monosubstituted 1-X-1-silacyclohexanes has been investigated by various methods including NMR, electron diffraction, microwave, infrared, Raman spectroscopy and theoretical calculations.[2,3] The principal differences from the corresponding cyclohexanes are much lower conformational energies *A* for alkyl and aryl substituents (Me, *t*-Bu, Ph),[2] axial preference of electronegative substituents (Hal, CF_3, CN)[2–7] or those with long Si–X bond (X = SiH_3),[8] and low barriers to ring inversion.[2] The observed differences were assigned to the longer Si–C as compared to the C–C bond, more flattened silicon-containing ring, and strong influence of electrostatic and stereoelectronic effects.[9]

Phenyl-substituted cyclohexanes and six-membered heterocycles reveal specific conformational properties due to possible rotation of the phenyl group as an asymmetric rotor. The investigation of equatorial-axial conformational preferences in saturated six-membered ring of phenylcyclohexane[10–12] and 1-phenyl-heterocyclohexanes (heteroatom = N,[13] Si,[14,15] P[16]) are summarized in our previous work on *N*-phenylpiperidine.[13] The ratio of the conformers and the relative orientation of the phenyl and cyclohexane (or heterocyclohexane) rings depend on the X–C_{Ph} bond distance and orbital interaction between the electron lone pair on the heteroatom and the π-system of the phenyl ring. The population of the Ph_{ax} conformer increases with the atomic number of heteroatom X in the cyclohexane ring: C < N < Si < P.[13] For methylcyclohexane[17] and 1-methyl-1-heterocyclohexanes with the same heteroatoms[16,18–20]

* Corresponding author.
E-mail addresses: shlykov@isuct.ru (S.A. Shlykov), bagrat@irioch.irk.ru (B.A. Shainyan).

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the population of the Me_{ax} conformer increases in a somewhat different order: N < C < P < Si.

In case where both methyl and phenyl substituents are attached to the same atom of the saturated ring, the conformational preference may differ from that deduced from additive effect of the single substituents. For the geminally substituted 1-Me-1-R-cyclohexanes, there is a clear trend that the smaller the conformational energy of substituent R, the larger its axial preference.[21–23] However, a pronounced anomalous effect arises in the case of 1-methyl-1-phenylcyclohexane, which prefers the $Ph_{ax}Me_{eq}$ conformation (72:28%) in spite of much larger *A* value for the phenyl (2.87 kcal/mol)[11] than for the methyl group (1.80 kcal/mol).[17] This was explained by destabilization of the $Ph_{eq}Me_{ax}$ conformer due to non-bonded H···H interactions.[12,24] In 1-monosubstituted silacyclohexanes, the *A* values for the Me and Ph groups are almost equal in solution at low temperature[15,18] and differ slightly in the gas phase.[14,18] As a result, the $Ph_{eq}Me_{ax}$ conformer of 1-methyl-1-phenyl-1-silacyclohexane was found by low-temperature NMR study to predominate in solution.[15] Taking into account the absence of experimental data on the conformational composition of 1-methyl-1-phenyl-1-silacyclohexane **1** in gas phase and as a continuation of our systematic studies on conformational behavior of silacyclohexanes and silaheterocyclohexanes,[2] we report here the results of combined gas-phase electron diffraction/mass spectrometry (GED/MS) experiment, IR spectroscopy and extended quantum chemical calculations for compound **1**. The only related compound with geminal methyl and phenyl groups at silicon investigated so far was 3-methyl-3-phenyl-3-silatetrahydropyran, which was synthesized[25] and its structure and conformational preferences studied in the gas phase and in solution.[26] The opposite conformational preferences in gas phase and in solution for the latter compound make the problem of gas phase investigation of compound **1** even more challenging.

2. Results and discussion

2.1. Energy

The phenyl group rotation. The PES profiles were obtained by scanning the C_{Me}–Si–C_{Ph}–C_{ortho} dihedral angle responsible for rotation of the two cycles about the Si–C_{Ph} bond is plotted as the energy versus $\varphi = \angle(C_{Me}–Si–C_{Ph}–C_{ortho})–90°$ dihedral angle (Fig. 1). If $\varphi = 90°$, the phenyl and silacyclohexane rings are in orthogonal orientation to each other; it may also be twisted down to 0°. Hereinafter, they are abbreviated as **1**-Ph_{eq}-orth, **1**-Ph_{eq}-twist, **1**-Ph_{ax}-twist and **1**-Ph_{ax}-orth (see Fig. 2), with the terms 'equatorial' and 'axial' referred to the position of the phenyl ring.

For the Ph_{ax} structures, the PES profiles demonstrate minima at $\varphi = 90°$, **1**-Ph_{ax}-orth conformers, and at $\varphi = 18$, 19 and 9° from B3LYP-GD3, M062X and MP2 calculations, respectively, **1**-Ph_{ax}-twist conformers. In the case of the PES profiles of the equatorial conformer, two minima were observed: one minimum at $\varphi = 90°$, the **1**-Ph_{eq}-orth conformers, and at $\varphi = 23°$ (in case of MP2 calculations, $\varphi = 0°$), the **1**-Ph_{eq}-twist conformers. Such orientations of the phenyl ring relative to silacyclohexane ring also were observed for 1-phenylsilacyclohexane.[14] No imaginary frequencies were found for any of these conformers. The structures of two orthogonal conformers, **1**-Ph_{eq}-orth and **1**-Ph_{ax}-orth, have C_S

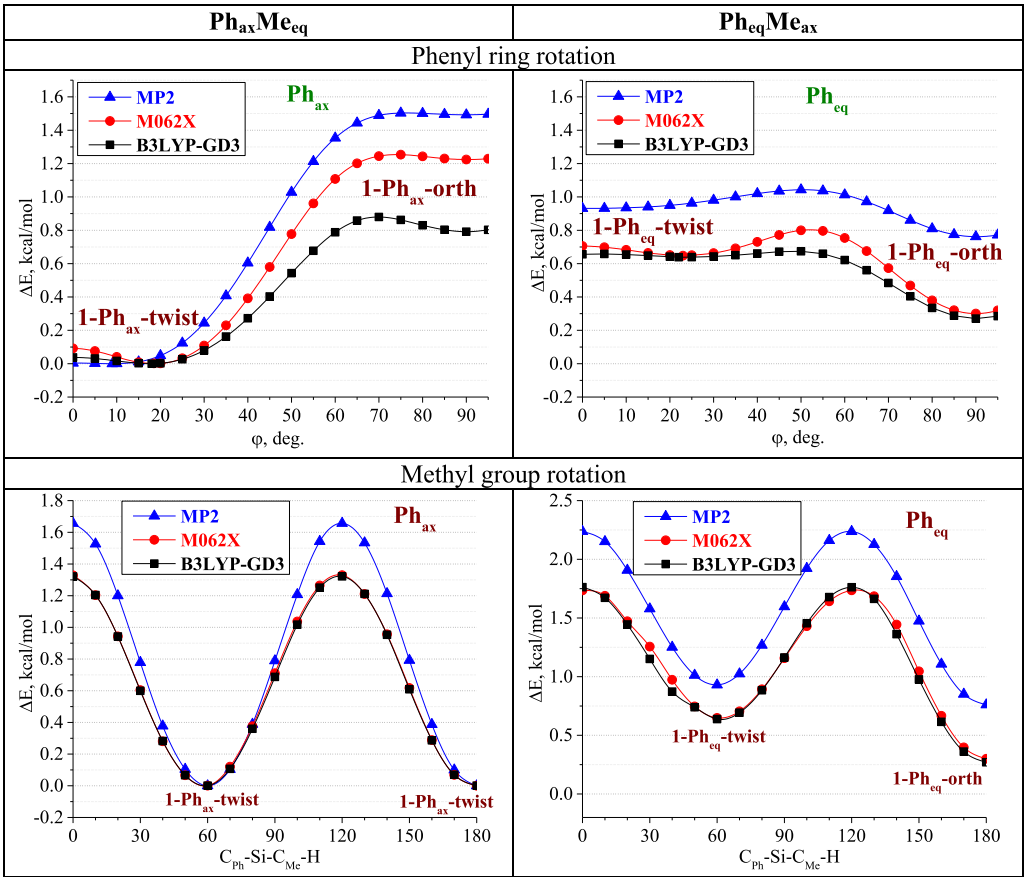

Fig. 1. Lowest energy pathways for axial and equatorial conformers by rotating the phenyl ring around Si–C_{Ph} bond (upper) and the methyl group around Si–C_{Me} bond (lower) calculated at DFT (B3LYP-GD3 and M062X) and MP2 levels with 6-311G** basis set. The φ angle was defined as $\varphi = \angle(C_{Me}–Si–C_{Ph}–C_{orth})–90°$.