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Molecular Structure and Conformational Preferences of 1-Chloro-1-silacyclohexane, $CH_2(CH_2CH_2)_2SiH–Cl$, as Studies by Gas-Phase Electron Diffraction and Quantum Chemistry

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Abstract—The molecular structure of axial and equatorial conformer of the 1-chloro-1-silacyclohexane molecule, $CH_2(CH_2CH_2)_2SiH–Cl$, as well as thermodynamic equilibrium between these species were investigated by means of gas-phase electron diffraction and quantum chemistry on the MP2(full)/AUG-cc-PVTZ level of theory. According to electron diffraction data, the compound exists in the gas-phase as a mixture of conformers possessing the *chair* conformation of the six-membered ring and Cs symmetry and differing in the axial and equatorial position of the Si–Cl bond at 352 K. NBO analysis revealed that axial conformer of 1-chloro-1-silacyclohexane molecule is an example of the stabilization of the form that is unfavorable from the point of view steric effects and effects of conjugations and that stabilization is achieved due to electrostatic interactions.

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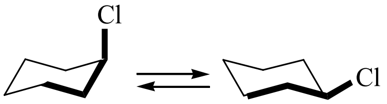
Substitution of carbon atom in cyclohexane molecule by silicon atom has a strong effect on the structure and conformational preferences of its derivatives. Chemical properties of functional groups are also changed remarkably when going from acyclic to cyclic molecules. Thus it is important to elucidate the effects which influence on the structure of cyclic and heterocyclic compounds.

Axial-equatorial equilibrium, as shown on Scheme, means that positive values of A correspond to predominance of equatorial conformer. In the case of molecule of monosubstituted cyclohexane, in general, the equatorial conformer is more preferred. Traditionally, this is attributed to the so called 1,3-diaxial repulsion between the substituent and the axial hydrogen atoms located in 3 and 5 positions that destabilizes the axial conformer. However, there are investigations which do not confirm the correctness of this explanation [1–5].



$$A = -\Delta G^0 = RT\ln K.$$

The authors of review [6] analyze the influence of heteroatom on the conformational stability of cyclohexane derivatives, where the effect of heteroatom, in a number of cases, is accounted by the orbital interactions. In the last few years there were conducted experimental and theoretical investigations a number of monoderivatives of 1-silacyclohexane molecules with the aim of investigation of the influence of silicon atom on the axial–equatorial equilibrium of silacyclohexane ring [7–16].

The aim of the present study is determination of geometric structure and conformational preferences of

1-chloro-1-sialcyclohexane molecule, $CH_2(CH_2CH_2)_2\cdot SiH–Cl$, by gas-phase electron diffraction method with the use of quantum chemical data on geometric and dynamic parameters. To increase our understanding of conformations realized in given free compounds we performed natural bond orbital andlysis (NBO) [17, 18].

The present contribution continues study of molecular structure and conformational preferences of monosubstituted 1-silacyclohexane molecules by experimental and theoretical methods. In order to better understand the reasons of conformational preference of 1-chloro-1-sialcyclohexane molecule we included the results of NBO analysis.

In monosubstituted cyclohexanes the axial and equatorial positions are unequal by energy. For example, in methylcyclohexane molecule the equatorial conformer by about 1.98 kcal mol^{-1} is more stable then the axial one [1]. The same is known for the other mono-substituted cyclohexanes. With exception of mercury substituted cyclohexane molecule [19], substituent always is more stable in equatorial position then in axial one.

The classical explanation of differences in energy between axial and equatorial conformations in monosubstituted cyclohexanes that is given in textbooks is the presence of steric tensions caused by 1,3-*syn*-diaxial interactions which are absent when substituents are located in equatorial positions. It is supposed that the value of the 1,3-*syn*-diaxial tension for particular substituents depends on their nature and size. It is also supposed that tension does not increase with increase in the size of alkyl group, because the stability of equatorial conformer increases [20]. However, it is to be noted that idea of 1,3-*syn*-diaxial interactions is intuitive one and there are no direct experimental and theoretical evidences of repulsion between atoms of axial substituent and 1,3-diaxial hydrogen atoms even in axial *tert*-butylcyclohexane molecule [3].

Substitution of carbon atom in cyclohexane molecule by a heteroatom may have a strong effect on the conformational properties of its derivatives due to changes in the size of atom, bond length, electronegativity, and electronic effects of different kind. Thus, for example, substitution of carbon atom in cyclohexane molecule by oxygen or sulfur leads to axial orientation mainly of an electronegative substituents in 2 position due to anomeric effect, that is due to delocalization of lone electron pair of oxygen atom into *anti*-bonding orbital of adjacent carbon–substituent σ-bond .

Substitution of carbon atom in cyclohexane molecule by the silicon atom leads to a change in the stability of axial and equatorial substituents even to opposite, so the axial conformer becomes more stable, as, for example, it is happened in the case of CF_3 derivative. If equatorial conformer remains more stable then its stability is remarkably reduced. Thus for trichloromethyl- and *tert*-butyl-substituents the difference of ΔE values is ~4.5 kcal mol^{-1} [20].

According to our calculations on the MP2(full)/AUG-cc-PVTZ level of theory the equatorial conformer of chlorocyclohexane molecule is more stable then axial conformer (ΔE 0.11 kcal mol^{-1}), whereas for 1-chloro-1-silacyclohexane molecule the axial conformer is more stable (ΔE –0.71 kcal mol^{-1}).

It is interesting to note that for 1-trifluoromethyl-1-silacyclohexane molecule, in spite of approximately equal steric demands of methyl and trifluorometyl groups and high electronegativity of the latter, that lies between chlorine and fluorine, the stability of axial conformer is remarkably higher then for 1-methyl- and 1-fluoro-1-silacyclohexane molecules. Higher conformational stability of axial conformer for a number of 1-monosubstituted silacyclohexane molecules also indicates that 1,3-*syn*-diaxial interactions do not play a decisive role [20].

Recently many attempts were made to account for revealed conformational preferences of 1-monosubstituted silacyclohexanes on the basis of calculations of energies of steric interactions and calculations in the framework of NBO analysis, considering effects of hyperconjugation, that is, the effects of delocalization of the electrons of the σ-bonds into *anti*-bonding orbitals of vicinal bonds located in *anti* positions. It was shown that such effects may play an important role but universal explanation is not found.

Recent work [7] analyzes the changes in the difference of electron and nuclear repulsion energies when going from axial to equatorial conformer in a pair of monosubstituted cyclohexanes and monosubstituted 1-silacyclohexanes as well as in the pairs of 1-substituted propanes and 1-substituted silapropanes for a number of substituents with the electronegativity varied in a wide range. It was revealed that in spite of absence of a remarkable correlations in the values of conformational energies when substituting carbon atom by silicon atom in this series of compounds, the changes of differences of conformational energies sufficiently well correlate with changes of differences of energies of nuclear repulsion. From the results of [7] follows that, in contrast to the electronegative and neutral substituents, the electropositive substituents such as alkaline metals and cations of alkaline-earth metals preferably occupy axial position in the cyclohexane molecule, in accordance with observed conformational preference of the cyclohexane mercury derivativese [19]. When going from cyclohexane to silacyclohexane derivatives, the conformational preference is changed to opposite. For them, conversely, the equatorial form becomes more stable.

In the present work with the use of NBO analysis the total electronic energy was decomposed into Lewis $E^{(L)}$ and non-Lewis $E^{(NL)}$ components (see the table). The Lewis component corresponds to the localized structure with two electron populations of each orbital. Thus, Lewis energy nearly exactly incorporates steric and electrostatic interactions and non-Lewis component corresponds to all conjugations. It is seen from the table that from the point of view of the conjugation effect the equatorial conformer is more preferable. Then using NBO analysis was calculated the total steric energy [21–23]. As follows from the data shown in the table, the steric interactions in axial conformer are remarkably higher then in equatorial conformer. Thus axial conformer of 1-chloro-1-silacyclohexane molecule is an example of stabilization of the form that is unfavorable from the point of view of steric and conjugation effects and is determined mainly by electrostatic interactions.

Structural parameters of molecule $CH_2(CH_2CH_2)_2SiH–Cl$

Parameter	Experiment (r_a, h_1 angles)	Calculation (MP2, r_e)
Si–C p_1[a], Å	1.859(2)	1.857
Si–Cl_{ax} p_2, Å	2.073(2)	2.075
Si–Cl_{eq} (p_2), Å	2.063(2)	2.065
C^2–C^3 p_3, Å	1.534(3)	1.530
C^3–C^4 (p_3), Å	1.529(3)	1.524
$(C–H)_{av}$ p_4, Å	1.116(4)	1.091
C^2SiC^6 p_5, deg	107.7(6)	105.8
$C^3C^4C^5$ p_6, deg	116.8(15)	114.2
$ClSiX^1_{ax}$ p_7, deg	126.1(15)[b]	120.1
$ClSiX^1_{eq}$, deg	127.5[c]	127.5
$(HCH)_{av}$, deg	106.4[c]	106.8
flap$(Si)_{ax}$ p_8	39.4(15)	43.1
flap$(Si)_{eq}$ (p_8)	41.9(15)	45.6
flap(C^4) p_9	54.9(12)	58.3
χ_{ax}, %	67(5)	73
R-Factor, %	5.9	
$A = (G^0_{ax} - G^0_{eq})$	–0.43(18)	–0.57
	ax	*eq*
$\Delta E^{(T)}$,[d] kcal mol^{-1}	0.0	0.89
$\Delta E^{(L)}$, kcal mol^{-1}	0.0	2.73
$\Delta E^{(NL)}$, kcal mol^{-1}	1.84	0.0
$\Delta E^{(ST)}$, kcal mol^{-1}	3.76	0.0
$\Delta E^{(L–ST)}$, kcal mol^{-1}	0.0	6.49

[a] (p_i) Independent parameter for axial (ax) and equatorial (eq) conformer; (p_i) difference equals MP2 theoretical one. [b] (X^i) dummy atom located on the bisector of the adjacent endocyclic angle. [c] Fixed. [d] Results of NBO analysis of decomposition of total electronic energy (T) into Lewis (L), non-Lewis (NL), steric (ST) and electrostatic (L–ST) energy.

EXPERIMENTAL

All quantum chemical calculations were carried out at the MP2(full)/AUG-CC-pVTZ level of theory (MP2) with the use of Gaussian 09 program system [24]. NBO analysis [17, 18] and calculations of total steric energy [21–23] were done using NBO 5.9 program [25] incorporated in NWChem 6.0 program [26] at the M062X/6-311++G** level.

Geometry optimizations of the axial and equatorial conformers were performed under *Cs* symmetry. Calculations of the molecular force fields confirmed that the optimized structures thus obtained correspond to minima on the potential energy hypersurface.

The theoretical force constants were used to calculate mean vibrational amplitudes of the pair of atoms and vibrational shrinkage corrections $D = r_h - r_a$, with the use of the program [27, 28]. Optimized set of geometrical parameters of the $CH_2(CH_2CH_2)_2SiH–Cl$ molecule is shown in the table.

Gas electron diffraction. The electron diffraction patterns were recorded on the EMR-100M electron diffraction apparatus at the nozzle temperature 46 and 54°C for the long and short nozzle-to-plate distances, respectively and accelerating voltage 60 kV with the use of cubic sector. For the scanning on the Epson Perfection 4870 Photo scanner were selected three plates for the long (362 mm) and three plates for the short (193 mm) nozzle-to-plate distances. The length of electron beam was determined with the use of scattering pattern from gaseous CCl_4. It was equal 0.049591 and 0.049402 Å for the long and short nozzle-to-plate distances, respectively. Atomic scattering factors were taken from [29]. Experimental backgrounds were drawn as cubic spline functions to the difference between experimental and theoretical molecular intensity data and theoretical background curves. Observed intensity curves were recorded in the range from 3.2 to 19.0 and from 7.6 to 38.0 $Å^{-1}$ for the long and short nozzle-to-plate distances, respectively. Both curves are with an increment of 0.2 $Å^{-1}$. Least-squares structure refinements were carried out with the use of modified virsion of the program KCED25M [30, 31]. Weight matrix was diagonal. The sort distance data were assign half weight and the long distance data 1.0. Estimated standard deviations calculated by the program were multiplied by a factor of three to include added uncertainty due to the data correlation and an estimated scale uncertainty of 0.1% [32]. The final set of structural parameters of $CH_2(CH_2CH_2)_2SiH–Cl$ molecule is listed in the table.

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