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Conformational preferences of fluorocyclohexane and 1-fluoro-1-silacyclohexane molecules: ab initio study and NBO analysis

Alexander V. Belyakov · Alexander A. Baskakov ·
Anatolii D. Ivanov · Alexander V. Garabadzhiu ·
Ingvar Arnason

Received: 28 November 2012 / Accepted: 7 January 2013 / Published online: 22 January 2013
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Abstract The molecular structure of the axial and equatorial conformers of fluorocyclohexane and 1-fluoro-1-silacyclohexane, $\text{H}_2\text{C}(\text{CH}_2\text{CH}_2)_2\text{XH-F}$ ($\text{X} = \text{C}$ or Si), as well as the thermodynamic equilibrium between these species were investigated by means of quantum chemical calculations up to MP2/aug-cc-pVTZ level of theory. According to MP2 data, these compounds consist of a mixture of conformers with chair conformation and C_s symmetry differing in the *axial* and *equatorial* position of the C–F/Si–F bonds (*axial* = 42/56 mol%, *equatorial* = 58/44 mol%) at $T = 298$ K. This corresponds to a free energy difference of $A = (G_{\text{ax}} - G_{\text{eq}}) = 0.19/-0.13$ kcal mol $^{-1}$ for $\text{X} = \text{C/Si}$. NBO analysis revealed that the *axial* conformer of 1-fluoro-1-silacyclohexane is an example of stabilization of the form that is unfavorable in terms of conjugation effects; stabilization is achieved mainly due to steric interactions. The *equatorial* conformer of fluorocyclohexane is an example of stabilization of the form that is unfavorable in terms of electrostatic interactions; stabilization is achieved due to steric and conjugation effects.

Keywords Cyclohexane · Silacyclohexane · Molecular structure · Conformational analysis · NBO analysis

We dedicate this paper to Professor Aldo Domenicano in connection with his 75th birthday.

A. V. Belyakov (✉) · A. A. Baskakov ·
A. D. Ivanov · A. V. Garabadzhiu
Saint-Petersburg State Technological Institute,
190013 Saint-Petersburg, Russia
e-mail: avbel@bmail.ru

I. Arnason
Science Institute, University of Iceland, Dunhaga 3, IS-107,
Reykjavik, Iceland

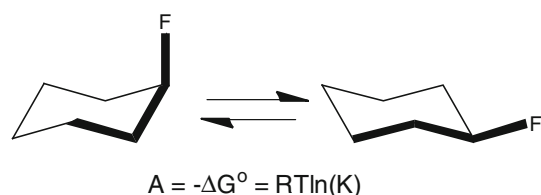
Introduction

Conformational analysis of cycloalkanes and heterocycles is a field that has contributed substantially to the understanding of the nature of the chemical bond. Understanding the conformational properties of cycloalkanes and heterocycles is crucial if one intends to understand the conformations of bioactive molecules like proteins and nucleic acids. Conformational analysis plays also a role in drug discovery.

The chair-to-chair inversion of the cyclohexane molecule is well known, the Gibbs free energy of activation for the step *chair* → *half-chair* → *twist* is generally accepted to be 10.1–10.5 kcal mol $^{-1}$. In the silacyclohexane molecule, the activation energy is about one-half of the value for cyclohexane [1, 2]. Unlike other cycloalkanes, the lowest energy conformer of cyclohexane has the ring in a *chair* form. The cyclohexane molecule is the most stable of the simplest cycloalkanes. The common explanation for this involves considering the lowest energy conformer of cyclohexane as having zero strain energy with almost perfect tetrahedral bond angles and staggered arrangement of vicinal bonds, thus resulting in no torsional strain and minimal steric strain as compared to the smaller cycloalkanes.

Substitution of a carbon atom in the cyclohexane molecule by a 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. It is therefore important to elucidate the effects which influence the structure of cyclic and heterocyclic compounds.

Axial-equatorial equilibrium, as shown in Scheme 1, means that positive values of A correspond to predominance of the equatorial conformer. In monosubstituted cyclohexanes, the equatorial conformers are generally



Scheme 1 Axial-equatorial equilibrium

preferred. This is traditionally attributed to the so-called 1,3-diaxial repulsion between the substituent in axial position and axial hydrogen atoms located in 1,3-positions that destabilizes the axial conformer. However, there are investigations which do not confirm the correctness of this explanation [3–7].

The authors of review [8] have analyzed the influence of a heteroatom on the conformational stability of cyclohexane derivatives where the effect of the heteroatom, in a number of cases, is accounted for by orbital interactions. In the last few years, a number of experimental and theoretic investigations of monosubstituted 1-silacyclohexanes have been carried out with the aim of rationalizing the influence of the silicon atom on the *axial-equatorial* equilibrium [9–24].

The aim of the present *ab initio* and DFT study is to elucidate differences in conformational preferences of fluorocyclohexane and 1-fluoro-1-silacyclohexane molecules by means of energy decomposition analysis in the frame of the Natural Bond Orbital method (NBO) [25–27].

Computational details

All quantum chemical calculations were carried out up to the MP2/aug-cc-pVTZ and M062x/aug-cc-pVTZ levels of theory with the use of the Gaussian 09 program system [28]. NBO analysis [25–27] and calculations of total steric energy [29–31] were done using the NBO 5.9 program [32].

Geometry optimizations of the axial and equatorial conformers were performed under C_s symmetry. Calculations of the molecular force fields confirmed that the optimized structures thus obtained correspond to minima on the potential energy hypersurface. Optimized sets of geometrical parameters of the $H_2C(CH_2CH_2)_2CH-F$ and $H_2C(CH_2CH_2)_2SiH-F$ molecules are shown in Table 1.

Lowest energy pathways for the *axial-to-equatorial* interconversion of fluorocyclohexane and 1-fluoro-1-silacyclohexane molecules were calculated with the use of the quadratic synchronous transit approach (STQN) [33, 34].

Results and discussion

In monosubstituted cyclohexanes, *axial* and *equatorial* positions are inequivalent in energy. For example, in

Table 1 Structural parameters of molecular models of C_s symmetry of $H_2C(CH_2CH_2)_2CH-F$ and $H_2C(CH_2CH_2)_2SiH-F$ calculated at the MP2/aug-cc-pVTZ level of theory (bonds r_e , Å; angles in °)

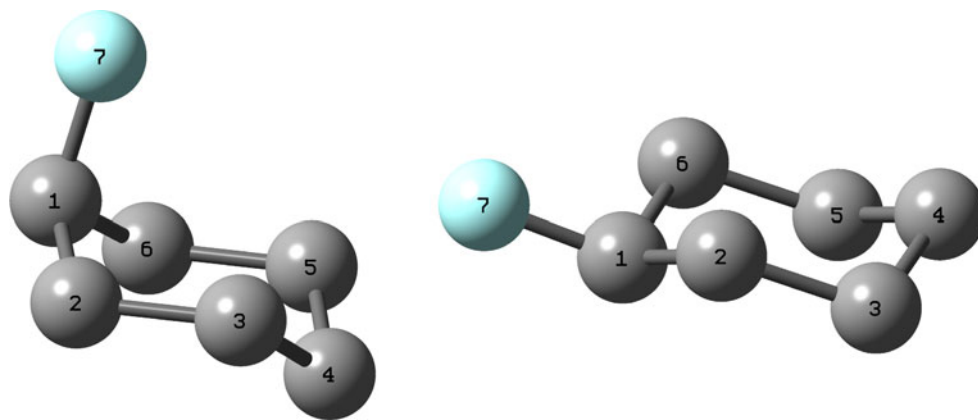
Parameters	$CH_2(CH_2CH_2)_2CH-F$		$CH_2(CH_2CH_2)_2SiH-F$	
	<i>ax.</i>	<i>eq.</i>	<i>ax.</i>	<i>eq.</i>
R(1,2)	1.516	1.513	1.867	1.867
R(1,7)	1.409	1.402	1.625	1.621
R(1,8)	1.092	1.095	1.481	1.483
R(2,3)	1.527	1.529	1.539	1.541
R(3,4)	1.527	1.527	1.531	1.531
A(2,1,6)	112.6	111.9	105.6	105.3
A(2,1,7)	108.1	109.1	108.3	111.5
A(2,1,8)	110.9	110.1	113.9	110.9
A(7,1,8)	106.0	106.3	106.6	106.9
A(1,2,3)	111.5	110.1	110.0	108.9
A(2,3,4)	110.8	110.9	113.2	113.2
A(3,4,5)	110.6	110.8	114.0	114.0
D(6,1,2,3)	53.1	−57.5	44.6	−47.5
D(7,1,2,3)	−66.3	−178.4	−71.2	−168.5
D(8,1,2,3)	177.9	65.2	170.3	72.5
D(2,1,6,5)	−53.1	57.5	−44.6	47.5
D(7,1,6,5)	66.3	178.4	71.2	168.5
D(8,1,6,5)	−177.9	−65.2	−170.3	−72.5
D(1,2,3,4)	−55.0	56.3	−55.7	57.1
D(2,3,4,5)	57.2	−56.1	66.7	−66.4
D(3,4,5,6)	−57.2	56.1	−66.7	66.4
D(4,5,6,1)	55.0	−56.3	55.7	−57.1
ΔE (kcal mol ^{−1})	0.12	0.0	0.0	0.18
ΔH° (kcal mol ^{−1})	0.15	0.0	0.0	0.19
ΔG° (kcal mol ^{−1})	0.19	0.0	0.0	0.13
χ , (%)	42	58	56	44

Atom numbering is shown in Fig. 1. Total (MP2) electronic energy is $E_{ax} = -334.4896487$ and -585.58610495277 a.e. for $CH_2(CH_2CH_2)_2CH-F$ and $CH_2(CH_2CH_2)_2SiH-F$ molecules respectively. Relative electronic energies at 0 K (ΔE); relative standard enthalpy (ΔH°), relative standard free energy (ΔG°) and mole fraction (χ) at 298 K

methylcyclohexane, the equatorial conformer is about 1.98 kcal mole^{−1} more stable than the *axial* one [3]. The same applies to other monosubstituted cyclohexanes. With exception of mercury-substituted cyclohexane molecules [35], the substituent is always more stable in the *equatorial* than in the *axial* position.

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 repulsion caused by 1,3-*syn*-diaxial interactions, which are absent when the substituent is located in the *equatorial* position. It is supposed that the value of the 1,3-*syn*-diaxial repulsion for a particular substituent depends on the nature and size of the substituent. It is also supposed that the repulsion has to increase with

Fig. 1 Molecular model and atom numbering for *axial* and *equatorial* conformers



increasing size of an alkyl group because the stability of the *equatorial* conformer increases [36]. Note, however, that the idea of 1,3-*syn*-diaxial interactions is an intuitive one and there is no direct experimental or theoretic evidence of repulsion between atoms of an *axial* substituent and 3,5-diaxial hydrogen atoms even in the *axial tert*-butylcyclohexane molecule [5].

Substitution of a carbon atom in the cyclohexane molecule by a heteroatom may have a strong effect on the conformational properties of its derivatives due to changes in atomic properties like radius, bond length, electronegativity, and other electronic effects. Thus, for example, substitution of a carbon atom in the cyclohexane molecule by an oxygen or sulfur atom leads to a preference for the *axial* position by electronegative substituents in ring position 2. This is due to delocalization of a lone electron pair of the oxygen atom into the antibonding σ -orbital of the adjacent carbon-substituent bond (the anomeric effect).

Substitution of a carbon atom in cyclohexane by a silicon atom may lead to reversal of the stability of *axial* and *equatorial* substituents, i.e., the *axial* conformer becomes more stable, as, for example, is the case for the CF_3 derivative [10]. If the *equatorial* conformer remains more stable, then its stability is remarkably reduced. Thus, for trichloromethyl- and *tert*-butyl- substituents, the difference of ΔE values amounts to about $\sim 4.5 \text{ kcal mole}^{-1}$ [36].

According to our calculated results at the MP2/aug-cc-pVTZ level of theory, the *equatorial* conformer of fluorocyclohexane molecule is more stable than the *axial* one ($\Delta E = 0.12 \text{ kcal mole}^{-1}$), whereas for 1-fluoro-1-silacyclohexane the *axial* conformer is more stable ($\Delta E = -0.18 \text{ kcal mole}^{-1}$).

It is interesting to note that for 1-trifluoromethyl-1-silacyclohexane, in spite of the approximately equal steric demands of methyl and trifluoromethyl groups and the high electronegativity of the trifluoromethyl group (lying between those of chlorine and fluorine), the relative stability of the *axial* conformer is remarkably higher than for 1-methyl- and 1-fluoro-1-silacyclohexane molecules.

Higher conformational stability of the *axial* conformer for a number of 1-monosubstituted silacyclohexanes also indicates that 1,3-*syn*-diaxial interactions do not play a decisive role [36].

Recently many attempts were undertaken to account for the conformational preferences of 1-monosubstituted silacyclohexanes on the basis of calculations of energies of steric interactions and calculations in the frame of NBO analysis, considering the effects of hyperconjugation (that is, the effects of delocalization of the electrons of the σ -bonds into antibonding orbitals of vicinal bonds located in *anti*-positions). It is shown that for some molecules such effects may play an important role, but a general explanation is not found.

In Ref. [9], the change in the differences of electronic and of nuclear repulsion energies when going from *axial* to *equatorial* conformers has been analyzed for the cyclic pairs of monosubstituted cyclohexanes, monosubstituted 1-silacyclohexanes and for the acyclic pairs of 1-substituted propanes, 1-substituted silapropanes, and a range of substituents with a wide variety of electronegativities. Despite the absence of remarkable correlations in the values of conformational energies when substituting the carbon by silicon atoms in these series of compounds, the changes of differences of conformational energies correlate reasonably well with the changes of differences in nuclear repulsion energies. It was concluded that electropositive substituents such as alkaline metals and cations of alkaline-earth metals prefer to be *axially* oriented substituents in cyclohexane in accordance with the observed conformational preference of mercury derivatives [35]. Moving from cyclohexane derivatives to silacyclohexane derivatives reverses the conformational preference and makes the *equatorial* form the preferred one.

Figure 2 presents a 3-D relative energy surface of the fluorocyclohexane molecule that was obtained by changing two opposite dihedral angles of the ring in small steps. When considering the *axial-to-equatorial* interconversion, the starting point is the *axial* conformer, which is located at

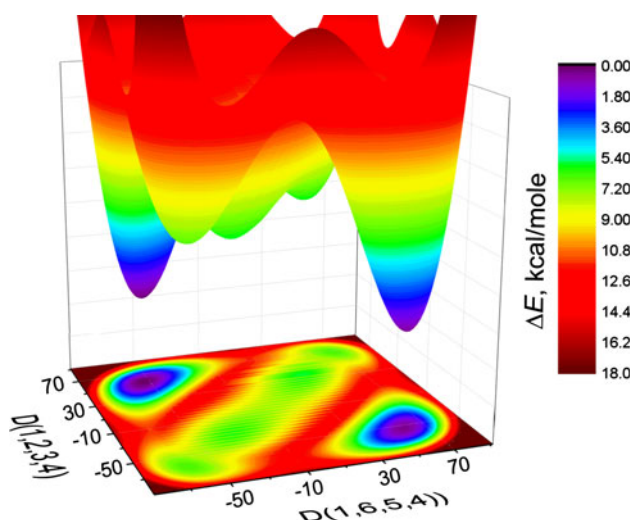


Fig. 2 3-D presentation of the relative energy surface of the fluorocyclohexane molecule calculated at the M062X/6-31G* level of theory, shown as a function of two dihedral angles

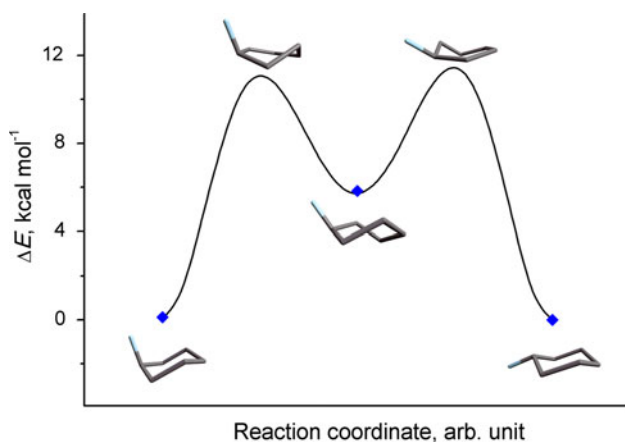


Fig. 3 Lowest energy pathway for the *axial-to-equatorial* interconversion of the fluorocyclohexane molecule calculated by the STQN method at the M062X/aug-cc-pVTZ level of theory and molecular models for minima and transition states. The *diamonds* correspond to relative energies at the MP2/aug-cc-pVTZ level of theory

the lower right corner and the final point is the *equatorial* conformer, which is located at the upper left corner. A lowest energy path is found from the *axial* form over a *half-chair* transition state to a *twist-boat* form (which is located at the lower left corner) and then over a second *half-chair* transition state to the *equatorial* form. Owing to symmetry reasons, there is a second enantiomeric lowest energy path, which goes through a *twist-boat* form which is located at the upper right corner.

Figures 3 and 4 show the minimum energy path of the interconversion between *axial* and *equatorial* conformers for the fluorocyclohexane and 1-fluoro-1-silacyclohexane molecules, respectively, calculated by the quadratic

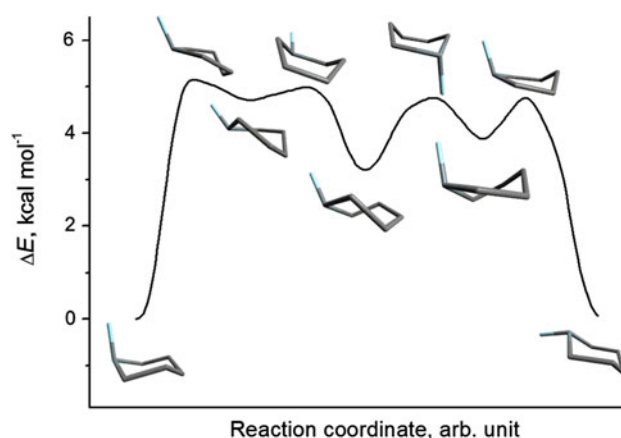


Fig. 4 Lowest energy pathway for the *axial-to-equatorial* interconversion of the 1-fluoro-1-silacyclohexane molecule calculated by the STQN method at the M062X/6-31G** level of theory

Table 2 Results of the NBO analysis and energy decomposition of total electronic energy $E^{(T)}$ into Lewis $E^{(L)}$, non-Lewis $E^{(NL)}$, total steric $E^{(ST)}$, and electrostatic $E^{(L-ST)}$ energies

	CH ₂ (CH ₂ CH ₂) ₂ CH-F		CH ₂ (CH ₂ CH ₂) ₂ SiH-F	
	<i>ax.</i>	<i>eq.</i>	<i>ax.</i>	<i>eq.</i>
$\Delta E^{(T)}$	0.1	0.0	0.0	0.2
$\Delta E^{(L)}$	0.0	2.7	0.0	2.7
$\Delta E^{(NL)}$	2.7	0.0	2.5	0.0
$\Delta E^{(ST)}$	19.1	0.0	0.0	2.6
$\Delta E^{(L-ST)}$	0.0	21.8	0.0	0.01

Relative energies are in kcal mol^{−1} (see text)

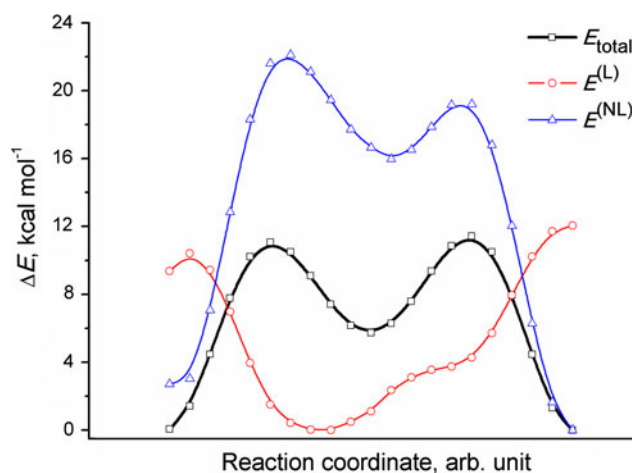


Fig. 5 Barrier to internal rotation along the lowest energy path for the *axial-to-equatorial* interconversion of the fluorocyclohexane molecule, showing the total energy $E^{(total)}$ (*squares*), the localized Lewis component $E^{(L)}$ (*circles*), and the delocalized non-Lewis component $E^{(NL)}$ (*triangles*) as a function of the reaction coordinate. $E^{(L)}$ reflects steric and electrostatic interactions and $E^{(NL)}$ reflects all conjugations

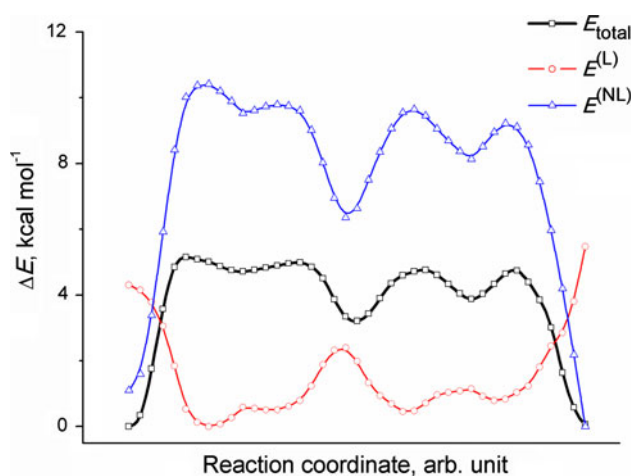


Fig. 6 Barrier to internal rotation along the lowest energy path for the *axial-to-equatorial* interconversion of the 1-fluoro-1-silacyclohexane molecule, showing the total energy $E^{(\text{total})}$ (squares), the localized Lewis component $E^{(\text{L})}$ (circles), and the delocalized non-Lewis component $E^{(\text{NL})}$ (triangles) as a function of the reaction coordinate. $E^{(\text{L})}$ reflects steric and electrostatic interactions and $E^{(\text{NL})}$ reflects all conjugations

synchronous transit approach (STQN) [33, 34]. The conformations corresponding to the minima and transition states on the potential energy hypersurface are also shown. Figure 3 compares M062X results with those calculated at the MP2/aug-cc-pVTZ level of theory. It is shown that relations of energies of all minima are the same for both methods.

In the present work, the decomposition of total electronic energy $E^{(\text{total})}$ into Lewis $E^{(\text{L})}$ (orbital population $n_i = 2.0$) and non-Lewis $E^{(\text{NL})}$ parts (see Table 2; Figs. 5 and 6) is performed using the concept of NBO analysis. The localized Lewis component $E^{(\text{L})}$ corresponds to more than 99.5 % of the full electron density, and thus incorporates in good approximation all steric and classic electrostatic effects. The non-Lewis $E^{(\text{NL})}$ part describes all types of conjugation.

Conclusion

The conformational preferences of fluorocyclohexane and 1-fluoro-1-silacyclohexane molecules are determined by a subtle balance of electronic, steric, and electrostatic effects. As it follows from Table 2, the *axial* conformer of the 1-fluoro-1-silacyclohexane molecule is an example of stabilization of the form that is unfavorable in terms of conjugation effects; stabilization is achieved mainly due to steric effects. The *equatorial* conformer of the fluorocyclohexane molecule is an example of stabilization of the form that is unfavorable in terms of electrostatic interactions; stabilization is achieved due to steric and conjugation

effects. In a similar way, it was shown in [19–21] that the more abundant *axial* conformers of the molecules of the series $\text{H}_2\text{C}(\text{CH}_2\text{CH}_2)_2\text{SiHX}$, (where $\text{X} = \text{Cl}$, Br , and I) are examples for electrostatic stabilization of the forms which are unfavorable in terms of steric and conjugation effects.

Acknowledgments Support from Russian Foundation for Basic Research (projects 10-03-00320a and 12-03-91330-NNIOa) and Russian Government (project 11.G34.31.0069) is gratefully acknowledged.

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