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Quantum-Chemical Study of Silacyclohexanes $C_5H_{10}SiHCN$, $C_5H_{10}SiH(t\text{-}Bu)$, $C_5H_{10}Si(t\text{-}Bu)CN$, and $C_5H_{10}SiHF$

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Abstract—By quantum-chemical calculations at the M06-2X/aug-cc-pVTZ level of theory geometrical parameters, dipole moments, polarizabilities, first hyperpolarizabilities and relative energies of the axial and equatorial conformers in gaseous phase were determined for 1-cyano-1-silacyclohexane, 1-*tert*-butyl-1-silacyclohexane, 1-*tert*-butyl-1-cyano-1-silacyclohexane, and 1-fluoro-1-silacyclohexane. For the cyano group and fluorine atom the axial position is more preferable whereas for *tert*-butyl group, equatorial one. Polarizabilities of conformers are similar but optical anisotropy of equatorial conformers of $C_5H_{10}SiHCN$ and $C_5H_{10}SiH(t\text{-}Bu)$ molecules is much larger than that of axial conformers. Upon substitution in nitriles of C^1 atom by Si atom the hyperpolarizability is many times increased.

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Conformational aspects of stereochemistry of mono- and disubstituted cyclohexanes can be regarded as well-studied problems of structural chemistry [1]. The substitution of a carbon atom in cyclohexane molecule by silicon atom has a strong effect on the structure and physicochemical characteristics of its derivatives. Particularly, it affects dipole moments and polarizabilities, electric properties responsible for intermolecular interactions and interactions of molecules with uniform electric field. It also results in the changes of the conformational composition in the equilibrium mixture.

In the last years results were published of the research on the conformational composition, relative energies, and structural parameters of 1-silacyclohexane derivatives in the gas phase [2–14]. With the use of electron diffraction, NMR, and quantum chemical methods relative energies and structural differences of conformers of 1-fluoro-1-silacyclohexane [2–4, 11], 1-methyl-1-silacyclohexane [5, 6, 11], 1-trifluoromethyl-1-silacyclohexane [7], 1-silyl-1-silacyclohexane [8], 1-hydroxy-, 1-methoxy- and 1-chloro-1-silacyclohexane [11, 13], 1-bromo-1-silacyclohexane [12], 1-iodo-1-silacyclohexane [14] were determined. The microwave spectrum of unsub-stituted silacyclohexane was recorded and interpreted [15].

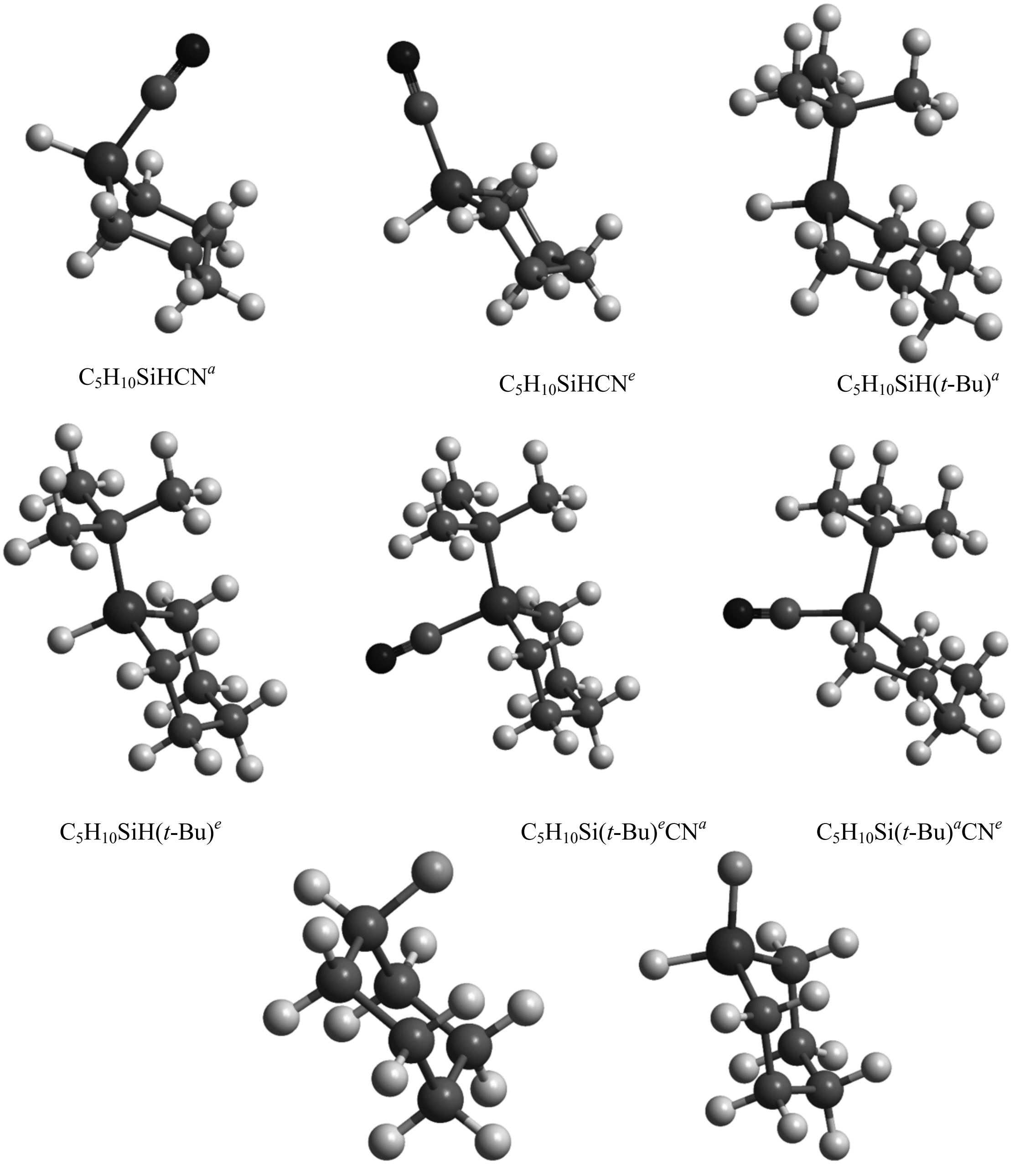
In the present study at the M06-2X/aug-cc-pVTZ level of theory [16] with the use of Gaussian-09 computer program [17] equilibrium structural parameters, energies, dipole moments, static dipole polarizabilities and first hyperpolarizabilities of axial and equatorial conformers of cyanocyclohexane, 1-cyano-1-silacyclohexane, 1-*tert*-butyl-1-silacyclohexane, 1-*tert*-butyl-1-cyano-1-silacyclohexane, and 1-fluoro-1-silacyclohexane molecules were calculated (see figure)

The results of these DFT studies were confirmed by *ab initio* calculations at the MP2(full)/aug-cc-pVTZ level of theory. Both methods were carried out with the use of *int = ultrafine* and *opt = tight* parameters which give higher precision of calculations compared to the standard procedure.

The revealed conformational minima were confirmed by calculation of vibrational frequencies. Zero point vibrational frequencies and energies were calculated in harmonic approximation without use of any empiric scale coefficients.

The atomic charges were calculated with the use of populations of the natural atomic orbitals [18].

Tables 1–3 show calculated equilibrium structural parameters of the molecules under study. The molecular structure of the 1-fluoro-1-silacyclohexane was presented formerly [2–4].



$C_5H_{10}SiHCN^a$ $C_5H_{10}SiHCN^e$ $C_5H_{10}SiH(t\text{-Bu})^a$

$C_5H_{10}SiH(t\text{-Bu})^e$ $C_5H_{10}Si(t\text{-Bu})^eCN^a$ $C_5H_{10}Si(t\text{-Bu})^aCN^e$

$C_5H_{10}SiHF^a$ $C_5H_{10}SiHF^e$

Conformers of 1-cyano-, 1-*tert*-butyl-, 1-*tert*-butyl-1-cyano-, and 1-fluoro-1-silacyclohexane.

As it follows from the comparison of the calculated energies, CN-axial and (*t*-Bu)-equatorial conformers are more preferable (see Table 4). These effects are not additive: the difference in the energies of conformers of 1-*tert*-butyl-1-cyano-1-silacyclohexane (1.73 kcal mol^{-1}) is by 0.36 kcal mol^{-1} lower than the sum of differences of energies of conformers of 1-cyano-1-silacyclohexane (0.94 kcal mol^{-1}) and conformers of 1-*tert*-butyl-1-silacyclohexane (1.15 kcal mol^{-1}).

In agreement with the results of [2–4] the energy of the axial conformer of 1-fluoro-1-silacyclohexane is lower than that of equatorial conformer. At the M06-2X/aug-cc-pVTZ and MP2(full)/aug-cc-pVTZ levels

Table 1. Equilibrium bond lengths (Å) in substituted cyclohexanes $H_2C(CH_2CH_2)_2ZX^aX^e$ calculated by MP2(full) and M06-2X methods

Molecule	Z–X^a	Z–X^e	Z–C^2	C^2–C^3	C^3–C^4	C≡N
			MP2(full)/aug-cc-pVTZ			
$C_5H_{10}SiHCN^a$	1.859	1.475	1.859	1.531	1.524	1.171
$C_5H_{10}SiHCN^e$	1.478	1.851	1.859	1.532	1.524	1.171
			M06-2X/aug-cc-pVTZ			
$C_6H_{11}CN^a$	1.468	1.091	1.538	1.526	1.527	1.147
$C_6H_{11}CN^e$	1.094	1.464	1.536	1.526	1.527	1.147
$C_5H_{10}SiHCN^a$	1.876	1.475	1.867	1.539	1.531	1.149
$C_5H_{10}SiHCN^e$	1.478	1.870	1.867	1.540	1.531	1.149
$C_5H_{10}SiH(t\text{-}Bu)^a$	1.901	1.489	1.886	1.536	1.530	–
$C_5H_{10}SiH(t\text{-}Bu)^e$	1.491	1.894	1.881	1.538	1.531	–
$C_5H_{10}Si(t\text{-}Bu)^eCN^a$	1.884	1.883	1.870	1.539	1.531	1.150
$C_5H_{10}Si(t\text{-}Bu)^aCN^e$	1.889	1.882	1.876	1.539	1.530	1.149

Table 2. Equilibrium bond angles (deg) in substituted cyclohexanes $H_2C(CH_2CH_2)_2ZX^aX^e$ calculated by MP2(full) and M06-2X methods

Molecule	X^aSiX^e	X^aSiC^2	X^eSiC^2	C^2SiC^6	SiC^2C^3	$C^2C^3C^4$	$C^3C^4C^5$
			MP2(full)/aug-cc-pVTZ				
$C_5H_{10}SiHCN^a$	106.6	106.0	115.6	106.1	108.8	113.3	114.3
$C_5H_{10}SiHCN^e$	106.6	110.8	111.4	105.9	108.0	113.3	114.1
			M06-2X/aug-cc-pVTZ				
$C_6H_{11}CN^a$	106.7	110.1	109.6	110.7	111.5	111.2	111.1
$C_6H_{11}CN^e$	107.0	108.6	110.6	111.1	110.4	111.3	111.0
$C_5H_{10}SiHCN^a$	106.2	106.5	115.3	106.3	109.4	113.5	114.2
$C_5H_{10}SiHCN^e$	106.0	112.1	110.4	106.0	108.8	113.5	114.2
$C_5H_{10}SiH(t\text{-}Bu)^a$	105.9	114.1	109.4	104.7	112.8	113.2	113.8
		112.2	110.5		112.4	113.6	
$C_5H_{10}SiH(t\text{-}Bu)^e$	108.0	108.7	113.6	104.3	110.1	113.4	114.1
$C_5H_{10}Si(t\text{-}Bu)^eCN^a$	106.2	105.8	116.1	105.9	110.0	113.4	114.1
$C_5H_{10}Si(t\text{-}Bu)^aCN^e$	104.4	115.2	107.8	106.0	111.7	113.4	113.7

of theory the energy differences are 0.16 and 0.17 kcal mol^{-1} that is practically equal to the value of 0.18 kcal mol^{-1} found in [4] at the MP2/aug-cc-pVTZ level of theory with “frozen” core orbitals of carbon and silicon atoms. Coupled cluster CCSD(T)/CBS method revealed lower value of 0.09 kcal mol^{-1} [10].

In spite of large absolute values of atomic charges in cyanides and fluorides (Table 5), the relative energies of their conformers are insensitive to the dielectric characteristics of the media (vacuum and solvent). The absence of the strong dependence of the energy difference between the axial and equatorial conformers on the dielectric constant, in general, it does not mean, that contribution of intramolecular electrostatic interactions into this difference has to be small, because dielectric shielding of such interactions to some extent is compensated by the increase in the absolute values of atomic charges due to the polarization of the molecule by reactive electric field.

Dipole polarizability of molecule is characterized by main values of the polarizability tensor (α_1, α_2, α_3), mean value α_{av} and optical anisotropy δ^2 [19], evaluated by formula (1)

$$\delta^2 = [(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2]/(\alpha_1 + \alpha_2 + \alpha_3)^2. \quad (1)$$

Mean polarizability is a measure of molecular volume and is increased at the replacement of carbon atom C^1 by the silicon atom. The difference in the polarizabilities of axial and equatorial conformers is not large. The following relation $\alpha^a_{av} \le \alpha^e_{av}$ is valid for

Table 3. Equilibrium dihedral angles (deg) in substituted cyclohexanes $H_2C(CH_2CH_2)_2ZX^aX^e$ calculated by MP2(full) and M06-2X methods

Molecule	$C^2ZC^6C^5$	$ZC^2C^3C^4$	$Y^3C^4C^5C^6$
MP2(full)/aug-cc-pVTZ			
$C_5H_{10}SiHCN^a$	46.4	56.2	66.6
$C_5H_{10}SiHCN^e$	48.4	57.3	66.6
M06-2X/aug-cc-pVTZ			
$C_6H_{11}CN^a$	54.8	55.7	56.1
$C_6H_{11}CN^e$	56.4	56.1	56.1
$C_5H_{10}SiHCN^a$	44.8	55.4	66.4
$C_5H_{10}SiHCN^e$	46.7	56.3	66.2
$C_5H_{10}SiH(t\text{-}Bu)^a$	38.3	53.0	67.1
	38.1	53.0	67.3
$C_5H_{10}SiH(t\text{-}Bu)^e$	45.8	56.4	66.1
$C_5H_{10}Si(t\text{-}Bu)^eCN^a$	43.9	55.1	66.6
$C_5H_{10}Si(t\text{-}Bu)^aCN^e$	38.6	53.0	67.6

Table 4. Relative energies (ΔE and ΔG; kcal/mole) and mole fractions (P, %) of most abandant conformers at 298.15 K calculated at the M06-2X/aug-cc-pVTZ and MP2(full)/cc-pVTZ (in parentheses) levels of theory

Molecule	ΔE	ΔG	P
$C_6H_{11}CN^a$	–0.150	–0.061	52.57
$C_5H_{10}SiHCN^a$	–0.936	–0.848	80.73
	(–0.975)	(–0.877)	(81.48)
$C_5H_{10}SiH(t\text{-}Bu)^e$	–1.153	–1.304	90.05
$C_5H_{10}Si(t\text{-}Bu)^eCN^a$	–1.730	–1.584	93.56
$C_5H_{10}SiHF^a$	–0.167	–0.130	55.47

them. With increase in the polarizability the strengthening of van-der-Waals attraction of the molecules is expectable [20].

The optical anisotropy of axial conformers of cyanocyclohexane and 1-cyano-1-silacyclohexane molecules is much smaller than that of the equatorial ones. In the case of equatorial conformers it is insensitive to the replacement of the carbon atom C^1 by the silicon atom (Table 6). Main values of polarizability tensors of axial and equatorial conformers of $C_5H_{10}Si(t\text{-}Bu)CN$ molecule are nearly equal, and δ^2 values for them are close to the optical anisotropy of cyclohexane.

The accuracy of the quantum-chemical calculations on the level M06-2X/aug-cc-pVTZ is demonstrated in Table 7 by comparison of the calculated and experimental data on the polarizabilities of cyclohexane and trimethylsilane molecules.

The electric asymmetry of the molecule is characterized by dipole moment $\boldsymbol{\mu}$ and first hyperpolarizability $\boldsymbol{\beta}$. Components of the vectors $\boldsymbol{\mu}$ and $\boldsymbol{\beta}$ are dependent on the orientation of the axes of coordinate system. Invariant values are μ, the norm of the vector $\boldsymbol{\mu}$, b, the norm of the vector $\boldsymbol{\beta}$ that is obtained by the contraction of the third-rank tensor $\boldsymbol{\beta}$, and $b_\mu = \mathbf{b}\cdot\boldsymbol{\mu}/\mu$, the projection of the vector **b** onto the direction of the dipole moment $\boldsymbol{\mu}$ [25–27].

The calculated results permit to expect many time increase in the hyperpolarizability upon substitution of carbon atom C^1 by silicon atom. In both conformers of 1-fluoro-1-silacyclohexane molecule vectors $\boldsymbol{\beta}$ and $\boldsymbol{\mu}$ are nearly orthogonal, while in both conformers of fluorocyclohexane molecule they are parallel. In axial conformer of cyanocyclohexane molecule vectors $\boldsymbol{\beta}$ and $\boldsymbol{\mu}$ are nearly parallel, but in equatorial one they are antiparallel. Upon substitution of C^1 atom by Si atom in the axial cyanocyclohexane molecule mutual location of $\boldsymbol{\beta}$ and $\boldsymbol{\mu}$ vectors becomes close to orthogonal.

As it is seen from the data on compounds presented in Table 8 both conformers of 1-*tert*-butyl-1-silacyclohexane molecule possess considerable values of b and b_μ (at small dipole moment μ and negative projection b_μ). However $C_5H_{10}SiH(t\text{-}Bu)$ molecule has smaller values of these characteristics as compared with *m*-nitroaniline, the crystals of which are used as a standard when estimating nonlinear optic properties of compounds [25].

Table 5. Atomic charges (a.u.) calculated at the M06-2X/aug-cc-pVTZ level of theory

Molecule	C^1/Si	F, CN	H^{3a}, H^{5a}	C^2, C^6	C^3, C^5	C^4
$C_5H_{10}SiHCN^a$	1.37	–0.45	0.20	–0.86	–0.39	–0.39
$C_5H_{10}SiHCN^e$	1.37	–0.44	0.19	–0.87	–0.39	–0.39
$C_5H_{10}Si(t\text{-}Bu)^eCN^a$	1.75	–0.47	0.20	–0.90	–0.38	–0.39
$C_5H_{10}Si(t\text{-}Bu)^aCN^e$	1.73	–0.46	0.19	–0.90	–0.38	–0.39
$C_5H_{10}SiHF^a$	1.79	–0.67	0.20	–0.91	–0.39	–0.39
$C_5H_{10}SiHF^e$	1.80	–0.66	0.19	–0.91	–0.39	–0.39

Table 6. Main values of polarizability tensor (α_1, α_2, α_3), mean polarizability (α_{av}), and optical anisotropy (δ^2, %), (a.u.) calculated at the M06-2X/aug-cc-pVTZ level of theory

Molecule	α_1	α_2	α_3	α_{av}	δ^2
C_6H_{12}	69	69	60	66	0.4
$C_6H_{11}CN^a$	89	79	78	82	0.4
$C_6H_{11}CN^e$	102	80	70	84	2.4
$C_5H_{10}SiHCN^a$	101	93	91	95	0.2
$C_5H_{10}SiHCN^e$	117	91	81	96	2.5
$C_5H_{10}SiH(t\text{-Bu})^a$	146	126	120	131	0.7
$C_5H_{10}SiH(t\text{-Bu})^e$	152	127	117	132	1.3
$C_5H_{10}Si(t\text{-Bu})^eCN^a$	157	140	131	143	0.6
$C_5H_{10}Si(t\text{-Bu})^aCN^e$	157	140	131	143	0.6
$C_5H_{11}F^a$	73	72	64	70	0.4
$C_5H_{11}F^e$	75	72	63	70	0.5
$C_5H_{10}SiHF^a$	88	83	70	80	0.9
$C_5H_{10}SiHF^e$	86	83	72	80	0.6

Table 7. Calculated and observed main values of polarizability tensors (α_1, α_2, α_3, A^3), mean polarizability (α_{av}, A^3) and values of optical anisotropy (δ^2, %), of cyclohexane and trimethylsilane molecules

Method	α_1	α_2	α_3	α_{av}	δ^2
Cyclohexane molecule C_6H_{12}					
[21]	11.7	11.7	9.3	10.9	1.1
[22, 23]	11.2	11.2	9.8	10.7	0.4
M06-2X/aug-cc-pVTZ	10.9	10.9	9.4	10.4	0.5
Trimethylsilane molecule $SiH(CH_3)_3$					
[24]	9.6	9.6	9.9	9.7	0.0
M06-2X/aug-cc-pVTZ	10.2	10.2	8.9	9.7	0.4

Owing to the presence of lone electron pairs and a considerable electric charge of the cyano group and fluorine atom the dipole moments of the equatorial cyanides and fluorides are larger than those of axial conformers (Table 8).

The performed quantum-chemical energy calculations make it possible to conclude on the conformers ratio of cyclohexane and silacyclohexane derivatives under the condition of the thermodynamic equilibrium. In the equilibrium mixtures of cyanocyclohexane, 1-cyano-1-silacyclohexane and 1-fluoro-1-silacyclohexane conformers the axial conformer prevails, but in the case of *tert*-butylcyclohexane molecule the equatorial conformer is more preferable. Difference in energies of conformers is insensitive to the influence of reactive field of solvent on the molecules under study.

Table 8. Norms of hyperpolarizability vectors (b), their projections onto direction of dipole moments (b_μ) and values of dipole moments (μ) calculated at the M06-2X/aug-cc-pVTZ[a]

Molecule	b, a.u.	b_μ, a.u.	μ, D
$C_6H_{11}CN^a$	22	18	4.13 (4.32)
$C_6H_{11}CN^e$	31	–31	4.58 (4.76)
$C_5H_{10}SiHCN^a$	152	–14	4.37 (4.38)
$C_5H_{10}SiHCN^e$	132	–101	4.71 (4.66)
$C_5H_{10}SiH(t\text{-Bu})^a$	177	–140	0.54
$C_5H_{10}SiH(t\text{-Bu})^e$	178	–89	0.49
$C_5H_{10}Si(t\text{-Bu})^eCN^a$	163	42	4.34
$C_5H_{10}Si(t\text{-Bu})^aCN^e$	125	–26	4.61
$C_5H_{11}F^a$	85.7	85.4	1.85
$C_5H_{11}F^e$	72.6	72.4	2.24
$C_5H_{10}SiHF^a$	147	36	1.92
$C_5H_{10}SiHF^e$	80	28	2.13
m-Nitroaniline	379	–348	5.62

[a] Exclusion from the aug-cc-pVTZ basis of diffusion functions (aug) at the calculation of hyperpolarizability of *m*-nitroaniline leads to the decrease of b value by 15% and b_μ by 20%.

Polarizabilities of 1-cyano- and 1-fluoro-1-silacyclohexanes are larger than those of the corresponding monosubstituted cyclohexanes and are nearly isotropic for dominant axial conformers. Upon replacement in cyclohexyl of carbon atom C^1, that is connected to electron-withdrawing F atom or CN group, by silicon atom the first hyperpolarizability is many times increased.

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