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Conformational Analysis of 2,2-Dimethyl-5-alkyl-1,3-dioxa-2-silacyclohexanes

S. A. Bochkor[a] **and V. V. Kuznetsov**[a,b]

[a] *Ufa State Petroleum Technological University, ul. Kosmonavtov 1, Ufa, 45062, Russia*
e-mail: kuzmaggy@mail.ru

[b] *Ufa State Aviation Technical University, Ufa, Russia*

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Abstract—Study of conformational isomerization of 2,2-dimethyl-5-alkyl-1,3-dioxa-2-silacyclohexanes using quantum-chemical HF/6-31G(d) and PBE/3z approximations showed that its route involves an equilibrium between the *chair* conformers with different orientation of substituent at C^5 ring atom and proceeds through a transition state corresponding to the 2,5-*twist* conformation. Molecular dynamics method showed that at room temperature this conformation transforms into the equatorial or axial *chair* conformers through 1,4-*twist* or *sofa* forms. Based on the experimental and theoretical values of vicinal ^{1}H NMR coupling constants we determined quantitative conformational composition of the molecules of these compounds and the values of ΔG^0 of the conformational equilibrium.

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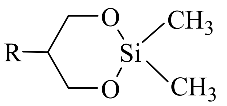
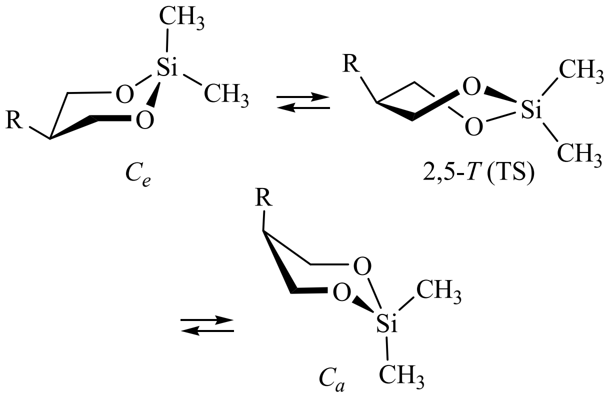
Interest to the six-membered cyclic silicon esters of 1,3-diols, the 1,3-dioxa-2-silacyclohexanes, is due to widespread use of these compounds in fine organic synthesis and their practically useful properties and structural features [1–4]. The latest traits to the great extant are conditioned by the presence to a great extent originate from the presence of a silicon atom with its vacant *d*-orbitals and electron-donor oxygen heteroatoms in one molecule. We previously used the data of ^{1}H NMR spectroscopy and empirical and semiempirical calculations to show that the potential energy surface (PES) of alkyl-substituted 1,3-dioxa-2-silacyclohexanes has minima corresponding to the *chair* conformers and flexible forms [5–8]. The aim of this paper is to study the conformational isomerization and to estimate the conformational composition of the molecules of 2,2-dimethyl-5-alkyl-1,3-dioxa-2-sila-cyclohexanes **I–III** using non-empitrical HF/6-31G(d) and DFT approximations of PBE/3z method within the HyperChem [9] and PRIRODA [10] softwares, respec-tively, as well as the data of ^{1}H NMR spectroscopy.



R = CH_3 (**I**), *i*-C_3H_7 (**II**), *t*-C_4H_9 (**III**).

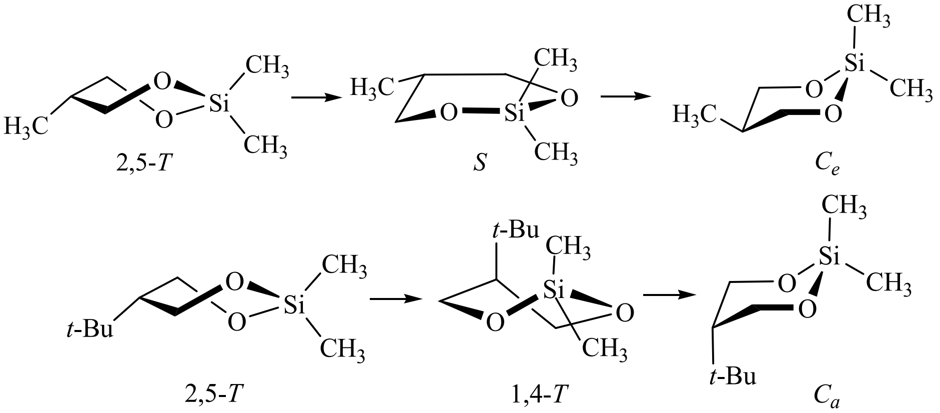
Recently [11] it was found that, in contrast to the multistep conformational equilibrium of the nearest hetero-analogs, the substituted 1,3-dioxanes [12–18], the interconversion of the *chair* conformers of 2,2-dimethyl-1,3-dioxa-2-silacyclohexanes is realized in one step via a transition state (TS) of 2,5-*twist* form (2,5-*T*), similar to that of six-membered cyclic carbonates, boric esters [19–24], and 1,3-dioxa-2-germacyclohexanes [25]. The conformational isomerization of compounds **I–III** proceeds by a similar route:



According to the obtained results (Table 1), the most stable form of the molecules of esters **I–III**, as expected, is the equatorial *chair* C_e. The prevalence of this form is also confirmed by ^{1}H NMR data [4, 8].

Note the low value of the ΔH of conformational isomerization of ether **II.** According to the PBE/3z calculations, the C_e and C_a conformers are almost degenerate in energy. The calculated potential barrier $\Delta H^{\neq}$ between the forms C_e and C_a is several times lower than in 1,3-dioxane (10.3–12.0 kcal mol^{-1} [15, 18]) and 1,3,2-dioxaborinanes (6.9–8.1 kcal mol^{-1} [23]). At the same time, with an increase in the conformational volume of the substituent at the C^5 atom the values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ monotonically decrease. It should also be noted that the conformational $C_e \leftrightarrow C_a$ isomerization of esters **I–III** is characterized by negative values of changes in entropy ΔS and activation entropy $\Delta S^{\neq}$. The latter indicates a more compact nature of the transition state and its sensitivity to the steric requirements of the system.

Using the method of molecular dynamics to simulate the conformational behavior of these compounds at room temperature (HyperChem, 295–300–295 K) we found that the 2,5-*T* forms of esters **I** and **III**, corresponding to the transition state, are converted into *chair* conformers with a period of 1–2 ps.



In the case of ester **I** the C_e conformer is formed through the *sofa* (*S*), while ether **III** transforms into C_a form through the flexible 1,4-*T* conformation. The latter suggests the location of the transition state on the reaction coordinate closer to the axial conformer.

To estimate the relative occupancy of alternative conformations and the ΔG^0 values of conformational equilibrium in the molecules of ethers **I–III** by an independent method we used the experimental ($^3J_{\mathrm{AX}}$, $^3J_{\mathrm{BX}}$ from ^{1}H NMR spectra [4, 8]) and theoretical (J_{aa}, J_{ae}, and J_{ee}) vicinal spin-spin coupling constants of alternative conformers with relative content N and 1–N, respectively (equation from [26]):

$$^3J_{\mathrm{AX}} + {}^3J_{\mathrm{BX}} = N(J_{aa} + J_{ae}) + (1 - N)(J_{ae} + J_{ee}),$$

$$\Delta G^0 = -RT\ln[N/(1 - N)].$$

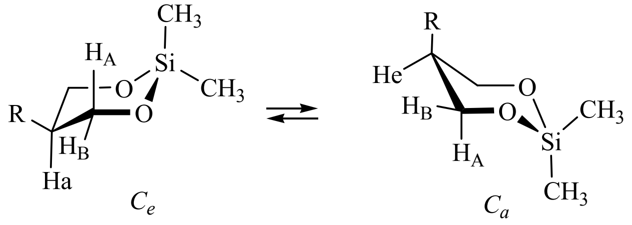
In turn, the theoretical coupling constants can be determined by the modified Karplus equation [27],

Table 1. Thermodynamic parameters of conformational equilibrium of esters **I–III**

Comp. no.	Method	T, K	ΔH,$^{\mathrm{a}}$ kcal mol^{-1}	$-\Delta S$, cal mol^{-1} K^{-1}	ΔG^0,$^{\mathrm{a}}$ kcal mol^{-1}	$\Delta H^{\neq}$,$^{\mathrm{a}}$ kcal mol^{-1}	$-\Delta S^{\neq}$, cal mol^{-1} K^{-1}	$\Delta G^{\neq}$,$^{\mathrm{a}}$ kcal mol^{-1}
I	HF/6-31G(d)	0	1.0	–	–	4.8	–	–
	PBE/3z	0	1.1	–	–	4.3	–	–
		298	1.1	0.04	1.1	3.8	4.1	5.3
II	HF/6-31G(d)	0	0.1	–	–	3.8	–	–
	PBE/3z	0	0.1	–	–	3.1	–	–
		298	–0.06	1.7	0.4	2.4	8.2	4.9
III	HF/6-31G(d)	0	1.5	–	–	3.0	–	–
	PBE/3z	0	1.2	–	–	2.3	–	–
		298	1.0	0.7	1.2	1.6	7.0	3.7

$^{\mathrm{a}}$ Relative to the C_e conformer.

Table 2. The relative occupancy of conformations and the values of ΔG^0 for the conformational equilibria of esters **I–III**



Compound	Conformer	Torsion angles, deg		Spin-spin coupling constants, Hz		N^a	$-\Delta G^0$, kcal mol^{-1}
		$\varphi_{aa(ea)}$	$\varphi_{ae(ee)}$	$^3J_{aa(ea)}$	$^3J_{ae(ee)}$		
I	K_e	177.5	59.6	11.6	4.2	0.76	0.7
	K_a	52.1	66.0	2.9	3.3		
II	K_e	176.5	58.2	11.6	4.4	0.73	0.6
	K_a	55.8	61.9	2.4	3.8		
III	K_e	177.1	63.6	11.6	3.6	0.94	1.6
	K_a	46.5	70.4	4.0	2.7		
Experimental coupling constants		**I**: $^3J_{AX}$ 9.49 Hz, $^3J_{BX}$ 3.97 Hz [4]; **II**: $^3J_{AX}$ 9.8 Hz, $^3J_{BX}$ 3.6 Hz [8]; **III**: $^3J_{AX}$ 10.55 Hz, $^3J_{BX}$ 4.06 Hz [4]					

[a] Relative to the C_e conformer.

using torsion angles between the protons in the conformers involved in the binary equilibrium [the optimum geometry data of HF/6-31G(d) calculation].

The results (Table 2) showed a significant (24–27%) concentration of the molecules of esters **I** and **II** in the C_a form. Accordingly, the values of ΔG^0 for Me and *i*-Pr substituents at the atom C^5 do not exceed 0.6–0.7 kcal mol^{-1}. This result is in good agreement with the data of [7] for ester **I**. However, ΔG^0 for these substituents in the 5-alkyl-1,3-dioxane and 1,3,2-dioxaborinanes is shifted to the greater values (0.9–1.1 kcal mol^{-1} [15, 23, 28]). On the other hand, the value of ΔG^0 of *t*-Bu group in ether **III** corresponds to the range of values of this parameter in 2-R-5-*t*-Bu-1,3-dioxanes (1.4–1.8 kcal mol^{-1} [28]). Thus, the changed geometry of the heteroatomic ring of cyclic silicon esters due to the increased length of Si–O bond compared with C–O and the participation of vacant *d*-orbitals of the silicon atom in the electron exchange with the oxygen heteroatoms lead to a certain decrease in the conformational free energy of substituents small and medium-sized by the conformational volume (Me and *i*-Pr), and virtually do not change the ΔG^0 value of bulky *t*-Bu group at C^5 atom compared with 1,3-dioxane. At the same time attention is drawn to the difference between calculated (Table 1) and found from the coupling constants (Table 2) values of ΔG^0. The obvious reason for such discrepancy is connected with fact that ^{1}H NMR spectra – the stage for the experimental coupling constants employed in the determination of ΔG^0 values – were recorded in the solutions of $CHCl_3$, $CDCl_3$ and CS_2 [4,8]. Therefore, for the more correct estimate of the calculated ΔG^0 and other parameters of the conformational equilibrium (Table 1) the calculations of the continuum or discrete models of specific solvents should be used in future.

EXPERIMENTAL

Esters **I–III** and their NMR spectral characteristics were described in [4, 8]. The routes and barriers to the interconversion are found using HyperChem [9] and PRIRODA [10] softwares. Belonging of the PES minima to the stationary points is confirmed by the absence of imaginary frequencies, and to transition states, by the presence of one imaginary frequency in the corresponding Hessian.

Thermal conformational transformation were investigated by molecular dynamics [HyperChem, HF/6-31G(d)] in the course of integration of the equations of motion at a constant temperature. The temperature regime sequence included a heating from the initial (295 K) to a given (300 K) temperature, keeping at 300 K, and cooling to 295 K, each of the three phases duration was 2 ps.

Modified Karplus equation has the form [27]:

$$^3J_{HH} = P_1\cos^2\varphi + P_2\cos\varphi + P_3 + \Sigma\Delta\chi_i[P_4 + P_5\cos^2(\xi_i\varphi + P_6\,|\,\Delta\chi_i\,)].$$

Here, $\Delta\chi_i$ is the difference in electronegativity between a substituent and hydrogen at the corresponding fragment of ethane, φ is the calculated torsion angle between the interacting protons, ξ_i takes the value ±1 depending on the orientation of the substituents at the carbon atoms of ethane fragment, and P_1–P_6 are the parameters depending on the degree of substitution of this fragment. To solve the equation the numerical values of the parameters P_1 to P_6 for fragments with three substituents were used: $P_1 = 13.22$, $P_2 = -0.99$, $P_3 = 0$, $P_4 = 0.87$, $P5 = -2.46$, $P_6 = 19.90$, as well as the values of electronegativity from [29]. Determination of ΔG^0 was performed for a temperature of 298 K, at which the ^{1}H NMR spectra were recorded. The applicability of computational methods to the determination of the free conformational energy values of substituents in the saturated 1,3-heterocycles has been discussed in [30] by the example of 1,3-dioxanes.

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