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Conformational Analysis of 2-Methyl-5-nitro-1,3,2-dioxaborinane

O. Yu. Valiakhmetova[a], S. A. Bochkor[a], and V. V. Kuznetsov[a,b]

[a] *Ufa State Oil Technical University, ul. Kosmonavtov 1, Ufa, 450062 Russia*
phone: (347)2431655
[b] *Institute of Molecular and Crystal Physics of Ufa Scientific Centre, Russian Academy of Sciences, pr. Octyabrya 151, Ufa, 450075 Russia*
phone: (347)2921417
e-mail: kuz@anrb.ru

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Abstract—Quantum-chemical methods HF/6-31G(d), HF/6-31+G(d), MP2/6-31G(d)//HF/6-31G(d), and MP2/6-31+G(d)//HF/6-31+G(d) were used to investigate the conformational isomerization of 2-methyl-5-nitro-1,3,2-dioxaborinane. It has been shown that a potential energy surface of this compound includes two minima: an axial form of *semi-chair* and equatorial *sofa* together with a transition state belonging to the conformation of 2,5-*twist*-form. A comparison between experimental NMR ^{1}H and theoretical vicinal coupling constants was used to determine the quantitative conformational composition of cyclic boric acid ester and a value of ΔG^0 for nitro group at the ring carbon atom C^5 in CCl_4 and $C_6D_5NO_2$ solutions.

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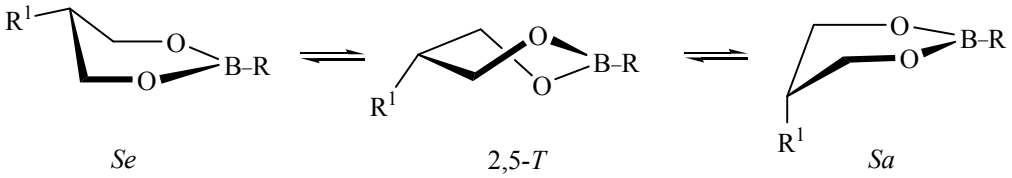
Interest in cyclic esters of boric acids is caused by the growing importance of these compounds for the fine organic synthesis (synthesis of enantiomeric alcohols and polyenes), by the combination of their practically useful properties (biologically active substances, corrosion inhibitors, components of polymer materials and fuels and lubricants) and also by structural features (electronic and steric intramolecular interactions) [1–9]. The latter is caused by the presence of electron-deficient boron atom and electron-donating oxygen heteroatoms in one molecule. It is known that the potential energy surface (PES) of 2,5-disubstituted 1,3,2-dioxaborinane molecules contains two minima: conformers of equatorial and axial *sofa* (*Se* and *Sa*) and also a transition state (TS), 2,5-*twist* form (2,5-*T*). In so doing, in the case of 5-alkyl- and 5-phenyl analogs the equilibrium is shifted to *Se* form [1, 5, 9–11].



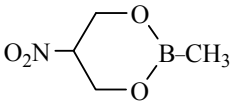
Se 2,5-*T* *Sa*

The presence of electron-withdrawing nitro group at the ring atom C^5 leads to appreciable rearrangement of electron density in the molecule of boric acid ester. As a result, by ^{1}H NMR data and X-ray diffraction and dipole measurements, the conformer with the axial nitro group becomes a main minimum on PES [6, 10, 12–14]. It is confirmed by results of empirical, semi-empirical, and *ab initio* (HF/STO-3G) calculations [15, 16].

This work deals with studying stationary points on PES of 2-methyl-5-nitro-1,3,2-dioxaborinane **I** by means of nonempirical approximations HF/6-31G(d), HF/6-31+G(d), MP2/6-31G(d)//HF/6-31G(d), and MP2/6-31+G(d)//HF/6-31+G(d) using HyperChem program package [17], and also with the determination of quantitative conformational composition of ester **I** by quantum-chemical calculations and ^{1}H NMR spectroscopy.

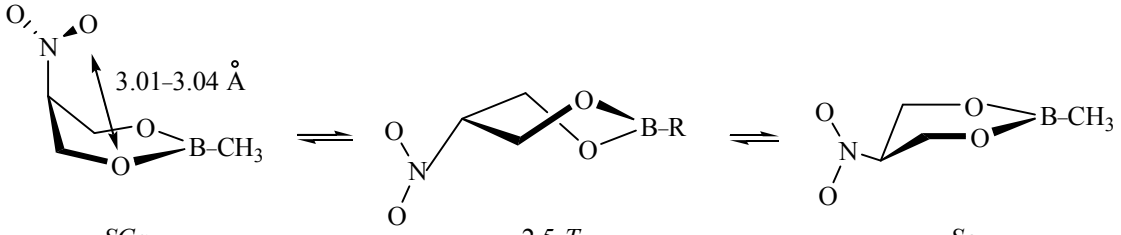
Table 1. Relative stability of minima and transition states on PES of ester **I** (kcal mol^{-1}) and values of dipole moments (D)

Method	Main minimum	ΔE	$\Delta E^{\neq}$	μ	
				SCa	*Se*
HF/6-31G(d)	*SCa*	0.3	6.5	4.50	1.85
HF/6-31+G(d)	*Se*	0.2	6.0	4.60	2.01
MP2/6-31G(d)//HF/6-31G(d)	*SCa*	1.4	7.8		
MP2/6-31+G(d)//HF/6-31+G(d)	*SCa*	0.6	6.8		



I

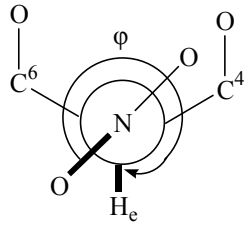
PES of ester **I** was established to include minima: conformer *Se* and *semi-chair* with an axial nitro group (*SCa*), which is the main in the majority of cases, and TS 2,5-*T* (Table 1).



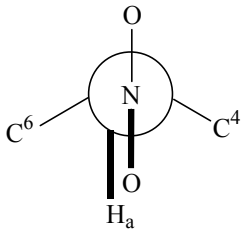
SCa 2,5-*T* *Se*

In this case the energy difference between forms *SCa* and *Se* (ΔE) depends on the selected calculation approximation, and potential barrier height ($\Delta E^{\neq}$) established within MP2 approximation is closed to the known experimental values $\Delta G^{\neq}$ for substituted 1,3,2-dioxaborinanes [12].

Interaction of the nitro group oxygen atoms with ring heteroatomic fragment is a probable reason of axial conformer predominance. This is confirmed by a fact that in the nitrocyclohexane equatorial form prevails [18], and in nonboric analog, 5-nitro-1,3-dioxane, axial *chair* [19-21]. Form *SCa* differs by asymmetrical arrangement of nitro group relative to bisectral plane of valence angle C^4–C^5–C^6. In this case interatomic distance between NO_2 group oxygen with a partial charge –0.470 and nearest heteroatom with a charge –0.636 [HF/6-31G(d)] is 3.01–3.04 Å depending on the calculation method. In spite of electrostatic repulsion of the oxygen atoms, this orientation of substituent corresponds to the main minimum on a diagram of potential energy dependence on the value of the angle between the bonds N–O and C^5–H (φ, see the figure).



SCa φ 320°



Se φ 0°

Initial reference point on a curve *1* corresponds to eclipsed arrangement of the mentioned bonds. The local maximum (ΔE = 3.7 kcal mol^{-1}) is at φ = 30^0, then the local minimum (ΔE = 0.5 kcal mol^{-1}, φ = 140°), the main maximum (ΔE = 4.5 kcal mol^{-1}, φ = 220°) and the main minimum (ΔE = 0, φ = 320°) follow. Calculation in HF/6-31+G(d) approximation leads to similar dependence of *E* on φ.

This fact of existing main and local minima and maxima, differing by the value of angle φ = 180°, is caused by additional conformational rearrangement of the cycle, which accompanies NO_2-group rotation. This circumstance and also sufficiently high barrier to the rotation around the C^5–N bond indicates appreciable stabilizing effect of COBOC fragment on the axial nitro group. Its nature, as in the case of 5-nitro-1,3-dioxanes, is probably due to the effect of dipole-dipole stabilization of polar substituent relative to dipoles of C–O bonds, and also by interaction of *p*-electrons of heteroatom oxygen with π-system of nitro group [20–22].

Eclipsed orientation of N–O and C^5–Ha bonds is characteristic for the minimum of internal rotation of nitro group in conformer *Se*. In so doing, NO_2 plane is oriented on bisector of C^4–C^5–C^6 angle. Symmetrical character of curve *2* similar to the corresponding potential function for nitropropane [23] and relatively low rotation barrier (< 0.6 kcal mol^{-1}) indicate that no appreciable interaction exists between the equatorial group NO_2 and heteroatom fragment.

It was of interest to evaluate relative content of alternative conformers and ΔG^0 value for conformational equilibrium in the molecule of ester **I** by means of independent method using experimental (from the ^{1}H NMR spectrum: $^3J_{AX}$, $^3J_{BX}$) and theoretical (J_{ae}, J_{ee}, $J_{a'e}$, $J_{e'e}$, J_{aa}, J_{ea}) vicinal spin–spin coupling constants of alternative conformers with relative content N and 1 – N respectively [24]:

$$2\,{}^3J_{AX} + 2\,{}^3J_{BX} = \mathrm{N}(J_{ae} + J_{a'e} + J_{ee} + J_{e'e}) + (1 - \mathrm{N})(2\,J_{aa} + J_{ea}),$$

$$\Delta G^0 = -RT \ln \frac{\mathrm{N}}{1 - \mathrm{N}}.$$

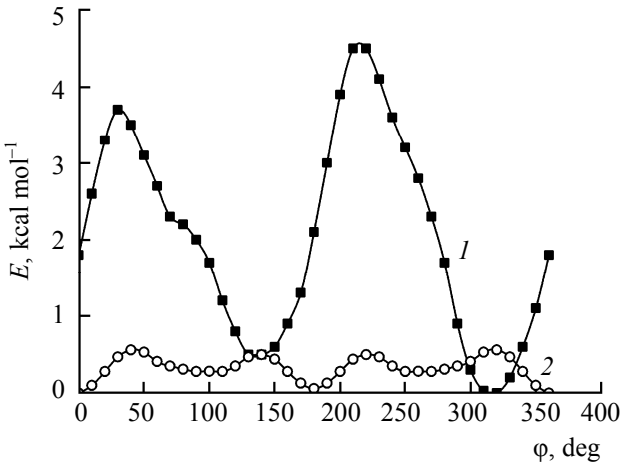
In its turn, theoretical coupling constants can be determined by modified Karplus equation [25] using torsion angles between the corresponding protons in conformers involved in a binar equilibrium (optimal geometry data). Note that due to the higher value of dipole moment of conformer *SCa* (Table 1) its stability and content in the equilibrium mixture should be increased as the solvent polarity increases. Value ΔG^0 of axial *chair* equals 0.38 kcal mol^{-1} in CCl_4 and 1.0 kcal mol^{-1} in acetonitrile for 2-isopropyl-5-nitro-1,3-dioxane with similar differences in dipole moments of axial and equatorial forms [19–21]. In this work we used experimental coupling constants from the ^{1}H NMR spectrum of ester **I** in CCl_4 ($^3J_{AX}$ 3.4, $^3J_{BX}$ 2.9 Hz) and in $C_6D_5NO_2$ ($^3J_{AX}$ 2.9, $^3J_{BX}$ 1.9 Hz) to calculate N.

The obtained results (Table 2) attest that *SCa* form prevails (86–98%) in conformational equilibrium of 2-methyl-5-nitro-1,3,2-dioxaborinane molecules. As expected, axial conformer content increases as the medium polarity rises. Assuming that the presence of solvent will not essentially affect the geometric characteristics of canonic forms *SCa* and *Se* optimized for the rarefied gas phase (this assumption is justified at least for nonpolar CCl_4), one can state the more stable than in 1,3-dioxanes interaction of axial nitro group and COBOC fragment of cycle.

EXPERIMENTAL

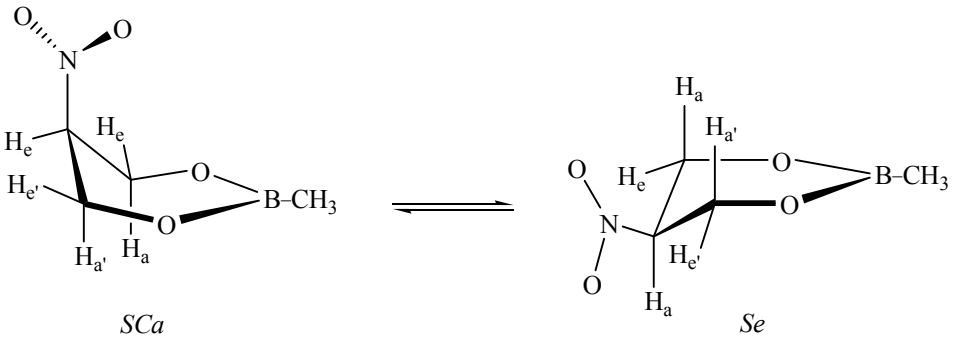
The ^{1}H NMR spectra of the nearest analog of ester **I,** 2-isopropyl-5-nitro-1,3,2-dioxaborinane, described in [26], were registered on a AM-250 Bruker spectrometer (250 MHz) using 10% solution of ester **I** in CCl_4 (with addtion of small amount of $CDCl_3$) and $C_6D_5NO_2$ relative to external TMS.

The route and value of interconversion barriers were established by the procedure “transition state” within HyperChem package [17]. Belonging of PES stationary points to minima was confirmed by the absence of imaginary frequencies, and to transition state (form 2,5-*T*), by the presence of one imaginary



Dependence of potential energy of conformers of ester **I** on the internal rotation angle H–C^5–N-O (φ) established by approximation HF/6-31G(d); (*1*) form *SCa* and (*2*) form *Se*.

Table 2. Relative content of conformers and ΔG^0 value (kcal mol^{-1}) of conformational equilibrium for ester **I**



SCa *Se*

Calculation method	Form	Torsion angles (deg)[a]		Coupling constant (Hz)		N[b] (solvent, NMR)	$-\Delta G^0$
		$\varphi_{ae(a'e)}$	$\varphi_{ee(e'e)}$	$^3J_{ae(a'e)}$	$^3J_{ee(e'e)}$		
MP2/6-31G(d)//HF/6-31G(d)	*SCa*	43.1	74.9	2.9	1.9	0.86	1.1
	Se	54.6	63.9	1.5	2.8	(CCl_4)	
		171.4	51.2	10.6	6.2	0.98	2.3
	Sca					($C_6D_5NO_2$)	
MP2/6-31+G(d)//HF/6-31+G(d)		42.3	75.8	3.0	1.8	0.86	1.1
	Se	54.0	64.6	1.6	2.8	(CCl_4)	
		171.7	51.1	10.6	6.2	0.98	2.3
						($C_6D_5NO_2$)	

[a] *a* and *e* are axial and equatorial orientation of the hydrogen atoms in the corresponding ethane fragment. [b] Relative to the most stable conformer.

frequency in the corresponding Hessian. The dependence of the potential energy of ester **I** on the internal rotation angle φ was examined in the range from 0° to 360° by calculating energy in the desired points using 10° step.

Modified Karplus equation takes the form [25]:

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

where $\Delta\chi_i$ is the electronegativity difference between substances of the corresponding ethane fragment and hydrogen, φ is the calculated torsion angles between interacting protons, ξ_i takes values ±1 depending on the orientation of substituents at the carbon atoms of ethane fragment, and P_1–P_6 are parameters depending on substitution extent of this fragment. In solving the equation we used numerical values of parameters P_1 – P_6 for fragment with three substituents: P_1 = 13.22, P_2 = –0.99, P_3 = 0, P_4 = 0.87, P_5 = –2.46, P_6 = 19.9°, and also electronegativities values of carbon, oxygen and hydrogen atoms from [27], and for NO_2-group, from [28]. Determination of ΔG^0 value was made for temperature 298 K, at which the ^{1}H NMR spectra were recorded.

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