Simulation of Potential Energy Surface
of 2-Methyl-1,3,2-dioxaborinane and Its Oxonium Ion

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The interest in cyclic esters of boric acids with oxygen heteroatoms, 1,3-dioxa-2-boracycloalkanes, is due to the features of their structure, the complex of useful properties, and also to the growing importance of these compounds for the fine organic synthesis [1–6]. The oxonium ions of 1,3-dioxa-2-heterocycloalkanes are known to serve as intermediates in numerous acid-catalyzed heterolytic reactions leading to the formation of esters, 1,3-diols, 5,6-dihydro-1,3-oxazines and other valuable products of the organic and petrochemical synthesis [7, 8]. Yet under the experimental conditions these intermediates may be detected only at the temperature below –50°C impeding the application of physicochemical methods to the estimation of fine features of their structure. Therefore the study of the structure and conformational behavior of these species by quantum-chemical procedures becomes very urgent [9]. We report here on the investigation of the character of conformational transitions in 2-methyl-1,3,2-dioxaborinane (**I**) and its oxonium ion **II** by Hartree–Fock method in semiempirical (AM1) and also ab initio [STO-3G, 3-21G, 6-31G(d) and 6-31G(d,p)] quantum-chemical approximations in the framework of HyperChem software [10] under the conditions simulating the behavior of these molecules in the gas phase.

The potential energy surface (PES) of 2-substituted 1,3,2-dioxaborinanes is known to contain a minimum [degenerate by energy forms *sofa* (*S*)] and a maximum [2,5-*twist*-form (2,5-*T*)] [4–6]. We established that also for ion **II** degenerate by energy forms *sofa* correspond to the minimum on PES (in AM1 case a distorted *sofa*), and to the maximum, conformation 2,5-*T*.
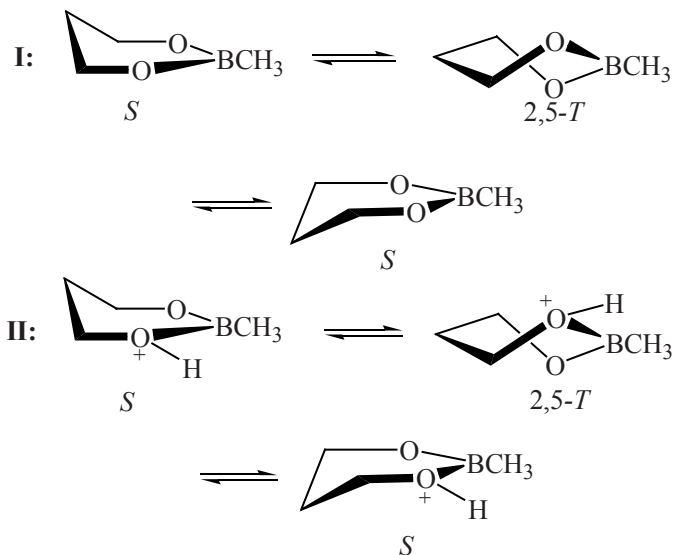
Therewith in contrast to 1,3-dioxane [9] the calculated values of the activation barrier to conformational isomerization of molecules **I** and **II** ($\Delta E^{\neq}$) are sufficiently close (see the table). Besides the values of the maximum for ester **I** calculated applying approximations 3-21G, 6-31G(d), and 6-31G(d,p) are well consistent with the experimental findings for the compounds of this class

Calculated energy parameters for inversion in 2-methyl-1,3,2-dioxaborinane (**I**) and its oxonium ion **II** (kcal mol^{-1})

Calculation methods	$\Delta E^{\neq}$		$-\Delta H_b -$	ΔH_d
	I	**II**		
AM1	3.2	2.4	135.8	139.6
STO-3G	6.5	6.3	256.9	255.5
3-21G	7.9	8.3	212.8	217.4
6-31G(d)	7.5	7.2	201.0	206.1
6-31G(d,p)	7.5	7.3	205.6	210.4

(7–8 kcal mol^{-1}) [11]. Except for the data of STO-3G the calculated heat of protonation of cyclic boric ester (ΔH_b) is smaller than the value for the nonboron analog, 2-methyl-1,3-dioxane, (ΔH_d) corresponding to the minimum on its PES, axial-equatorial form.

This result is in agreement with the experimental data on measurement of the basicity of oxygen atoms in the 1,3,2-dioxaborinane ring that is considerably lower than in 1,3-dioxanes due to the presence of the p-π conjugation along the B–O bond [12].

The results obtained suggest a higher conformational lability of the molecules of six-membered cyclic boric esters and their oxonium ions compared with 1,3-dioxanes mainly because of the absence of additional steric interactions in the heteroatomic fragment of the ring.

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