

SHORT  
COMMUNICATIONS

# Quantum-Chemical Investigation of Conformational Isomerization of the Complex of 1,3,2-Dioxaborinane with a Hydroxyl Anion

O. Yu. Valiakhmetova<sup>a</sup> and V. V. Kuznetsov<sup>a,b</sup>

<sup>a</sup>Ufa State Petrolic Technical University, Ufa, 450075 Russia

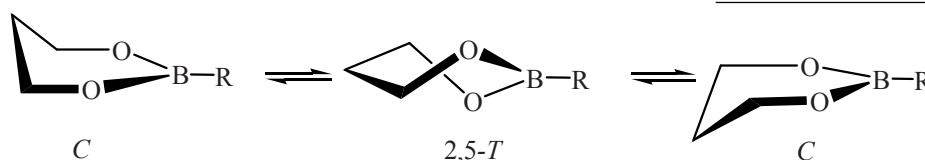
<sup>b</sup>Institute of Physics of Molecules and Crystals, Ufa Scientific Centre, Russian Academy of Sciences  
e-mail: kuz@anrb.ru

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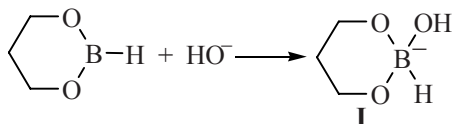
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Cyclic boric acid esters being weak Lewis acids are known to be able to form complexes with electron pair donors. The relative strength of these associates is governed mainly by the basicity of the donor, and the associates are capable of further transformations. In particular, the formation of an adduct with a hydroxyl anion is the first stage of the alkaline hydrolysis of a boric acid ester [1]. Besides the configurational transformation

of the boron atom ( $sp^2 \rightarrow sp^3$ ) caused by the complex formation should affect also the conformational characteristics of the whole cyclic system. The potential energy surface (PES) of unsubstituted or symmetrically substituted 1,3,2-dioxaborinanes with a trigonal boron atom contains two stationary points: sofa conformers degenerate by energy ( $S$ ) and a maximum corresponding to a 2,5-*twist* form (2,5- $T$ ) [2–4].

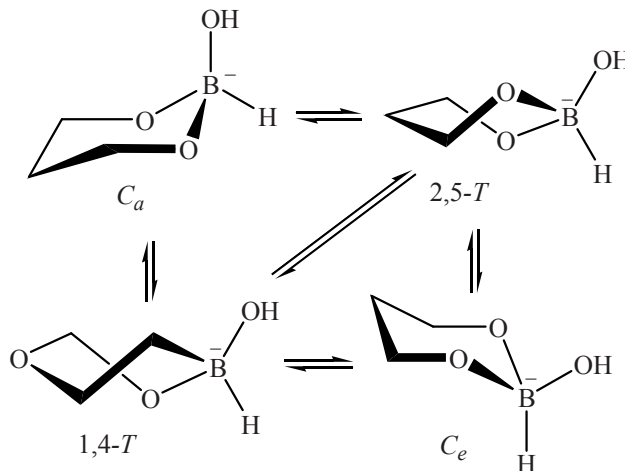


The conformational behavior of six-membered heterocyclic systems containing a tetrahedral boron atom has not been studied up till now. In this connection we report here on the study of conformational isomerization of an adduct of 1,3,2-dioxaborinane with a hydroxyl anion (**I**) performed by nonempirical [RHF/STO-3G, 6-31G(d)  $\theta$  MP2/6-31G(d)//RHF/6-31G(d)] quantum-chemical approximations in the framework of software HyperChem [5] under the conditions simulating the behavior of this substance in the gas phase.



It was established that the change in the configuration of the boron atom resulted in the complication of PES:

For associate **I** four maxima appeared nondegenerate in energy, and several routes of conformational isomerization.

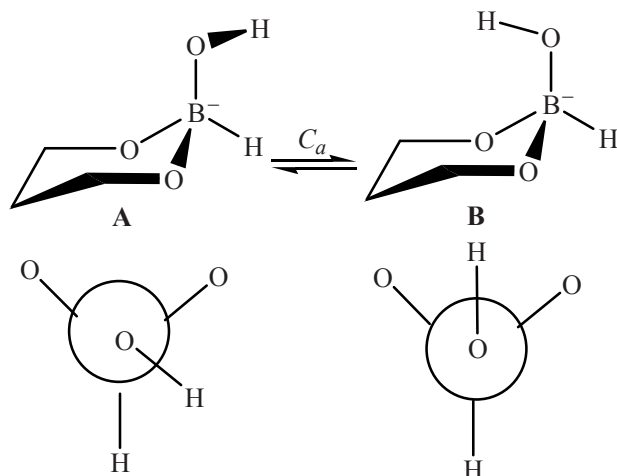


Energy parameters of 1,3,2-dioxaborinane complex with hydroxyl anion (**I**), kcal mol<sup>-1</sup>

Method	Minima				$-\Delta H^a$	$\Delta E_{AB}$	$\Delta E_{AB}^\ddagger$
	$C_a$	$C_e$	2,5- <i>T</i>	1,4- <i>T</i>			
RHF/STO-3G	0	2.2	4.6	3.4	155.5	1.4	2.3
RHF/6-31G(d)	1.2	0	4.6	4.8	77.4	2.9	5.8
MP2/6-31G(d)//RHF/6-31G(d)	1.2	0	4.6	5.0	87.7	2.7	6.4

<sup>a</sup> With respect to the most stable conformer.

It follows from the data in the table that in keeping with the results of STO-3G the main minimum on the PES corresponds to the conformer of the axial *chair* ( $C_a$ ), and in the approximation 6-31G(d), to the equatorial chair ( $C_e$ ). Therewith depending on the orientation of the fragment OH for all minima, in particular, for the form  $C_a$ , two conformers are probable: **A** and **B**.



They are characterized by relatively small energy difference ( $\Delta E_{AB}$ ) in favor of form **A** and by a low potential barrier ( $\Delta E_{AB}^\ddagger$ ). The calculated bond distance B–O (1.440–1.476 E) is comparable with the experimental value  $r_{B-O}$  for the four-valent boron atom (1.44–1.59 E [1]). For conformer  $C_e$  in the 6-31G(d) approximation exists only the form **B**. In agreement with the expectations the calculated enthalpy of formation of the exothermal complex **I**  $-\Delta H$  is fairly large and 2–3 times

larger than the known experimental values for the molecular associates of the acyclic boron compounds [6].

The obtained results show the increase in the conformational rigidity of molecules of six-membered cyclic esters of boric acid at the change of the boron atom configuration from  $sp^2$  to  $sp^3$  caused mainly by the appearance of additional steric interactions with the heteroatomic fragment of the ring. Therewith the conformational behavior of these systems and the stationary points on PES are analogous to those established for the nearest non-boron analogs, 1,3-dioxanes [7, 8].

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