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LETTERS TO THE EDITOR

Comparative Basicity of 1,3,2-Oxazaborinanes and Tetrahydro-1,3-Oxazines

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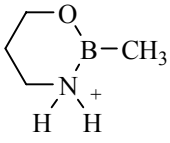
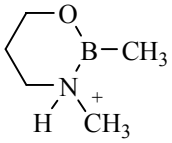
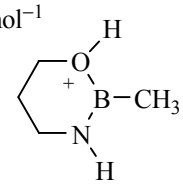
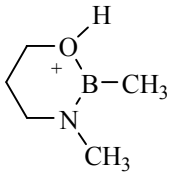
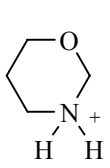
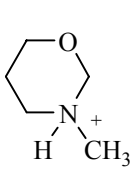
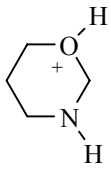
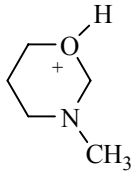
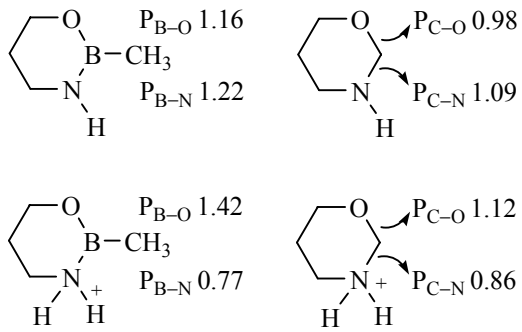
Substituted 1,3,2-oxazaborinanes and their non-boron analogues, tetrahydro-1,3-oxazines, are of interest for stereochemical studies and are used in organic synthesis [1–7]. The first stage of heterolytic reactions of the discussed compounds is known to be the formation of oxonium and ammonium ions [5]. However, the conjugation of *n*-electron pairs of heteroatoms with the vacant orbital of boron atoms in the cyclic molecules of the boron esters decreases their basicity, which was confirmed experimentally by the example of substituted 1,3,2-dioxaborinanes compared with 1,3-dioxanes [8]. If the heteroatoms are different, the redistribution of the electron density in the X–B–Y heteroatomic fragment should increase the basicity of one center at the expense of another. However, such systems remain unexplored so far. The purpose of this paper is to assess the relative basicity of 2-methyl- and 2,3-dimethyl-1,3,2-oxazaborinanes and tetrahydro-1,3-oxazine and its 3-methyl analog by calculating the heat of protonation using *ab initio* HF/6-31G(d) approach within a HyperChem software [9] and PBE/3z DFT-method (PRIRODA package [10]) for the most stable conformers of the studied compounds. The most stable conformers of cyclic boronic esters are the *halfchair* form [2] and in the case of tetrahydro-1,3-oxazines molecules, the *chair* conformers [11].

The protonation of these compounds is found to be an exothermic process ($\Delta H < 0$). The ammonium ions **I**, **II**, **V**, **VI** are more stable than the corresponding oxonium analogs **III**, **IV**, **VII**, **VIII**. This is especially true for the tetrahydro-1,3-oxazines, whose ions **VII**

	$-\Delta H$, kcal mol^{-1}			
				
	I	**II**	**III**	**IV**
HF/6-31G(d) (0 K)	222.5	226.5	209.2	210.3
PBE/3z (298 K)	207.6	210.6	196.2	197.9
				
	V	**VI**	**VII**	**VIII**
HF/6-31G(d) (0 K)	233.2	240.3	205.9	208.5
PBE/3z (298 K)	216.4	222.8	–	–

and **VIII** are not realized within a PBE/3z approach: in the course of geometry optimization they transformed into the acyclic carbocations. Therefore, studying the basicity of the discussed compounds it is advisable to compare the ΔH values only for ammonium ions.

These calculations show that the ions **I** and **II** are characterized by ΔH values reduced by 10–14 kcal mol^{-1} compared with the same type substituted ions of tetrahydro-1,3-oxazines. On the other hand, the dynamics of the change in the bond orders in the heteroatomic ring fragment (PBE/3z data) shows that the electron density redistribution in the protonated molecule of boron ester is more significant. This may be due only to removal of the nitrogen *n*-electron pair from the *p*–π-conjugation with the vacant orbital of boron atom at the protonation.



As expected, the presence of methyl moiety at the nitrogen atom increases its basicity compared to the unsubstituted analogs of boron ester [ion **II**] and tetrahydro-1,3-oxazine [ion **VI**].

The results confirm the reduced basicity of 1,3,2-oxazaborinanes compared with tetrahydro-1,3-oxazine. However, in an acidic medium these compounds should be easily subjected to protonation to form the ions of two types, therewith the calculations suggest that the oxonium ions of non-boron analogs are unstable.

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