Chemistry of Heterocyclic Compounds, Vol. 45, No. 7, 2009

THEORETICAL ESTIMATION OF THE ENTHALPY OF FORMATION OF COMPLEXES OF CYCLIC ESTERS OF METHYLBORIC ACID WITH THE HYDROXYL ANION

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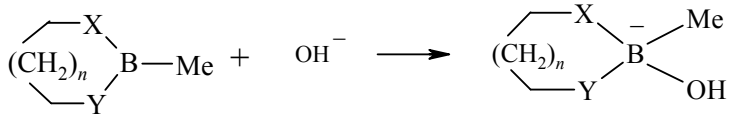
Keywords: 1,3-dihetero-2-methyl-2-boracycloalkane, quantum chemistry, enthalpy of formation.

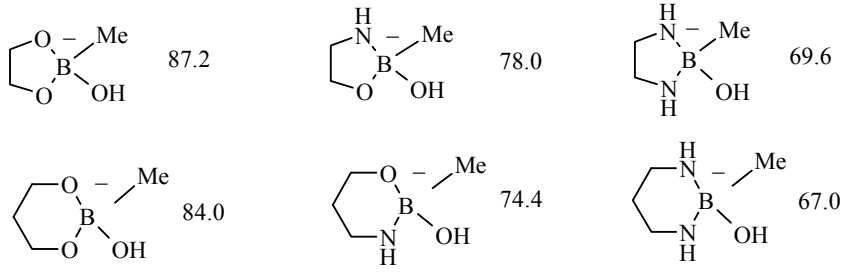
The capacity of cyclic esters of boric acids to form complexes both with electron pair donors and acceptors makes these compounds convenient objects for computer modeling of the mechanisms of interaction a boron-containing substrate with various solvents. In the present work, the enthalpy of formation of complexes of five- and six-membered cyclic esters of methylboric acid with the hydroxyl anion was studied for the first time using the MP2//6-31G(d) method in the framework of the HyperChem program package [1].



X, Y = O, NH; n = 0, 1

According to the calculation data, all the compounds are exothermal ($\Delta H < 0$).

$-\Delta H$, kcal/mol



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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1105-1106, July, 2009. Original article submitted December 24, 2008.

The ΔH values are two or three times greater than the experimental data for $R_3B{\cdot}XR^1_n$ molecular associates (X = O, N, P, S [2]). The formation of these adducts involves a configurational rearrangement of the boron and nitrogen heteroatoms from planar to tetrahedral. Conformational changes related to different orientation of the hydrogen atoms at the nitrogen atom (pseudoaxial or pseudoequatorial) are possible in the associated species itself. However, the differences in energies caused by these changes do not exceed 0.5 kcal/mol and, thus, are not important for estimating the values of ΔH. The calculated B–O bond length from 1.453 to 1.507 *E* is greatest for the 1,3,2-diazaborinane adduct and corresponds to the reported experimental data for compounds of tetravalent boron [3].

Our results show that the consecutive replacement of the oxygen heteroatoms by nitrogen leads to a decrease in ΔH values. The same effect is observed in going from five-membered analogs to six-membered analogs. Thus, in the framework of the calculation approximation, the cyclic esters of diols are stronger Lewis acids than esters of amino alcohols and diamines, while the acidity of the six-membered derivatives is weaker than of the five-membered derivatives. This conclusion was supported experimentally by quantitative evaluation of the strain energy of organoboron heterocycles relative to extent of intermolecular association [4, 5] and thermodynamically [6].

The formation of $[B–(R)OH]^-$ adducts is the first step in the hydrolysis of cyclic boric acid esters [3]. Therefore, this approach opens additional possibilities for evaluating the relative stability and chemical transformations of these compounds.

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