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LETTERS TO THE EDITOR

Conformational Behavior of 2-Methyl-1,3,2-oxathiaborinane Oxonium and Sulfonium Ions

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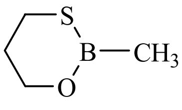
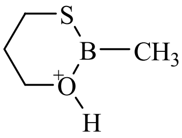
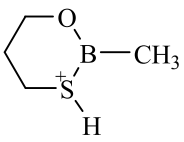
The protonation of the saturated 1,3- and 1,3,2-heterocyclic compounds is known to be the initial stage of the ring opening in a variety of heterolytic reactions [1, 2]. A study of the conformational mobility of the formed ions indicates that their parameters differ significantly from those of the electrically neutral compounds [3, 4]. In this communication we report on the study of the effect of protonation of 2-methyl-1,3,2-oxathiaborinane **I** at the oxygen or sulfur atoms (associates **II**–**IV** respectively) on the conformational properties of the adducts using an *ab initio* quantum-chemical classical approximation HF/6-31G (d) and PBE/3z within a HyperChem [5] and Nature [6] packages. Analogs of these compounds have been described [7].


I


II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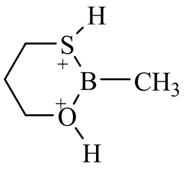
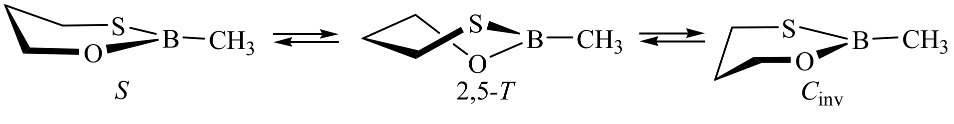

IV

The calculations indicated the formation of barrier-free exothermic associates. The energy of sulfonium ion formation is slightly higher than that of oxonium: $\Delta E_{\mathrm{III}} = -199.5$ kcal mol^{-1}, $\Delta E_{\mathrm{IV}} = -286.2$ kcal mol^{-1} [HF/6-31G(d)].

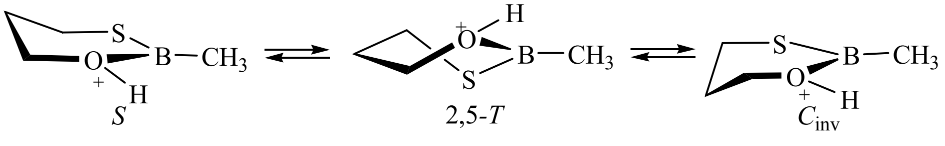
The results of the computer modeling of molecules **I** and **II**–**IV** show that they are in the equilibrium between conformers *sofa* (*S*), *semi-chair* (*HC*) or *chair* (*C*). In addition, for compounds **I** and **II** the forms corresponding to the minimum are energetically de-

I:



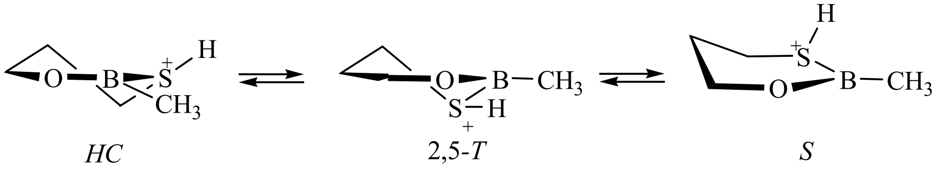
(0 K) $\Delta E^{\neq}$ 7.5 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 6.5 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 6.8 kcal mol^{-1} (PBE/3z)

II:



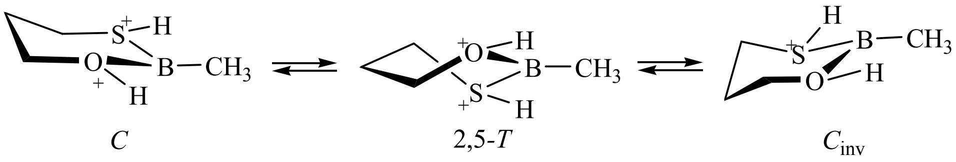
(0 K) $\Delta E^{\neq}$ 6.7 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 5.4 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 5.2 kcal mol^{-1} (PBE/3z)

III



(0 K)
$\Delta E^{\neq}$ 4.9 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 4.5 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 5.2 kcal mol^{-1} (PBE/3z)

IV:



(0 K)
$\Delta E^{\neq}$ 5.8 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 5.4 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 5.9 kcal mol^{-1} (PBE/3z)

generate, while in other cases there is a difference in the energy of 0.3–0.7 kcal mol^{-1} in favor of *sofa* and *chair* (C_{inv}) forms. The height of the interconversion potential barrier ($\Delta E^{\neq}$ at 0 K and $\Delta G^{\neq}$ at 298 K) in all cases is lower than that of the ester **I**. It depends significantly on the nature of the complex and is minimal for the adduct **III**.

Thus, the protonation of 1,3,2-oxathiaborinane molecule has a significant influence on the conformational behavior of the cyclic boric ether and decreases the transition state energy as in the case of 1,3,2-dioxa- [3] and oxazaborinanes [4].

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