ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 3, pp. 609–610. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.V. Kuznetsov, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 3, pp. 514–515.

LETTERS TO THE EDITOR

Conformational Behaviour of 2-Methyl-1,3,2-diazaborinane Ammonium Ions

V. V. Kuznetsov[a,b]

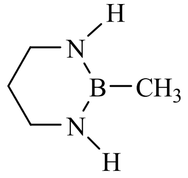
[a] *Institute of Physics of Molecules and Crystals, Ufa Scientific Centre, Russian Academy of Sciences,*
pr. Octyabrya 71, Ufa, 450054 Russia

[b] *Ufa State Petroleum Technological University, ul. Kosmonavtov 1, Ufa, 450062, Russia*
e-mail: kuz@anrb.ru

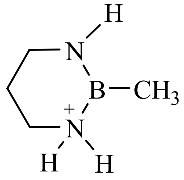
Received October 7, 2010

DOI: 10.1134/S1070363211030303

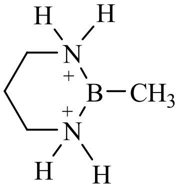
1,3,2-Diazaborinanes are known as important representatives of the boron-nitrogen-containing heterocycles possessing valuable pharmacological properties (potential anticancer drugs, antiseptics, and fungicides), and are convenient model compounds for the study of heteroatoms effect on the conformation and configuration characteristics of cyclohexane heteroanalogs [1, 2]. It was shown previously that the protonation of the oxygen and nitrogen heteroatoms in 1,3,2-dioxa- [3] and oxazaborinane [4] molecules affects to some extent the parameters of the conformational isomerization. In addition, the protonation is the initial stage of the reactions proceeding with the heterocycle ring opening [5]. In this paper we investigated the effect of 2-methyl-1,3,2-diazaborinane **I** protonation at the nitrogen atoms (associates **II** and **III**, respectively) on the conformational properties of the associates using quantum-chemical calculations in the non-empirical approximations HF/6-31G(d) and PBE/3z within HyperChem [6] and Nature [7] software.



I



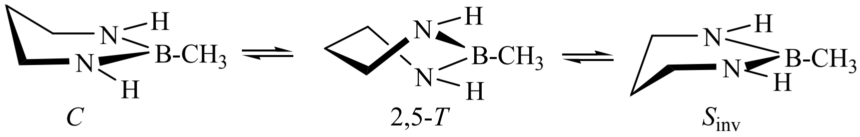
II



III

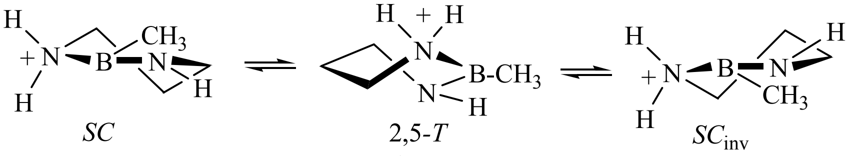
The calculations revealed that the exothermic formation of complexes **II** and **III** is barrier-free. As expected, in this case the energy of associate **II** is higher than a half of ΔE value for adduct **III**: $\Delta E_{\mathbf{II}}$ = –234 kcal mol^{-1}; $\Delta E_{\mathbf{III}}$ = –35 kcal mol^{-1} [HF/6-31G(d)].

I:



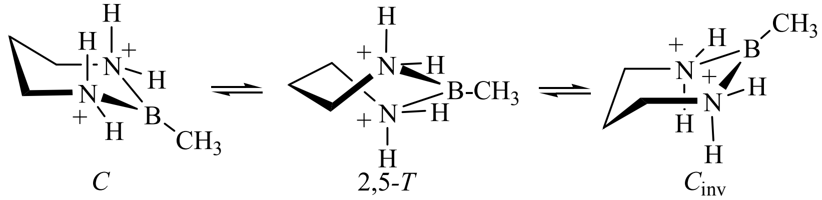
(0 K) $\Delta E^{\neq}$ 8.1 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 7.0 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 7.7 kcal mol^{-1} (PBE/3z)

II:



(0 K) $\Delta E^{\neq}$ 5.6 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 4.8 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 5.1 kcal mol^{-1} (PBE/3z)

III:



(0 K) $\Delta E^{\neq}$ 4.7 kcal mol^{-1} [HF/6-31G(d)]
$\Delta E^{\neq}$ 4.6 kcal mol^{-1}, $\Delta G^{\neq}_{298}$ 5.0 kcal mol^{-1} (PBE/3z)

It was shown formerly by the examples of 1,3,2-dioxa- and oxazaborinanes [3, 4] that the potential energy surface of cyclic boric ethers contains minima degenerate by energy corresponding to the *sofa* (*S* and S_{inv}) or *semi-chair* (*SC* and SC_{inv}) conformers, respectively, suffering invertion into each other through the 2,5-*twist* (2,5-*T*) transition state. The results of computer modeling of compound **I** and associates **II** and **III** also indicate that there is an equilibrium between the degenerate by energy conformers *sofa* **I** and *semi-chair* **II** or *chair* **III**. The values of the potential barrier for the interconversion ($\Delta E^{\neq}$ at 0 K and $\Delta G^{\neq}$ at 298 K) depend essentially on the nature of the complex: they are minimal for adduct **III** and maximal for compound **I**.

Thus, the protonation of the 1,3,2-diazaborinane molecule affects the conformational behavior of the 1,3,2-diazaborinanes and, as in the case of 1,3,2-dioxa- [3] and oxazaborinanes [4], lowers the transition state energy.

REFERENCES

1. Nidentsu, K. and Dawson, J., *Chemistry of Boron-Nitrogen Compounds*, Moscow: Mir, 1968.
2. Seip, R. and Seip, H.M., *J. Mol. Struct.,* 1975, vol. 28, p. 441.
3. Valiakhmetova, O.Yu. and Kuznetsov, V.V., *Zh. Obshch. Khim.,* 2008, vol. 78, no. 12, p. 2007.
4. Kuznetsov, V.V., *Zh. Obshch. Khim.,* 2010, vol. 80, no. 8, p. 1405.
5. Kuznetsov, V.V., *Izv. Akad. Nauk, Ser. Khim.,* 2005, no. 7, p. 1499.
6. *HyperChem 7.01. Trial version. www.hyper.com*.
7. Laikov, D.N., Ustynyuk, Yu.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2005, no. 3, p. 804.