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THEORETICAL BARRIERS TO THE INTERNAL ROTATION OF A NITRO GROUP IN 2-METHYL-5-NITRO-1,3,2-DIOXABORINANE

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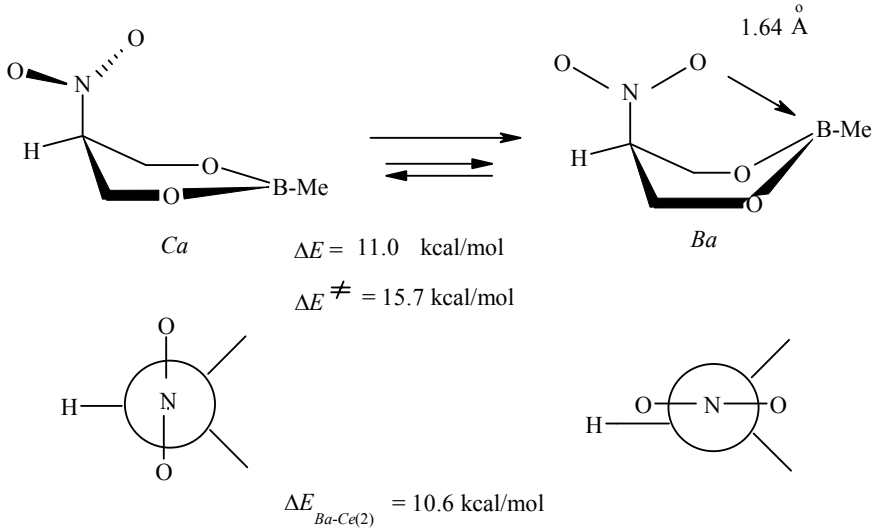
Interest in 1,3,2-dioxaborinane, linked with the special features of the structure, chemical behavior, and a complex of practically useful properties [1], makes the study of the potential energy surface (PES) of molecules of these compounds by computer modeling methods urgent [2, 3]. It was shown previously that molecules of 5-nitro-1,3,2-dioxaborinanes continue in the preferred conformation with an axial nitro group [2-5]. In the present work the barriers to internal rotation of the nitro group in axial and equatorial conformers of the molecule of 2-methyl-5-nitro-1,3,2-dioxaborinane have been investigated for the first time. This was carried out within the framework of the HyperChem package [6] by the RHF//STO-3G method.

The data obtained indicate the existence of two rotamers for both the axial and the equatorial conformers. In the case of the axial form the rotamer *Ba* is the most stable form to all appearances, stabilized by an intracoordinate O→B bond, the experimental size of which for tetraalkoxyboranes is 1.44-1.59 Å [1]. The



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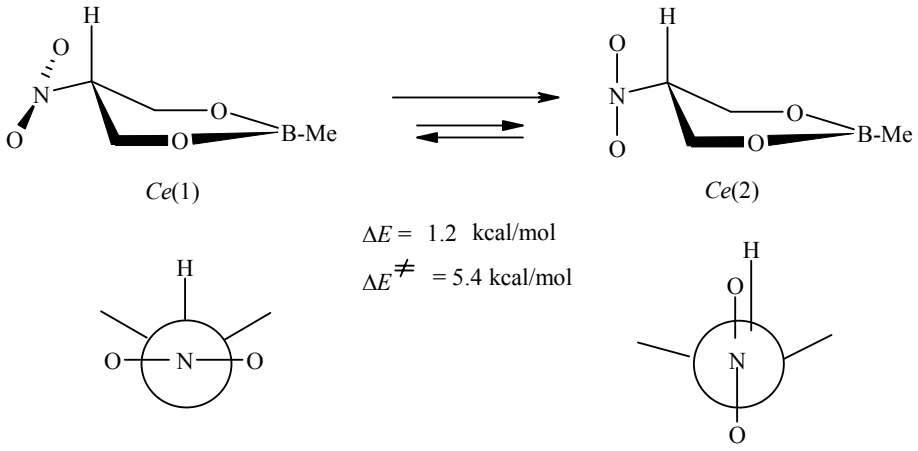

conformational equilibrium between the *Ca* and *Ba* forms is characterized by relative high values of ΔE and $\Delta E^{\neq}$. The most stable rotamer of the equatorial conformer *Ce*(2) is characterized by a "bissectral" orientation of the nitro group, which is stabilized by the "orthogonal" orientation of *Ce*(1). The *Ba* rotamer is therefore more than 10 kcal/mol more stable than the *Ce*(2) form. The results of the calculations therefore confirm the preferred existence of conformer *Ba*, the geometry of which is close to that observed, according to X-ray structural analysis data for the molecule of the cyclic phenylboron ester of bis(hydroxyalkyl)nitrone [7].

REFERENCES

1. A. I. Gren' and V. V. Kuznetsov, *Chemistry of Cyclic Esters of Boric Acids* [in Russian], Naukova Dumka, Kiev (1988), 160 pp.
2. V. V. Kuznetsov, O. Yu. Valiakhmetova, and S. A. Bochkor, *Khim. Geterotsikl. Soedin.*, 1860 (2007). [*Chem. Heterocycl. Comp.*, **43**, 1577 (2007)].
3. V. V. Kuznetsov and S. A. Bochkor, *Khim. Geterotsikl. Soedin.*, 1065 (1999). [*Chem. Heterocycl. Comp.*, **35**, 935 (1999)].
4. V. V. Kuznetsov, K. S. Zakharov, I. V. Petrovskii, and A. I. Gren', *Khim. Geterotsikl. Soedin.*, 1107 (1990). [*Chem. Heterocycl. Comp.*, **26**, 927 (1990)].
5. W. Kliegel, L. Preu, S. J. Rettig, and J. Trotter, *Can. J. Chem.*, **64**, 1855 (1986).
6. HyperChem 7.01. Trial Version. www.hyper.com.
7. W. Kliegel, L. Preu, S. J. Rettig, and J. Trotter, *Can. J. Chem.*, **63**, 509 (1985).