CONFIGURATIONAL AND CONFORMATIONAL PROPERTIES OF THE COMPLEX OF 2,5-DIMETHYL-1,3,2-DIOXABORINANE WITH HYDROXYL ANION

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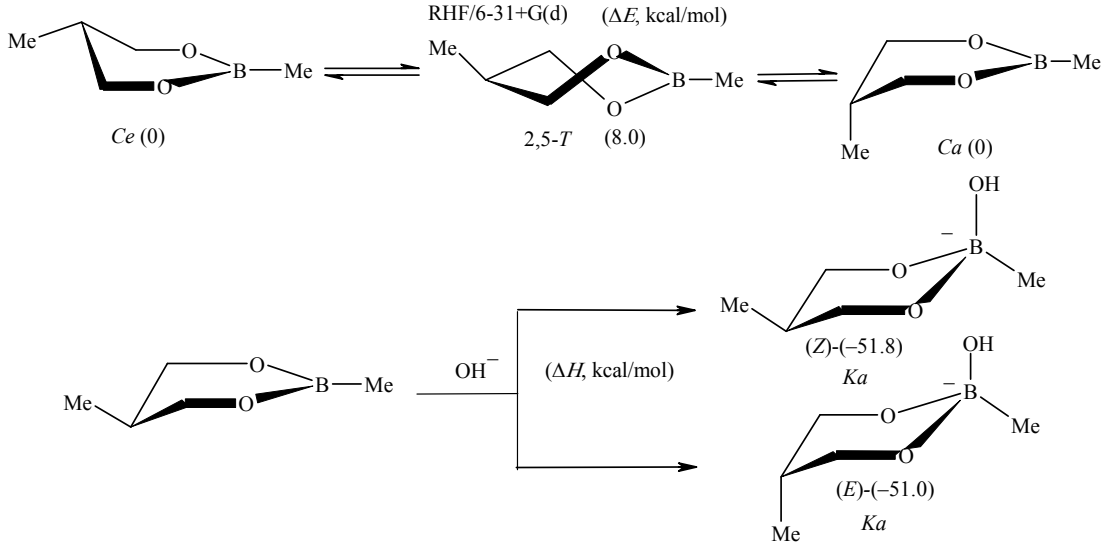
The ability of cyclic boron acid esters to form associates both with donors and acceptors of an electron pair makes these compounds suitable subjects for computer modelling of the mechanism of interaction of boron-containing substrates with various solvents, in particular with oxygen-containing bases [1-4]. Using the RHF/6-31+G(d) method within the terms of the HyperChem program suite [5] we have, for the first time, studied the stereochemical features of the complex of 2,5-dimethyl-1,3,2-dioxaborinane with the hydroxyl anion.

The potential energy surface of the starting boron ester contains minima, *viz*. the equatorial and axial *sofa* conformers (*Ce* and *Ca*) and the 2,5-twist form (2,5-*T*) transition state [6].



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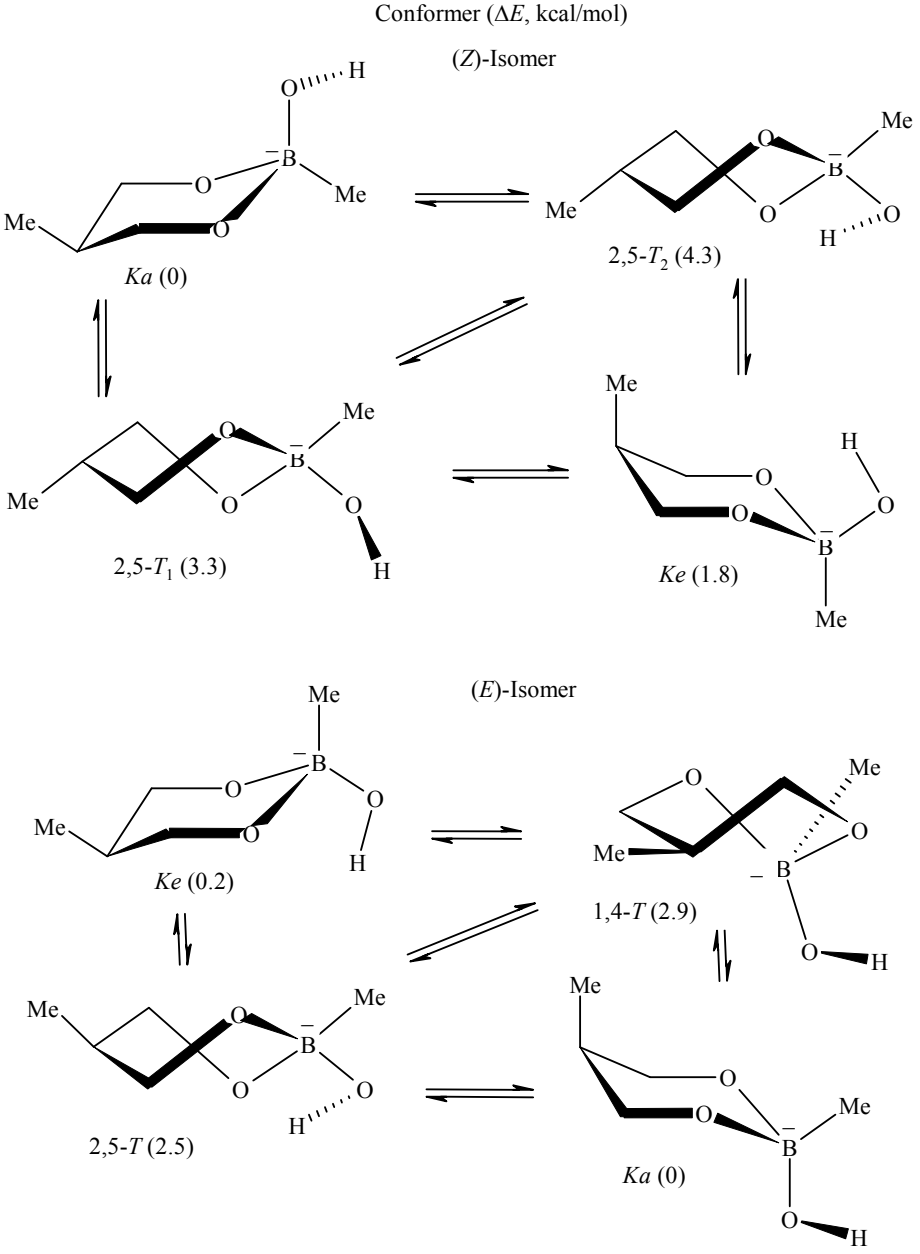
The formation of exothermic complexes with the hydroxyl anion leads to configurational restructuring of the boron atom. The principal conformation of the cyclic ester with an sp^3 boron atom changes from a *sofa* to a *chair* forming (*Z*)- and (*E*)-isomers. Moreover the number of minima on the potential energy surface in the associates formed is markedly increased due to the appearance of the flexible 1,4-*T* and 2,5-*T* conformers. The most stable (*Z*)-isomer form (*Ka* with an axial hydroxyl group) is more stable by 0.8 kcal/mol than the most stable of the (*E*)-isomer conformers (*Ka*).



The 2,5-T_1 and 2,5-T_2 conformers of the (*Z*)-isomer differ in the orientation of the hydroxyl group relative to the heterocyclic ring. The results obtained confirm the similarity of the associates studied with the closest non-boron analogs (the substituted 1,3-dioxanes [7]) and open up additional possibilities for a detailed study of the stereochemistry of cyclic boron esters with a tetrahedral boron atom.

REFERENCES

1. V. V. Kuznetsov, O. Yu. Valiakhmetova, and S. A. Bochkor, *Khim. Geterotsikl. Soedin.*, 1260 (2009). [*Chem. Heterocycl. Comp.*, **45**, 1004 (2009)].
2. O. Yu. Valiakhmetova, S. A. Bochkor, and V. V. Kuznetsov, *Zh. Org. Khim.*, **45**, 796 (2009).
3. V. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, 1105 (2009). [*Chem. Heterocycl. Comp.*, **45**, 886 (2009)].
4. O. Yu. Valiakhmetova and V. V. Kuznetsov, *Zh. Org. Khim.*, **45**, 1268 (2009)].
5. HyperChem 7.01. Trial version. www.hyper.com
6. V. V. Kuznetsov, A. N. Novikov, I. S. Rublev, and P. Yu. Markolenko, *Khim. Geterotsikl. Soedin.*, 426 (2003). [*Chem. Heterocycl. Comp.*, **39**, 379 (2003)].
7. M. G. Faizullin, A. E. Kuramshina, A. Kh. Mamleev, and V. V. Kuznetsov, *Zh. Obshch. Khim.*, **79**, 2046 (2009).