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ROUTES OF CONFORMATIONAL ISOMERIZATION OF 4-SUBSTITUTED 1,3,2-DIOXABORINANES

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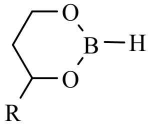
With the help of nonempirical quantum-chemical approximations we have studied the conformational equilibria in a series of 4-substituted 1,3,2-dioxaborinanes. It is shown that the route includes minima corresponding to the equatorial and axial sofa forms, and maxima corresponding to the equatorial and axial 2,5-twist conformations.

Keywords: 1,3,2-dioxaborinane, cyclic boron esters, conformer, quantum chemistry, conformational equilibria, potential energy surface.

Molecules of six-membered cyclic boron esters – 1,3,2-dioxaborinanes – contain an electron-deficient boron atom and electron-donor oxygen heteroatoms. Therefore the conformational properties of these compounds is determined not only by steric effects but also electronic effects of the substituents, and also the *p*-π conjugation with the heteroatom fragment of the ring. The position and character of the substituent groups have an effect which is not small [1-7]. We observed recently that for 4-substituted 1,3,2-dioxaborinanes inversion of the ring is possible through two energy nondegenerate transition states [8]. The present work is connected with the study of the path of conformational isomerization of model 4-R-1,3,2-dioxaborinanes **1-7** using nonempirical (RHF//STO-3G and 3-21G) methods within *HyperChem* suite of programs [9].



1–7

1 R = Me, **2** R = *i*-Pr, **3** R = *t*-Bu, **4** R = C_5H_{11}, **5** R = Ph, **6** R = $CH=CH_2$, **7** R = $C\equiv CH$

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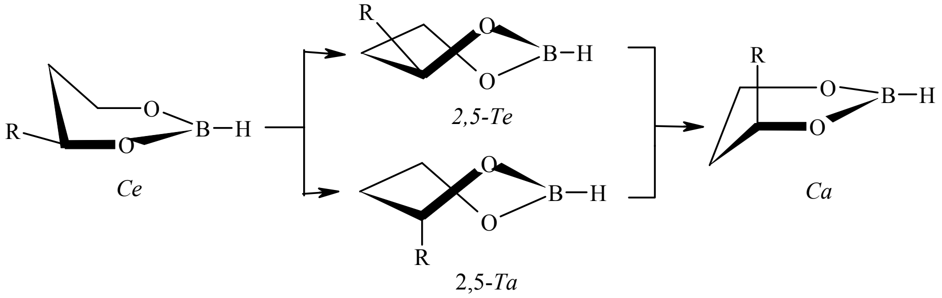
It is known [1,2,10,11] that the principal minimum on the potential energy surfaces (PES) of esters **1** and **4** is the equatorial *sofa* conformer (*Ce).* We observed that the conformational isomerization between the minima *Ce* and *Ca* (axial *sofa* conformer) may occur via two routes, including two transition states, 2,5-*Te* (equatorial conformer of the *twist* form) and 2,5-*Ta* (axial conformer of the *twist* form).



The data obtained (Table 1) indicate the energetic preference of the *Ce* forms for esters **1-6**. The relative advantage of the equatorial orientation of the substituent (ΔE) within the approximate calculations used is based on the volume of the substituents and in the majority of cases is found in the range from 0.5 (ester **6**) to 3.8 kcal/mol (ester **3**). Only the very small value of ΔE for the phenyl substituent in ester **5** (0.1 kcal/mol, *RHF//3-21G*) is excluded. It should be noted that the values obtained are considerably smaller then the calculated and experimental values for the conformational energies of substituents in their nonboron analogs – 4R-1,3-dioxanes [12-14]. This is in excellent agreement with the planar configuration of the trigonal boron atom and the decreased number of nonbonding interactions in the ring [1, 2]. The difference in energy between the transition states 2,5-*Te* and 2,5-*Ta* ($\Delta\Delta E^{\neq}$) depending on the method of calculation and the character of the substituent R varies from 0.1 to 2.0 kcal/mol. As would be expected, $\Delta\Delta E^{\neq}$ increases with the conformational size of the alkyl substituent (esters **1-4**). The methyl and pentyl groups (the conformation of the latter is treated as an undistorted fragment of hydrocarbon chain) are similar enough to one another. The decrease in the conformational volume of R as a result of the appearance of a double bond (ester **6**) also decreases the values of ΔE and $\Delta\Delta E^{\neq}$. In the case of 4-ethynyl-1,3,2-dioxaborinane (**7**) the axial orientation of the substituent R is preferable. The advantage in energy between *Ce* and *Ca* in this case is 2.1 kcal/mol in favor of the latter (3-21*G*). For the maxima the form 2,5-*Ta* is also more stable than 2,5-*Te*. However in all cases the character of the substituent R influences the calculated height of the potential barrier ($\Delta E^{\neq}$) relatively weakly which is in good agreement with the experimental data [15-17].

Table 1. Energetic Characteristics of the Conformational Equilibria of Esters **1-7** (kcal/mol).

Compound	Method	ΔE	$\Delta\Delta E$	$\Delta E^{\neq}$	Compound	Method	ΔE*	$\Delta\Delta E^{\neq}$*	$\Delta E^{\neq}$
1	STO-3G	0.9	0.4	7.0-8.0	**5**	STO-3G	1.0	1.0	7.2-8.2
	3-21G	0.6	0.1	8.3-8.4		3-21G	0.1	1.3	8.6-9.9
2	STO-3G	1.3	1.0	7.0-8.0	**6**	STO-3G	0.7	0.2	7.1-7.3
	3-21G	1.0	1.3	8.1-9.4		3-21G	0.5	0.3	8.5-8.8
3	STO-3G	3.5	1.1	6.9-8.0	**7**	STO-3G	-0.3	0	7.4
	3-21G	3.8	2.0	8.0-10.0		3-21G	-2.1	-1.4	9.1-10.4
4	STO-3G	1.0	0.6	6.9-7.5					
	3-21G	0.7	0.4	8.2-8.6					

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* Negative values indicate the more stable forms of *Ca* or 2,5-*Ta*.

Thus a detailed analysis of the conformational conversions of 4-substituted 1,3,2-dioxaborinanes indicates two different routes for the transition *Ce* ↔ *Ca*; their relative contributions are determined by the steric and electronic characteristics of the substituents at the atom C-4 of the heterocyclic ring.

EXPERIMENTAL

The route for inversion and the size of the barriers for interconversion were established by the "transition state" procedure within the *HyperChem* [9] program. Fixing the stationary points of the potential energy at the maxima (forms 2,5-*Te* and 2,5-*Ta*) confirmed the presence of a single negative frequency in the corresponding Hessian matrix. Using the calculated method to analyze the structural and energetic characteristics of cyclic boron esters similar to those reported elsewhere [18, 19].

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