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NONEMPIRICAL STUDY OF 2-METHYL-1,3,2-DIOXABORINANE–METHANOL COMPLEXES

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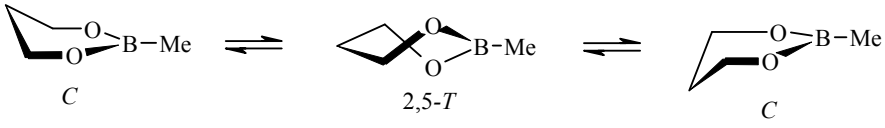
Computer modeling with the RHF/STO-3G, 3-21G, and 6-31G(d) nonempirical quantum-chemical approximations was used to study the properties of 1:1 molecular complexes of 2-methyl-1,3,2-dioxaborinane and methanol. Complexes are formed both with an O→B donor-acceptor bond and an OH···O intermolecular hydrogen bond. The relative stability and conformational behavior of these complexes are a function not only of the orientation of the molecules in this complex but also the assumptions of the calculation method used.

Keywords: 1,3,2-dioxaborinane, conformer, methanol, molecular complex, quantum chemistry, coordination bond, hydrogen bond, potential energy surface.

A current problem in conformational analysis concerns the correct consideration and prediction of the effect of solvent on the parameters of the conformational equilibrium in solution [1]. Cyclic esters of boric acids hold considerable interest in this study. These compounds contain and electron-deficient boron atom and electron-donor oxygen atoms. This combination of properties permits various types of associated species of these compounds with solvents due to the formation of molecular complexes with both electron pair acceptors and donors [2]. This opens broad possibilities for computer modeling of the mechanisms for the interaction of the borate esters with different types of solvents.

In previous work [3-5], we used semiempirical calculations to establish the possible existence of complexes of substituted 1,3,2-dioxaborinanes with water. The present work is devoted to computer modeling of the potential energy surface of 2-methyl-1,3,2-dioxaborinane (**1**) in the presence of methanol molecules using the nonempirical RHF/STO-3G, 3-21G, and 6-31G(d) approximations in the HyperChem program package [6].



C 2,5-*T* *C*

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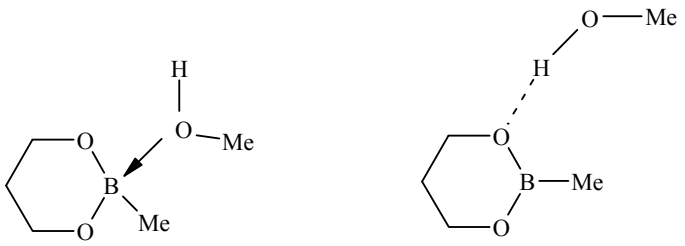
Molecules of 2-alkyl-1,3,2-dioxaborinanes at room temperature exist with ring inversion, which is rapid on the NMR time scale. This inversion has a relatively low barrier [7-10], while the potential energy surface of compound **1** contains minima (degenerate relative to the energy of the *sofa* conformers, *S*) and a transition state corresponding to a 2,5-*twist* form (2,5-*T*) [11].

We discovered that only the two most stable complexes **A** and **B** exist for the 1:1 complex of ester **1** and methanol among a multitude of various binary structures. Structure **A** has an O→B coordination bond and structure **B** has an intermolecular MeO–H···O hydrogen bond.



A **B**

Complex **A** may exist as two rotamers defined by the relative orientation of the methanol molecule and heterocyclic ring (**A_1** and **A_2**).

The nature of the conformational isomerization of the complexes hardly differs from that for ester **1** and involves interconversion between two conformers. On the other hand, the properties of the adducts studied are a function not only of the mutual orientation of the donor and acceptor molecules but also of the assumptions in the calculation basis.

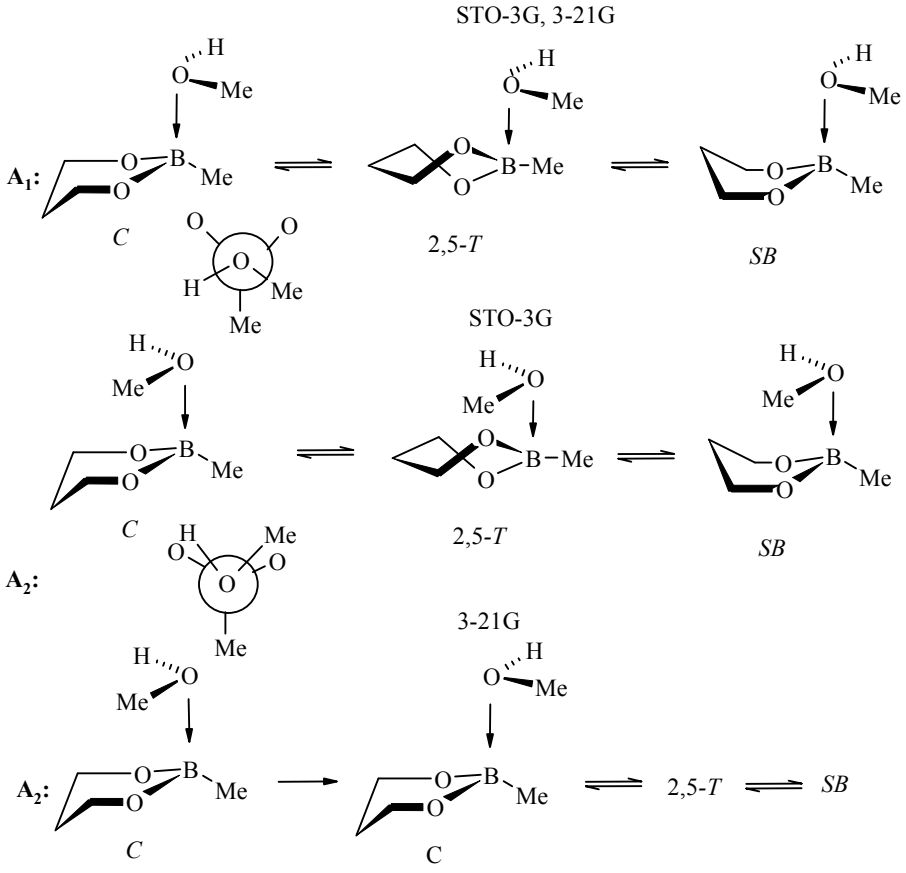
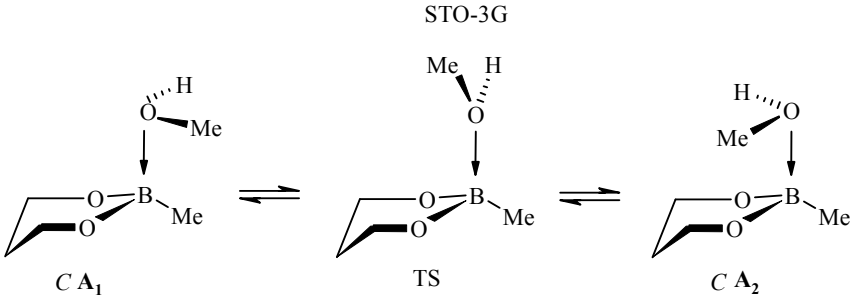


TABLE 1. Calculated Structural (Å) and Energy Parameters (kcal/mol) of Complexes **A₁**, **A₂** and **B**

Complex	Parameters	Calculated basis (method RHF)		
		STO-3G	3-21G	6-31G(d)
1	$\Delta E^{\neq}$ [11]	6.5	7.9	7.5
A₁	ΔE*	1.4	0.6	—
	$\Delta E^{\neq}$*	5.2	6.0	—
	$\Delta E^{\neq}_{O\rightarrow B}$*	2.1	-10.4	—
	$-\Delta H$	7.5	2.05-2.30 (1.78)	—
	$r_{O\rightarrow B}$ (TS)	1.80-1.83 (1.75)		—
A₂	ΔE*	1.1	—	—
	$\Delta E^{\neq}$*	4.2	—	—
	$-\Delta H$	5.3	—	—
	$r_{O\rightarrow B}$ (TS)	1.82-1.84 (1.73)		
B	$\Delta E^{\neq}$	6.5	7.6	7.6
	$-\Delta H$	5.1	10.1	5.0
	$r_{OH\cdot O}$ (TS)	1.75 (1.75)	1.86 (1.84)	2.03-2.04 (2.03)

Complex **A₁** features an equilibrium state between two nondegenerate minima ($\Delta E \neq 0$). In the STO-3G and 3-21G approximations, these minima correspond to a compressed *chair* (*C*) and *symmetrical boat* (*SB*), where the *C* form is the major minimum and the only transition state corresponds to the 2,5-*T* conformation. We should note that the potential barrier for the interconversion ($\Delta E^{\neq}$) of complex **A₁** is much lower than for ester **1** and this complex is 2.2 kcal/mol more stable than complex **A₂** according to the calculated energy of formation (ΔH) in the STO-3G approximation (Table 1).

The potential energy surface of complex **A₂** in the STO-3G approximation contains two minima differing in energy: compressed *C* and *SB* conformers separated by a potential barrier corresponding to the 2,5-*T* conformation. In this case, $\Delta E^{\neq}$ is also lower than the value calculated for ester **1**. The transition state (TS) between the *chair* forms relating to the major minima on the potential energy surface of adducts **A₁** and **A₂** ($\Delta E^{\neq}_{O\rightarrow B}$) corresponds to a *chair* conformation with orthogonal orientation of the methanol molecule.

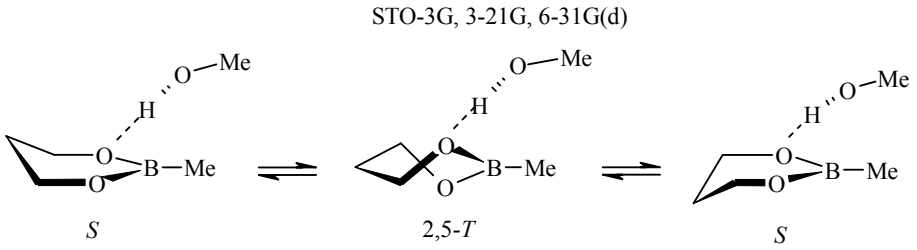


Complex **A₂** could not be located in the 3-21G approximation. In the minimization procedure, this complex irreversibly converts to the *C* conformer of complex **A₁**, which then reversibly isomerizes to the *SB* form through the 2,5-*T* transition state. The length of the O→B coordination bond in the transition state is slightly shorter than in the ground state and, regardless of the calculation basis employed, exceeds the experimental value $r_{O\rightarrow B}$ in the relatively most stable $Me_2O{\cdot}BF_3$ complex (1.75 Å [12, 13]).

Adducts **A₁** and **A₂** are not found using the 6-31G(d) basis. Optimization of the initial structure is accompanied by irreversible transformation to complex **B**. The potential energy surface of complex **B** contains two *sofa* invertomers almost degenerate relative to energy and a transition state corresponding to the 2,5-*T* form.

The intermolecular hydrogen bond is retained during the conformational transformations regardless of the calculation basis employed and has virtually the same length in the ground and transition states. The value

for $r_{OH\cdots O}$ obtained with the calculation approximations is shorter than the experimental length of the water hydrogen bond (2.74-2.77 Å [14]). The potential barrier for interconversion is virtually the same as for the isolated molecule of ester **1**.



Thus, expansion of the basis set used leads to a lowering of the relative stability of complexes $\mathbf{A_1}$ and $\mathbf{A_2}$ relative to complex **B**. The energy of the hydrogen bond in complex **B** calculated in the STO-3G and 6-31G(d) approximations is in good accord with the experimental value of $-\Delta H$ for water (4.8-6.0 kcal/mol [14]).

These results indicate a marked effect of the complexation on the potential energy surface of ester **1**. These species are considered weak complexes. Nevertheless, we may assume that the presence of several methanol molecules leads to the formation of a specific solvation shell about the borate ester molecule due to formation of both types of complexes.

EXPERIMENTAL

The conformational isomerization was carried out by optimization of the molecular geometry of the complexes upon varying the intracyclic OCCC torsion angle within a range of ±50°. The interconversion pathway and potential barriers were found using the transition state search procedure in the HyperChem program package [6]. The relationship of the stationary points of the potential energy surface to transition states was indicated by the existence of one imaginary frequency in the Hesse matrix.

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