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# Conformational Analysis of 2-Methyl-1,3,2-dioxaborinane in the Presence of an Ammonia Molecule

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**Abstract**—Nonempirical quantum chemical methods RHF//STO-3G, 3-21G and 6-31G(d) were used for the investigation of the conformational properties of molecular complexes of 2-methyl-1,3,2-dioxaborinane with ammonia (1:1). Two types of possible associates are revealed: with donor-acceptor N→B bond and with intermolecular NH···O hydrogen bond. Their calculated relative stability and conformational behavior are determined not only by the spatial orientation of the donor and the acceptor but also by the concepts of the used calculation approach.

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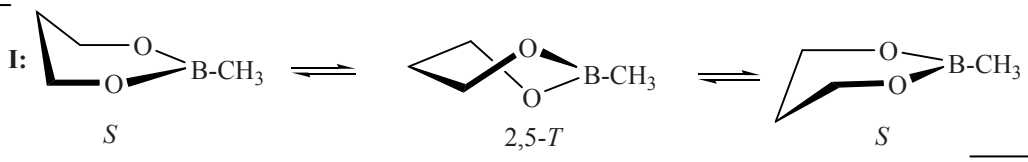
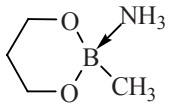
The interest in boric acids cyclic esters to a great extent is connected with the structural features caused by the presence of electron-deficient boron atom and electron-donor oxygen heteroatoms in the same molecule [1–6]. This leads to the formation of various types associates in solutions due to the complex formation with both donors and acceptors of electron pair. This circumstance offers possibilities for computer modeling of interaction mechanisms of boric acid esters with solvents of different nature.

2-Alkyl-1,3,2-dioxaborinane molecules are known to be in the state of fast ring inversion (an NMR time scale) at room temperature with relatively low barrier [1,2,6]. It is known also that potential energy surface (PES) of 2-methyl-1,3,2-dioxaborinane **I** includes minima (energetically degenerate *sofa* conformers, *S*) and a maximum corresponding to the conformation of *2,5-twist*-form (*2,5-T*) [7].

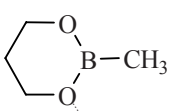



The fundamental possibility of the existence of substituted 1,3,2-dioxaborinane associates with water and ammonia molecules have been established earlier [8–11] by semiempirical calculations. This work deals with computer simulation of the ester **I** potential energy surface in the presence of ammonia molecule by nonempirical methods RHF//STO-3G, 3-21G and 6-31G(d) within HyperChem program package [12].

Boric acid esters are shown to manifest both acceptor and donor properties [13]. We found two types of molecular complexes **I** with ammonia (1:1): with donor-acceptor bond N→B (**A**) and with intermolecular hydrogen bond NH···O (**B**).



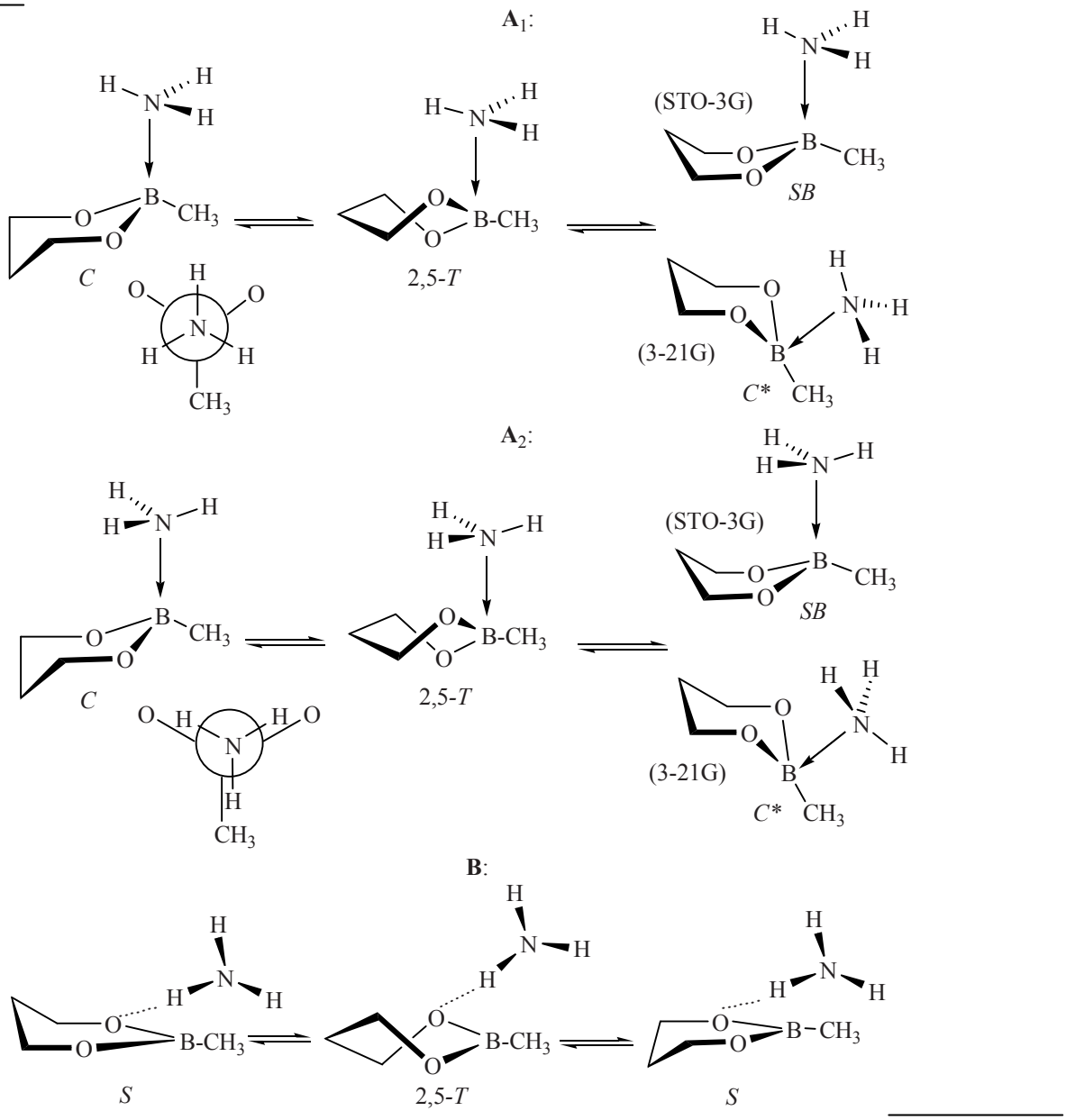

**A**




**B**

In this case complex **A** exists as two rotamers determined by the relative orientation of the ammonia

molecule and the heterocyclic ring ($\mathbf{A}_1$ and $\mathbf{A}_2$). Conformational conversions of the complexes differ little from the observed for the isolated molecule of ester **I**, and interconversion of the two isomers is assumed. At the same time the calculated properties of the studied associates are determined not only by the donor and acceptor spatial orientation but they are also affected by the concepts of the used calculation approach. The PES of the associates $\mathbf{A_1}$ and $\mathbf{A_2}$ contains minima corresponding to conformers of the flattened *chair C* and *symmetric boat SB*, or of the inverted *chair C**. They are separated by the potential barrier to which corresponds the flexible form *2,5-T* (see the table).




Invertomers *C* and *C** (*SB*) of $\mathbf{A}_1$ and $\mathbf{A}_2$ associates are energetically nonequivalent ($\Delta E \neq 0$). At the same time by STO-3G and 3-21G data, the value of interconversion potential barrier ($\Delta E^{\neq}$) is essentially lower than for ester **I**. We failed to calculate the rotation barrier around N→B bond due to the gently sloping profile of the two-dimensional PES section between rotamers *C* ($\mathbf{A}_1$) and *C* ($\mathbf{A}_2$). It may be only suggested that its value is practically by the order of magnitude lower than the experimental data for the donor-

Structural (Å) and energy (kcal mol$^{-1}$) parameters calculated for $\mathbf{A}_1$, $\mathbf{A}_2$, and **B** complexes

| Structure | Parameters | Calculation basis (RHF method) | | |
|---|---|---|---|---|
| | | STO-3G | 3-21G | 6-31G(d) |
| **I** | $\Delta E^{\neq}$ | 6.5 | 7.9 | 7.5 |
| $\mathbf{A}_1$ | $\Delta E$ [a] | 2.1 | 0.5 | 7.8 |
| | $\Delta E^{\neq}$ [a] | 3.8 | 4.1 | – |
| | $-\Delta H$ | 6.5 | 10.3 | 2.6 |
| | $r_{N\rightarrow B}$ (ПС) | 1.86–1.89 (1.79) | 1.68–1.83 (1.75) | 1.69 (*C**); 3.41 (*C*) |
| $\mathbf{A}_2$ | $\Delta E$ [a] | 1.8 | 1.4 | – |
| | $\Delta E^{\neq}$ [a] | 3.3 | 4.4 | – |
| | $-\Delta H$ | 6.0 | 10.6 | – |
| | $r_{N\rightarrow B}$ (ПС) | 1.88–1.92 (1.78) | 1.69–1.87 (1.75) | – |
| **B** | $\Delta E^{\neq}$ | 6.6 | 7.8 | 7.5 |
| | $-\Delta H$ | 3.2 | 6.8 | 2.9 |
| | $r_{NHO}$ (ПС) | 1.91 (1.91) | 2.14 (2.12) | 2.36–2.39 (2.37) |

[a] Relative to the more stable conformer.

acceptor adducts of borane (about 3.4 kcal mol$^{-1}$ [14]) and than the obtained by RHF//STO-3G calculation for $H_3N{\cdot}BH_3$ associates (3.0 kcal mol$^{-1}$ [15]). This fact shows indirectly that N→B coordination bond energy in the complexes studied is relatively low.

The enthalpies of formation ($\Delta H$) of $\mathbf{A}_1$ and $\mathbf{A}_2$ associates obtained by STO-3G and 3-21G approaches are practically equal. However, the values obtained are essentially lower than the experimental data for the adducts of amines with acyclic boranes (20–30 kcal mol$^{-1}$ [16]) and are comparable with the energy of intramolecular coordination N→B bond in the five-membered cyclic boric esters (9.6–12.9 kcal mol$^{-1}$ [17]). Hence it follows that **A**-type complexes are not featured by high stability. Experimental data of [18, 19] confirm that the heat effect of reaction of 1,3,2-dioxaborinanes with amines to give donor-acceptor associates is relatively low.

In some cases the N→B bond length ($r_{N\rightarrow B}$) is close to the experimental value for the acyclic adducts (1.57–1.64 Å [20, 21]). According to STO-3G results, in the transition state (TS) this bond is shorter than in conformers corresponding to the energy minimum.

With the calculation basis 6-31G(d), only associate $\mathbf{A}_1$ is realized; during minimization the $\mathbf{A}_2$ complex conformers transform irreversibly into the corresponding forms of $\mathbf{A}_1$ adduct. The latter conformers are appreciably different by energy in favor of *C* form; it is characterized by abnormally high value of N→B bond length in comparison with *C** (Table 1). However, the conformational isomerization procedure leads to destruction of this adduct: both conformers transform into **B** complex without transformation into each other. Intermolecular hydrogen bond of the latter is retained during conformational transformations regardless of the calculation basis used and does not change its length in the ground state as well as in the transition state. The value $r_{NH\cdot O}$ (2.36–2.39 Å) obtained with 6-31G(d) approach is fairly close to the experimental value of the hydrogen bond length for water (2.74–2.77 Å [22]). The invertomers *S* are energetically degenerate, and the value of the interconversion barrier is the same as the calculated for cyclic ester **I**. Beyond that point the complication of basic set leads to monotonous decrease in the enthalpy of formation of **A** complexes and to increase in $\Delta H$ value for **B** associate. The hydrogen bond energy calculated with 3-21G approach (6.8 kcal mol$^{-1}$) is relatively close to the experimental value $\Delta H$ for water (4.8–6.0 kcal mol$^{-1}$ [22]).

The results obtained demonstrated that complex formation affected appreciably the character of the potential energy surface of ester **I**. Associates studied are weak complexes. Nonetheless, it is believed that the presence of several ammonia molecules furnishes a specific solvate shell around the boric ester molecule by the formation of both types associates.

## EXPERIMENTAL

The conformational isomerization was carried out by optimization of associate molecules geometry under changes of intracyclic torsion angle OCCC within

±50°. The route and values of interconversion barriers are established by procedure of searching for the transition state within the framework of the HyperChem package [12]. The assignment of PES stationary points to maxima (*2,5-T* form) was confirmed by the presence of the one negative frequency in the corresponding Hesse matrix.

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