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Quantum-Chemical Study on Conformations of Molecular Complexes Formed by 2-Methyl-1,3,2-dioxaborinane with Methylamine

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Abstract—Conformations of 1 : 1 molecular complexes of 2-methyl-1,3,2-dioxaborinane with methylamine were studied in terms of restricted Hartree–Fock approximation using STO-3G, 3-21G, and 6-31G(*d*) bass sets. The results showed possible formation of two types of complexes, one with dative N→B bond, and the other with intermolecular hydrogen bond NH···O. Their relative stability and conformations are determined by both mutual orientation of the components and basis set used.

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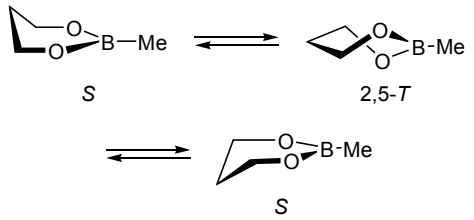
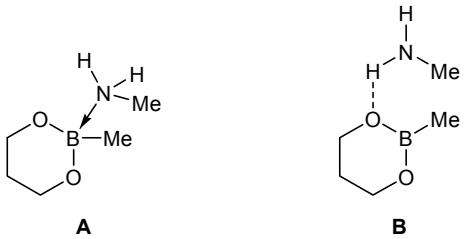
The ability of boric acid esters to form molecular complexes with both lone electron pair (LEP) donors and acceptors [1] makes these compounds convenient models for computer simulation of mechanisms of interactions with various solvents. It was shown previously [2–7] that molecules of 2-alkyl-1,3,2-dioxaborinanes at room temperature undergo fast (on the NMR time scale) ring inversion with a relatively low barrier. In addition, the potential energy surface (PES) of 2-methyl-1,3,2-dioxaborinane (**I**) includes minima (energy-degenerate *sofa* conformers *S*) and a maximum corresponding to 2,5-*twist* conformer 2,5-*T* (Scheme 1) [8].

Scheme 1.



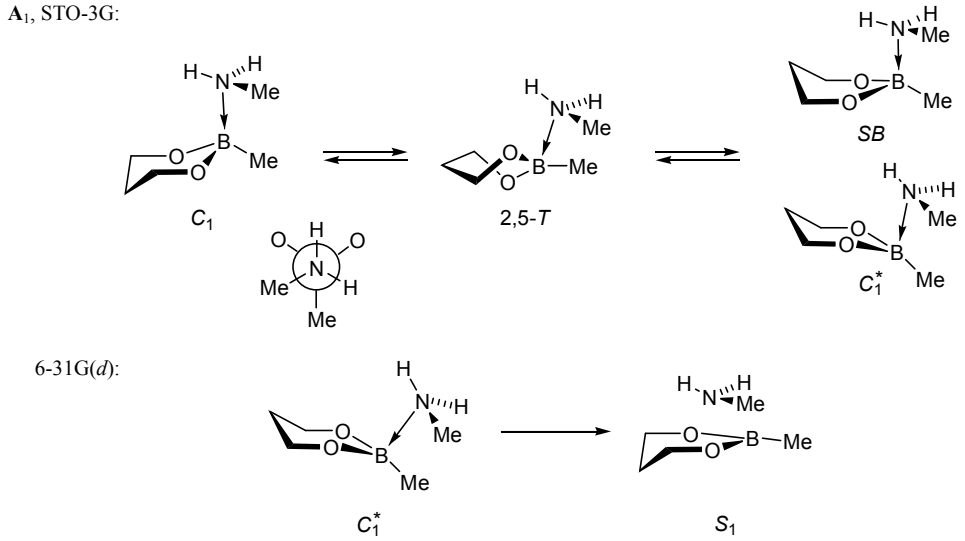
Semiempirical calculations [9–11] showed that substituted 1,3,2-dioxaborinanes are capable of forming molecular complexes with ammonia. In keeping with the results of relatively recent B3LYP/6-311+G* calculations, the formation of adducts by methyl- and phenylboronic acids with ammonia in solution is an endothermic processes [12]. In the present work we tried to simulate the potential energy surface of ester **I** in the presence of methylamine molecule in terms of the restricted Hartree–Fock approximation with STO-3G, 3-21G, and 6-31G(*d*) basis sets using HyperChem software package [13].

We found that the molecular system 2-methyl-1,3,2-dioxaborinane (**I**)–methylamine (1 : 1) could give rise to numerous binary structures and that there are only two most stable associates with dative N→B bond (**A**) and intramolecular hydrogen bond H–N···O (**B**).



Complex **A** can exist as three rotamers $\mathbf{A}_1$–$\mathbf{A}_3$ differing by mutual orientation of the amine molecule and heteroring). The conformational behavior of associates **A** differs from that found for ester **I** and implies interconversion of two non-degenerate conformers.

Scheme 2.



Complex $\mathbf{A}_1$ gives rise to equilibrium between two minima with different energies ($\Delta E \neq 0$), which correspond to flattened *chair* (C_1) and *symmetric boat* (*SB*) conformers (STO-3G) or *chair* conformers C_1 and C_1^* (3-21G) (Scheme 2). The global minimum is occupied by C_1 (STO-3G) or C_1^* (3-21G), and the maximum, by 2,5-*twist* conformer 2,5-*T* (Table 1). The potential barrier to interconversion ($\Delta E^{\neq}$) is appreciably lower as compared to ester **I**. The formation of the above complexes is accompanied by heat evolution. However, the calculated enthalpies of their formation (ΔH) are considerably lower than the experimental values reported for adducts of amines with acyclic boranes (20–30 kcal/mol [14]) and are comparable with the energy of dative N→B bond in five-membered cyclic boronic acid esters (9.6–12.9 kcal/mol [15]). The calculated (3-21G) N→B bond length ($r_{N\to B}$) approaches a value found experimentally for acyclic adducts (1.57–1.64 Å [16, 17]), and this bond in the transition state (TS) is shorter than in the conformers corresponding to the energy minima. According to the calculations with 6-31G(*d*) basis set, the most stable are

Scheme 3.

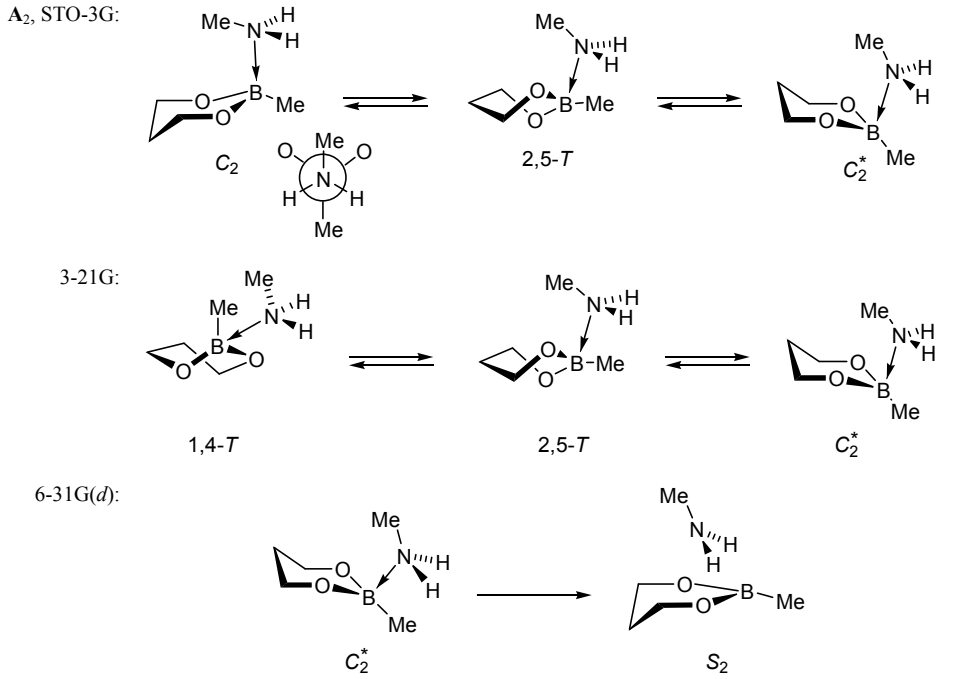


Table 1. Calculated structural and energy (kcal/mol) parameters of complexes $\mathbf{A}_1$–$\mathbf{A}_3$ and **B**

Compound no.	Parameter	STO-3G	3-21G	6-31G(*d*)
I	$\Delta E^{\neq}$	6.5	7.9	7.5
$\mathbf{A}_1$	ΔE[a]	2.1	1.3	–
	$\Delta E^{\neq}$[a]	3.8	4.4	–
	ΔH	–6.3	–13.1	–2.6 (S_1), 3.0 (C_1^*)
	$r_{N\to B}$ (TS),[a] Å	1.848 (1.776)	1.672 (1.722)	1.678 (C_1^*)
$\mathbf{A}_2$	ΔE[a]	2.3	1.8	–
	$\Delta E^{\neq}$[a]	2.9	6.0	–
	ΔH	–4.8	–14.1	–2.6 (S_2), 2.7 (C_2^*)
	$r_{N\to B}$ (TS),[a] Å	1.903 (1.799)	1.672 (1.710)	1.683 (C_2^*)
$\mathbf{A}_3$	$-\Delta H$	4.3	11.4	—
	$r_{N\to B}$,[a] Å	1.907	1.703	
B	$\Delta E^{\neq}$	6.5	9.3	7.5
	ΔH	–3.0	–6.6	–2.8
	$r_{NH\cdots O}$ (TS), Å	1.906 (1.903)	2.147	2.368

[a] Relative to the most stable structure.

chair (C_1^*) and *sofa* (S_1) conformers. The formation of the first of these, despite relatively short N→B bond (1.68 Å), requires an energy ΔH of 3.0 kcal/mol, and it is irreversibly converted into binary associate S_1 with no any intermolecular bonds; however, structure S_1 is formed with a gain in energy (ΔH = –2.5 kcal/mol).

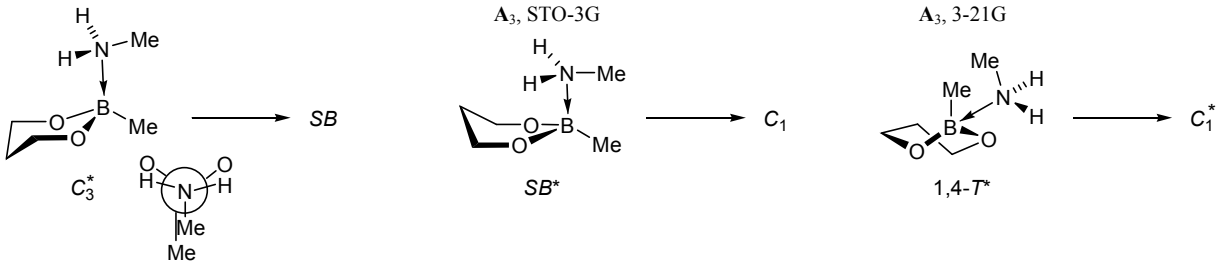
The potential energy surface for complex $\mathbf{A}_2$ also contains two non-degenerate minima (Scheme 3). In terms of the STO-3G approximation, these minima correspond to C_2 and C_2^* conformers, the former having a lower energy. The calculations with 3-21G basis set gave 1,4-*T* and C_2^* conformers, and the latter occupies the main minimum. The stable conformers are separated by an energy barrier corresponding to 2,5-*T*; and the $\Delta E^{\neq}$ value is also lower than that calculated for ester **I**. The calculated enthalpy of formation of adduct $\mathbf{A}_2$ and the N→B bond length are comparable with the corresponding parameters of structure $\mathbf{A}_1$. Conformers C_2^* and S_2 were identified as energy minima on the PES by calculations with 6-31G(*d*) basis set. The former is irreversibly converted into energetically more favorable S_2 conformer with no any intermolecular bond.

Complex $\mathbf{A}_3$ is less stable than adducts $\mathbf{A}_1$ and $\mathbf{A}_2$. Conformers C_3 and *SB** (STO-3G) or 1,4-*T** (3-21G) undergo irreversible conformational transformations into *SB* and C_1 (STO-3G) or C_1^* (3-21G) conformers of adduct $\mathbf{A}_1$. No complex $\mathbf{A}_3$ was localized by 6-31G(*d*) calculations (Scheme 4).

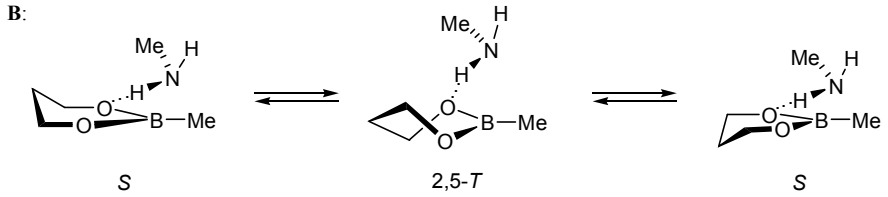
We can conclude that complexes **A** are not very stable. According to the experimental data reported in [18, 19], the heat of formation of donor–acceptor complexes of 1,3,2-dioxaborinanes with amines is fairly small.

The calculations with all basis sets used suggest the existence of associates like **B** (Scheme 5). Two energy minima (almost degenerate *sofa* conformers) and one maximum (2,5-*T*) were localized on its potential energy surface. Intermolecular hydrogen bond is conserved in both minima in the course of conformational transformations, but analogous bond in the maximum

Scheme 4.



Scheme 5.



was revealed only by calculations with STO-3G basis set. The calculated distance $r_{NH\cdots O}$ (Table 1) is shorter than the experimental hydrogen bond in water (2.74–2.77 Å) or ammonia (3.1 Å [20]). The potential barrier to interconversion either coincides with that found for isolated molecule **I** or exceeds it (3-21G).

Thus extension of the basis set leads to reduction in the stability of complexes $\mathbf{A}_1$–$\mathbf{A}_3$ relative to **B**. The energy of the hydrogen bond in associate **B** (3-21G) is higher than in ammonia (3.7–4.4 kcal/mol), and it approaches the experimental energy of hydrogen bond in water (4.8–6.0 kcal/mol [20]).

The stability of molecular complexes **A** and **B** was additionally characterized by calculation of the barriers to rotation about the C–N and N→B bonds ($\Delta E^{\neq}_{N-C}$ and $\Delta E^{\neq}_{N\to B}$) in their molecules and comparison of the calculated values with those for the molecular complex $MeNH_2 \cdot BMe_2$ (**C**) which is *a fortiori* stronger [17]. The results (Table 2) showed the lack of unambiguous relation between $\Delta E^{\neq}_{N-C}$ values for isolated methylamine molecule and that involved in complex formation. Calculations with STO-3G basis set gave lower potential barrier as compared to methylamine, the difference being greater for adducts **A**, whereas 3-21G calculations predicted a higher barrier, Obviously, the $\Delta E^{\neq}_{N-C}$ value is determined not only by strength of the dative bond in the adduct but also by the force field of the boron-containing molecule. The role of the basis set used is also important: the experimental $\Delta E^{\neq}_{N-C}$ value for free methylamine, determined by microwave spectroscopy (1.976 kcal/mol [21]), is better consistent with the results of 3-21G calculations.

By contrast, the parameter $\Delta E^{\neq}_{N\to B}$ is clearly related to the strength of the adducts and is lower for complexes **A** as compared to **C**. This is confirmed by the results of calculation of the potential barrier to rotation about the N→B bond in the strong molecular complex $H_3N \cdot BH_3$ (3 kcal/mol, STO-3G [22]) and experimental $\Delta E^{\neq}_{P\to B}$ value found for fairly strong $H_3P \cdot BH_3$ adduct (3.4 kcal/mol [23]).

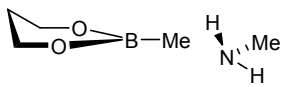
Apart from complexes **A** and **B**, some other binary associates of ester **I** with methylamine without intermolecular bonds are possible (structures **D**–**F**). Taking into account their relatively low stability, their conformational behavior was not considered.

Our results indicate appreciable effect of complex formation on the potential energy surface of ester **I**.

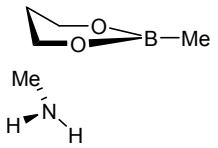
Table 2. Calculated barriers to rotation about the C–N and N→B bonds in complexes **A**–**C** and enthalpies of formation of complex **C** (kcal/mol)

Compound	Parameter and conformer	STO-3G	3-21G	6-31G(*d*)
$\mathbf{A}_1$	$\Delta E^{\neq}_{N-C}$: C_1	1.9	2.4	–2.6
	C_1^* or *SB*	1.8	2.9	
$\mathbf{A}_2$	$\Delta E^{\neq}_{N-C}$: C_2^*	1.2	3.9	2.8
	1,4-*T*	–1.5	3.9	–
	$\Delta E^{\neq}_{N\to B}$: $C_1 \to C_2$	–	–2.4	–2.1
	$C_1^* \to C_2^*$			
$\mathbf{A}_3$	$\Delta E^{\neq}_{N-C}$: 1,4-*T*	–	2.6	–
B	$\Delta E^{\neq}_{N-C}$	2.6	2.3	2.3
C	ΔH	–30.9	–21.8	–10.9
	$\Delta E^{\neq}_{N-C}$	2.5	2.4	2.4
	$\Delta E^{\neq}_{N\to B}$	2.5	3.0	2.5
Methylamine	$\Delta E^{\neq}_{N-C}$	2.8	2.0	2.4
	Exptl. 1.976 [21]			

D, ΔH = 0.1 kcal/mol



E, ΔH = –0.2 kcal/mol



F, ΔH = –1.7 kcal/mol

The examined adducts may be regarded as weak complexes. Nevertheless, it may be presumed that the presence of several amine molecules could give rise to a specific solvate shell around the boronic acid ester molecule due to formation of various associates.

EXPERIMENTAL

Conformational transformations were studied by performing optimization of geometric parameters of associates upon variation of the torsion angle OCCC in molecule **I** in the range ±50°. The interconversion paths and potential barriers were determined by the procedure for searching for transition states built in HyperChem software [13]. Stationary points on the potential energy surface were identified as maxima by the presence of one imaginary frequency in the corresponding Hesse matrix.

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