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# Conformational Analysis of 1,3,2-Polymethyl-Substituted Dioxaborinanes

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**Abstract**—Study of conformational isomerization of 4,4,6-trimethyl- and 4,4,6,6-tetramethyl-1,3,2-dioxaborinanes containing hydrogen, as well as methyl and vinyl groups at the boron atom, by means of non-empirical quantum-chemical calculation in HF/6-31G (d) and PBE/3z approximations, as well as by analysis of $^1$H NMR spectroscopic data was carried out. The molecules of the analogs with three methyl groups in the ring are in equilibrium between the *half-chair* and *sofa* conformers, the equilibrium is shifted almost completely toward the latter form. For the 4,4,6,6-tetramethyl-substituted cyclic boronic esters is characteristic the conformational equilibrium between energetically degenerated forms of either *sofa,* or *half-chair*.

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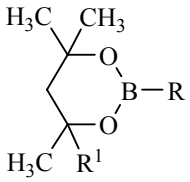
Interest in cyclic boric acid ester is due to a significant role of these compounds in fine organic synthesis (preparation of enantiomeric alcohols and polyenes), a scope of their practically useful properties (bioactive substances, corrosion inhibitors, polymer components, and lubricants), as well as their structural features [1–8]. In addition, 4,4,6-trimethyl-1,3,2-dioxaborinane is used as a borinating and hydroborinating agent [1, 9–12], and a precursor of functionally substituted derivatives at the boron atom [13]. Its 2-vinyl-substituted analogs is used for the stereoselective synthesis of 1,3,5-hexatrienes [14], substituted styrenes and dienes [15], many products of the addition at the double bond [16–18]. 2-Chloro- and 2-alkoxy-4,4,6-trimethyl-1,3,2-dioxaborinanes are used for the synthesis of new cyclic boronic esters [1, 13, 19–22].

From the data of $^1$H NMR spectroscopy and ab initio calculations was revealed that the molecule of 2-substituted 1,3,2-dioxaborinanes exists in a state of equilibrium between the degenerate *sofa* invertomers [1, 23]. The potential energy surface (PES) of their 2,5-disubstituted analogs includes the equatorial and axial *sofa* conformers that turn into each other through the 2,5-*twist* transition state [24]. At the same time, the conformational behavior of 4,4,6-trimethyl- and 4,4,6,6-tetramethyl-1,3,2-dioxaborinanes has not been studied in detail. Only is know that $^1$H NMR data, as well as the data of empirical and semiempirical calculations suggest the existence of equilibrium between the *half-chair* invertomers of the molecules of tetramethyl-substituted analogs and between the *sofa* and *half-chair* forms for the trimethyl-derivatives [25]. The aim of this paper is to study the conformational isomerization of the molecules of 4,4,6-trimethyl- and 4,4,6,6-tetramethyl-1,3,2-dioxaborinanes and their 2-methyl- and 2-vinyl-derivatives **I–VI** using the data of $^1$H NMR spectroscopy and ab initio approximations HF/6-31G (d) and PBE/3z within the HyperChem [26] and Nature [27] softwares.



**I**, R = R$^1$ = H; **II**, R = CH$_3$, R$^1$ = H; **III**, R = CH=CH$_2$, R$^1$ = H; **IV**, R = H, R$^1$ = CH$_3$; **V**, R = R$^1$ = CH$_3$; **VI**, R = CH=CH$_2$, R$^1$ = CH$_3$.

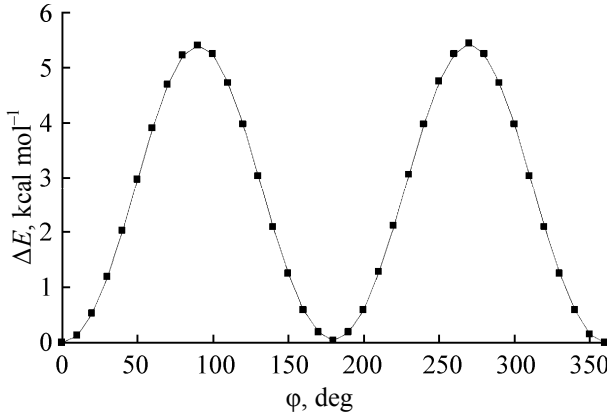
Estimated parameters of conformational equilibrium of the compounds are listed in Table 1. The PES of the esters **I–III** molecules includes the *sofa*

**Table 1.** Thermodynamic parameters of conformational equilibrium of esters **I–VI**

| Comp. no. | Method | $T$, K | $\Delta H$, kcal mol$^{-1}$ [a] | $\Delta S$, cal mol$^{-1}$ K$^{-1}$ | $\Delta G^0$, kcal mol$^{-1}$ [a] | $\Delta H^{\neq}$, kcal mol$^{-1}$ [a] | $\Delta S^{\neq}$, cal mol$^{-1}$ K$^{-1}$ | $\Delta G^{\neq}$, kcal mol$^{-1}$ [a] |
|---|---|---|---|---|---|---|---|---|
| **I** | HF/6-31G(d) | 0 | 4.0 | – | – | 7.6–8.6 | – | – |
| | PBE/3z | 0 | 3.8 | – | – | 7.2–8.4 | – | – |
| | | 298 | 3.8 | 0.6 | 3.6 | 6.8–7.9 | 3.4–3.1 | 7.8–8.8 |
| **II** | HF/6-31G(d) | 0 | 4.1 | – | – | 7.4–8.3 | – | – |
| | PBE/3z | 0 | 3.9 | – | – | 6.9–8.1 | – | – |
| | | 298 | 3.9 | 0.1 | 3.9 | 6.4–7.6 | 4.9–5.1 | 7.9–9.1 |
| **III** | HF/6-31G(d) | 0 | 4.1 | – | – | 7.1–8.1 | – | – |
| | PBE/3z | 0 | 3.8 | – | – | 6.7–7.9 | – | – |
| | | 298 | 3.8 | 1.3 | 3.4 | 6.2–7.4 | 3.8–4.0 | 7.3–8.6 |
| **IV** | HF/6-31G(d) | 0 | 0 | – | 0 | 4.0 | – | – |
| | PBE/3z | 0 | 0 | – | 0 | 4.2 | – | – |
| | | 298 | 0 | 0 | 0 | 3.6 | 5.7 | 5.3 |
| **V** | HF/6-31G(d) | 0 | 0 | – | 0 | 3.7 | – | – |
| | PBE/3z | 0 | 0 | – | 0 | 3.9 | – | – |
| | | 298 | 0 | 0 | 0 | 3.2 | 11.2 | 6.5 |
| **VI** | HF/6-31G(d) | 0 | 0 | – | 0 | 3.5 | – | – |
| | PBE/3z | 0 | 0 | – | 0 | 3.6 | – | – |
| | | 298 | 0 | 0 | 0 | 3.0 | 6.6 | 5.0 |

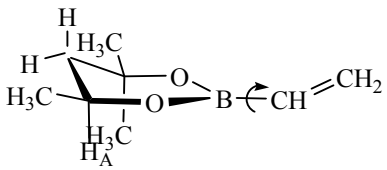
[a] Conformer relative to $S_e$ (esters **I–III**).

conformers with an equatorial methyl group at C$^6$ atom ($S_e$, the main minimum) and *half-chair*. For the ester **III** was also studied a dependence of the energy of $S_e$ conformer on the angle of rotation of vinyl group around the B–C bond (the figure). The energy minima correspond to the conformers with coplanar arrangement of ethylene and heteroatomic fragments of the molecule, while the maxima to the orthogonal orientation of the vinyl substituent. The rotation barrier (5.4 kcal mol$^{-1}$) is relatively close to the experimentally observed in vinyldifluoroborane (4.2 kcal mol$^{-1}$) [28].



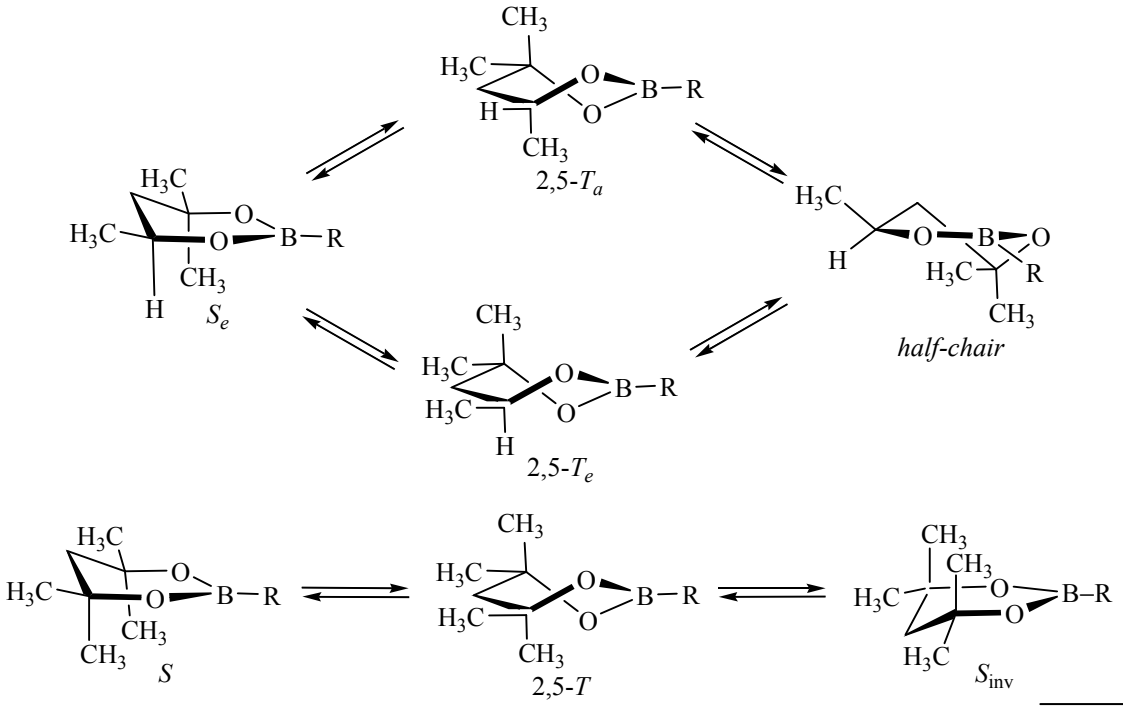

Dependence of the potential energy of *sofa* conformer of ester **III** on the internal rotation angle O–B–C=C (φ), calculated in HF/6-31G(d) approximation.

The differences in enthalpies ($\Delta H$) of the $S_e$ and *half-chair* forms of compounds **I–III** at the approximations used in the calculation vary little with temperature, 3.8–4.1 kcal mol$^{-1}$ in the range between 0 and 298 K (Table 1). We should also note a fairly high value of $\Delta G^0$ of the $S_e \leftrightarrow$ *half-chair* equilibrium at room temperature (3.4–3.9 kcal mol$^{-1}$ in favor of the $S_e$ form). Previously on the examples of 4- and 2,4-substituted 1,3,2-dioxaborinanes has been found that the conformational isomerization of the $S_e$ form may occur by two routes: through the transition states of 2,5-twist form 2,5-$T_e$ and 2,5-$T_a$, which differ in energy by 0.9–1.2 kcal mol$^{-1}$ [29–32].

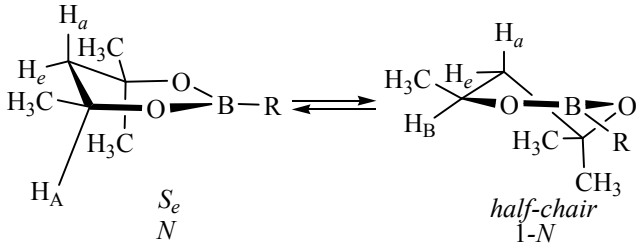



$^1$H NMR data for the molecules of esters **IV–VI** at room temperature indicate a state of equilibrium between the energetically degenerate forms corresponding to a minimum on the PES [1, 25].

According to the results of calculations performed in this study, for the molecules of esters **IV** and **V** these conformers are *S* and $S_{inv}$, while for the ester **VI** the *half-chair* forms. Note that the estimated value of the activation barrier for this process ($\Delta G^{\neq}$) is 1.2–1.6 times lower than the calculated and experimental data for 2-, 2,5- and 2,5,5-substituted 1,3,2-dioxaborinanes [ 23, 24, 33, 34]. Entropy of the main minimum is always higher than that for the alternative conformers and the transition state (Table 1).




The relative content of alternative conformers of the esters **I–III** molecules (*N* and 1–*N*) can be evaluated by an independent method based on the experimental ($^1$H NMR: the constants $^3J_{AX}$ and $^3J_{BX}$ [25]) and theoretical ($J_{Aa}$, $J_{Ae}$, $J_{Ba}$, $J_{Be}$) vicinal spin-spin coupling constants [35]:




In turn, the theoretical coupling constants can be determined by the modified Karplus equation [36], using torsion angles between the related protons in the conformers involved in the binary equilibrium ($\varphi_{Aa}$, $\varphi_{Ae}$, $\varphi_{Ba}$, $\varphi_{Be}$, the data of the optimum geometry). Substituent at the boron atom practically not affects the values of these torsion angles: the maximum difference for esters **I–III** in both used approximations are ±0.3°.

The *N* value thus found exceeds unity (*N* > 1, Table 2) indicating a negligible concentration of the *half-chair*

**Table 2.** Calculated torsion angles between the protons (deg), calculated and experimental spin-spin coupling constants (Hz) and relative content of predominant conformers of compounds **I–III**

| Torsion angles | | Calculated coupling constants | | Experimental spin-spin coupling constant | | *N* |
|---|---|---|---|---|---|---|
| $\varphi_{Aa}$ ($\varphi_{Ba}$) | $\varphi_{Ae}$ ($\varphi_{Be}$) | $^3J_{Aa}$ ($^3J_{Ba}$) | $^3J_{Ae}$ ($^3J_{Be}$) | $^3J_{Aa}$ | $^3J_{Ae}$ | |
| 172.1 (35.3) | 55.2 (80.1) | 11.7 (7.5) | 2.6 (1.7) | 11.5 | 3.7 | 1.18 |

conformer with pseudoaxial methyl group at the $C^4$ atom of the ring. This result confirms the calculated values of $\Delta G^0$ for the $S_e \leftrightarrow$ *half-chair* equilibrium and indicate a high conformational rigidity of the molecules of 4,4,6-trimethyl-1,3,2-dioxaborinanes compared with 2-, 2,5- and 2,5,5-substituted analogs [23, 24, 34] due to additional steric interactions in the carbon fragment of the ring.

## EXPERIMENTAL

Compounds **I–III** have been described in [11, 16], the analogue of esters **IV–VI,** 2-isopropyl-4,4,6,6-tetramethyl-1,3,2-dioxaborinan in [37]. The experimental values of vicinal coupling constants of esters **I–III** were published in [25]: $^3J_{AX}$ = 11.5 Hz, $^3J_{BX}$ = 3.7 Hz.

Simulation of conformational isomerization was carried out by optimizing the geometry of the molecules of esters **I–VI** at varying the intra-cyclic torsion angle OCCC within ± 50°. To investigate the relationship between the energy of the ester **III** *sofa* conformer on the vinyl group rotation angle around the B–C bond we used the procedure of scanning the OBCC torsion angle with the 10° step. Routes of interconversion and the value of the potential barriers are revealed using the standard procedure of searching the transition states within the HyperChem [26] and Nature [27] software. Belonging of the PES minima to the stationary points was confirmed by the absence of imaginary frequencies, and to the transitional state by the presence of a single imaginary frequency in the corresponding Hessian.

The modified Karplus equation has the form [36]:

$$^3J_{HH} = P_1\cos^2\varphi + P_2\cos\varphi + P_3$$
$$+ \Sigma\Delta\chi_i[P_4 + P_5\cos^2(\xi_i\varphi + P_6|\Delta\chi_i|)],$$

where $\Delta\chi_i$ is the difference in electronegativity between the substituents in the respective ethane fragment and hydrogen, φ is the calculated torsion angle between the interacting protons, $\xi_i$ takes the value ±1 depending on the orientation of substituents at the carbon atoms of ethane fragment, and $P_1$–$P_6$ are the parameters depending on the degre of substitution in this fragment. At solving this equation were used the following numerical values of the parameters for the fragments with three substituents: $P_1$ = 13.22°, $P_2$ = –0.99°, $P_3$ = 0°, $P_4$ = 0.87°, $P_5$ = –2.46°, $P_6$ = 9.19°, and the electronegativity values from [38].

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