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Conformational Analysis of 2,4,5-Trimethyl-1,3,2-dioxaborinane Individual Stereoisomers

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Abstract—The study of the conformational isomerization of *cis*- and *trans*-isomers of 2,4,5-trimethyl-1,3-dioxaborinane **I** by means of RHF//STO-3G, 3-21G and 6-31G(d) quantumchemical methods led to the conclusion that its route includes equilibrium between *sofa* conformers with a different steric orientation of substituents at the C-4 and C-5 ring atoms. These conformers are interconverted through the maxima, the conformations of equatorial and axial 2,5-*twist*-forms. A comparison between experimental ^{1}H NMR and theoretical vicinal spin-spin coupling constants was used to determine the quantitative conformational composition of stereoisomers and a value of ΔG^0 for conformational equilibrium.

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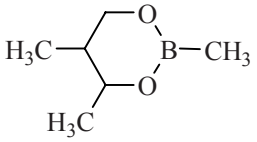
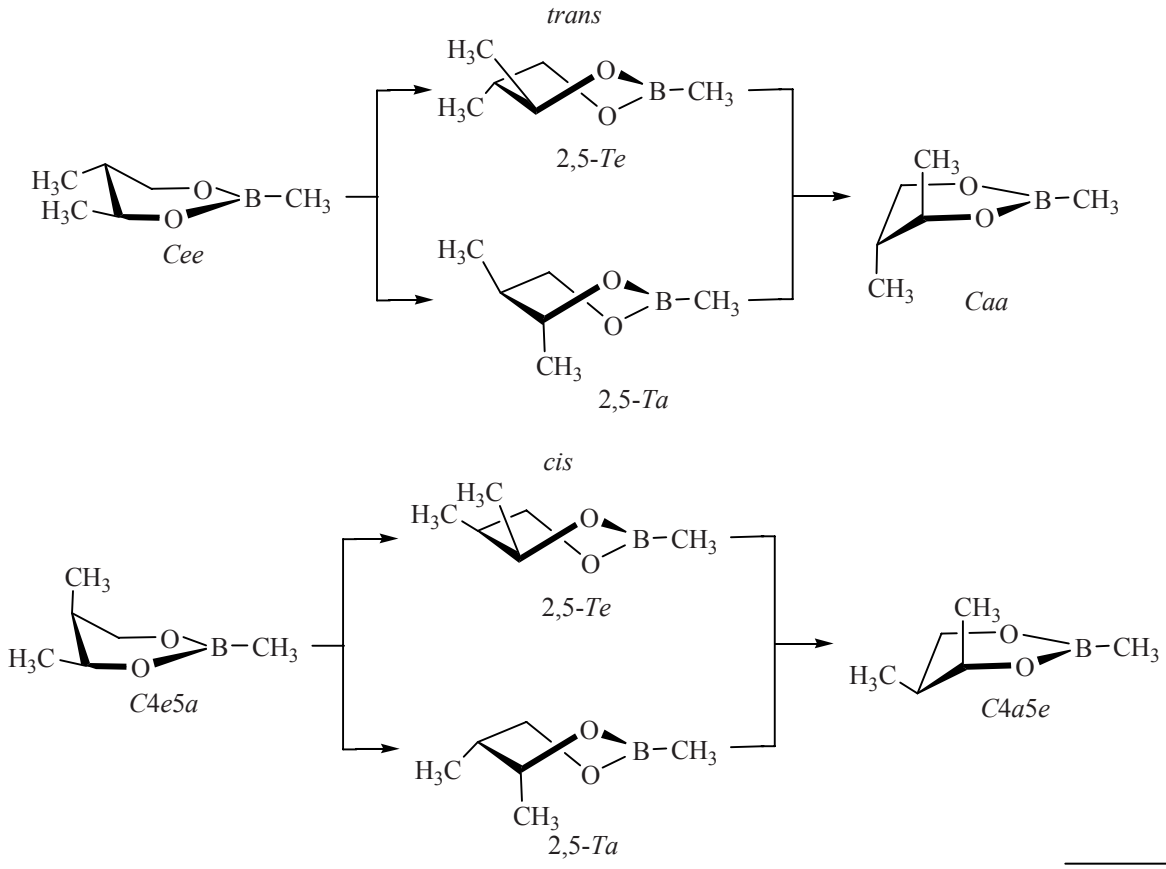
Interest in cyclic esters of boric acids containing the oxygen heteroatoms, 1,3-dioxa-2-boracycloalkanes, is caused by increasing importance of these compounds for the fine organic synthesis (preparation of enantiomeric alcohols and polyenes), by complex of practically useful properties (biologically active substances, corrosion inhibitors, the components of polymers, fuels and lubricants), and also by the structural features (electronic and steric intramolecular interactions) [1–11]. The latter is considerably conditioned by the presence of electron-deficient boron atom and electron-donor oxygen heteroatoms in one molecule. Potential energy surface (PES) of the six-membered boric esters, 1,3,2-dioxaborinanes, contains one or two (for substituted derivatives) minima corresponding to the *sofa* conformers (*S*), and one or two (for asymmetrically substituted com-pounds) maxima of 2,5-*twist* form (2,5-*T*). Unlike the non-boric analog 1,3-dioxane, the conformation iso-merization assumed existence of maximally two minima [1, 4, 5, 8–12].

We studied in detail applicability of quantum-chemical methods to determination of structural and geometrical characteristics of the cyclic boric esters molecules [13, 14]. Relative conformation stability of stereoisomers of 2,4,5-substituted 1,3,2-dioxaborinanes was also examined [4, 5, 15, 16]. The aim of this work is to analyze conformation isomerization routes and to determine quantitative conformation composition of 2,4,5-trimethyl-1,3,2-dioxaborinane **I** *cis*- and *trans*-isomeric molecules by means of non-empirical quantum-chemical approaches RHF//STO-3G, 3-21G and 6-31G(d) with HyperChem program package [17] and ^{1}H NMR spectral data.



I

As in the case of 4-substituted 1,3,2-dioxaborinanes [12], conformation isomerization of *cis*- and *trans*-isomers of the molecules of ester **I** was established to proceed by two ways involving 2,5-*Te* and 2,5-*Ta* transient states.



According to the data obtained (Table 1), the *sofa* (*Cee*) diequatorial form is the more stable conformer of *trans*-**I** molecule. Its prevalence was proved also by the ^{1}H and ^{13}C NMR spectroscopy [18]. As this takes place, the differences between 2,5-*Te* and 2,5-*Ta* maxima are relatively small (0.3–0.8 kcal mol^{-1}). By 3-21G data both routs of conformation isomerization are energetically equivalent. In the case of *cis*-isomer the alternative forms *C*4*e*5*a* and *C*4*a*5*e* are practically degenerated by energy irrespective of the basis used. At the same time the conformation equilibrium is characterized by higher potential barrier and the more significant (1.0–3.2 kcal mol^{-1}) distinctions in energy between two probable routs in comparison with *trans*-isomer.

Our interest was in estimating the relative content of alternative conformers and the conformation equilibrium value ΔG^0 in *cis*- and *trans*-**I** molecules by independent method using experimental (from ^{1}H NMR spectrum: $^{3}J_{AX}$, $^{3}J_{BX}$, $^{3}J_{A'X}$ [18]) and theoretical (J_{aa}, J_{ae}, $J_{a'e}$, J_{ae}, J_{ee}, $J_{e'e}$) vicinal spin-spin coupling constants (SSCC) for alternative conformers with the relative content N and 1-N respectively [19].

Table 1. Relative stability of minima and maxima on potential energy surface (PES) for individual stereoisomers of ester **I** (kcal mol^{-1})

Isomer	Calculation basis	Minima				Maxima	
		Cee	*Caa*	*C*4*a*5*e*	*C*4*e*5*a*	2,5-*Te*	2,5-*Ta*
trans	STO-3G	0	1.1	–	–	7.0	7.3
	3-21G	0	0.6	–	–	8.2	8.2
	6-31G(d)	0	1.7	–	–	6.1	6.9
cis	STO-3G	–	–	0	0.1	8.1	9.1
	3-21G	–	–	0	0.1	9.4	10.4
	6-31G(d)	–	–	0	0.1	6.8	10.0

$$^3J_{AX} + {}^3J_{BX} + {}^3J_{A'X} = N(J_{aa} + J_{ae} + J_{a'e}) + (1 - N)(J_{ae} + J_{ee} + J_{e'e}),$$

$$\Delta G^0 = -RT\ln [N/(1 - N)].$$

In its turn the theoretical SSCC can be determined by modified Karplus equation [20] using torsion angles between the corresponding protons in conformers involved into binary equilibrium (optimal geometry data).

The obtained results (Table 2) bears witness to appreciable (near 20%) concentration of *Caa* form in the conformation equilibrium of *trans*-**I** molecules. On the other hand, in accordance with calculations the *cis*-isomer *C*4*a*5*e* and *C*4*e*5*a* conformers are presented in equal amounts, and the corresponding value of ΔG^0 is close to zero.

This fact confirms the high conformation flexibility of the six-membered cyclic boric acid esters molecules in comparison with other 1,3-dioxa-2-heterocyclohexanes due to the absence of steric interactions in the cycle heteroatomic fragment [1, 5, 10].

EXPERIMENTAL

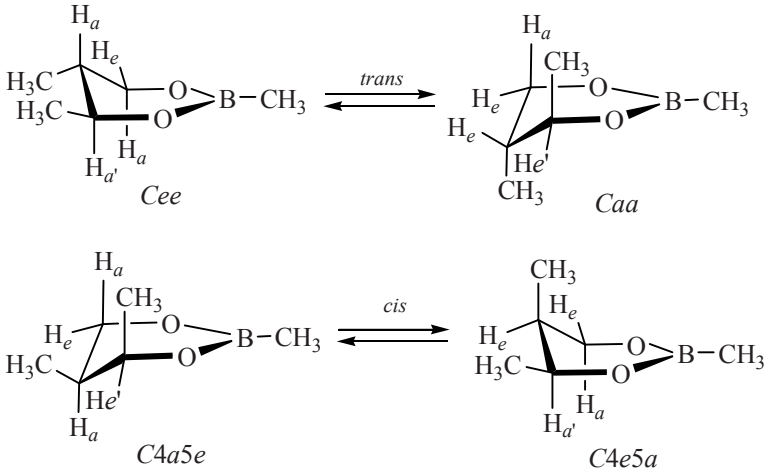
Individual stereoisomers of ester **I** were described in [21], and its NMR spectral characteristic are given in [18]. The routes and values of interconversion were established by means of "transition state" procedure with HyperChem program package [17]. The assignment of PES stationary points to maxima (2,5-*T* form) was confirmed by the presence of the one negative frequency in the corresponding Hesse matrix.

The modified Karplus equation is presented as [20]:

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

where $\Delta\chi_i$ is electronegativities difference between substituents at the corresponding ethane fragment and hydrogen, φ is calculated torsion angles between interacting protons, ξ_i takes values ±1 depending on the substituents orientation at the ethane fragment carbon atoms, P_1–P_6 are parameters depending on this fragment substitution extent. On solving this equation

Table 2. Relative content of conformers and ΔG^0 value (kcal mol^{-1}) for conformation equilibrium of ester **I** *cis*- and *trans*-



Isomer, conformer	Torsion angles (deg)[a]			SSCC (Hz)			N[b]	$-\Delta G^0$
	$\varphi_{aa(ea)}$	$\varphi_{ae(ee)}$	$\varphi_{a'e(e'e)}$	$^3J_{aa(ea)}$	$^3J_{ae(ee)}$	$^3J_{a'e(e'e)}$		
trans							0.78	0.7
Cee	174.4	55.7	176.9	11.7	4.8	11.6		
Caa	47.7	71.2	77.5	3.5	2.6	1.2		
cis							0.53	0
*C*4*a*5*e*	174.0	55.2	51.5	11.7	4.8	4.6		
*C*4*e*5*a*	48.6	70.6	52.6	3.4	2.7	3.0		

[a] Optimal geometry 6-31G(d) data were used; *a* and *e* are axial and equatorial orientation of the hydrogen atoms in corresponding ethane fragment. [b] Relatively to the more stable conformer.

the computational values of P_1–P_6 parameters were used for fragments containing three substituents [calculation of SSCC $^3J_{aa(ea)}$ and $^3J_{ae(ee)}$]: P_1 = 13.22, P_2 = –0.99, P_3 = 0, P_4 = 0.87, P_5 = –2.46, P_6 = 19.9°, and four substituents [calculation of spin–spin coupling constants $^3J_{a'e(e'e)}$]: P_1 = 13.24, P_2 = –0.91, P_3 = 0, P_4 = 0.53, P_5 = –2.41, P_6 = 15.5°, and also the electronegativity values from [22]. In the case of tetrasubstituted frag-ment one more parameter (P_7 = 0.19) was used to additional correction data for β-substituents effect: $\Delta\chi_i = \Delta\chi(\alpha) - P_7\sum\Delta\chi(\beta)$. Numerical values of experimental SSCC were: $^3J_{AX}$ =10.5 Hz, $^3J_{BX}$ =4.4 Hz, and $^3J_{A'X}$ =8.6 Hz for *trans*-**I**; $^3J_{AX}$ = 7.5 Hz, $^3J_{BX}$ = 4.2 Hz, and $^3J_{A'X}$ =3.8 Hz for *cis*-**I** [18]. The ΔG^0 value determination was carried out for temperature 298 K, at which the ^{1}H NMR spectra were registered.

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