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PSEUDOROTATION AND BARRIERS TO INVERSION OF 1,3,2-DIOXABORINANE RINGS

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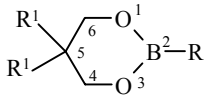
It has been shown by empirical, semiempirical, and nonempirical methods that the interconversion of the rings of 1,3,2-dioxaborinanes goes via transition state with the 2,5-twist form and differs from the monotypic substituted 1,3-dioxanes in having a lower potential barrier.

Keywords: 1,3,2-dioxaborinanes, conformer, interconversion barrier, transition state.

A basic area of study in the field of conformational analysis of heterocyclic compounds is concerned with the discovery of stable conformers and also the determination of possible routes for their interconversion and the corresponding potential barriers. It is known that the most stable form of the ring of six-membered cyclic esters of boric acid is the *sofa,* and that for molecules of 2- and symmetrical 2,5,5-substituted 1,3,2-dioxaborinanes the characteristic state at room temperature is an equilibrium between two *sofa* invertomers [1-4]. The present paper is concerned with the study of probable routes and calculations of the barriers in interconversion of unsubstituted, 2-, 5,5- and 2,5,5-substituted 1,3,2-dioxaborinanes **1-7** using empirical (MM+), semiempirical (AM1), and nonempirical (the Hartree–Fock approximation (HF) with differences in the number and width of the basic sets) methods within the HyperChem 5.02 program [5].



1–7

1 R = R^1 = H; **2** R = OMe, R^1 = H; **3** R = *i*-Pr, R^1 = H; **4** R = H, R^1 = Me; **5** R = OMe, R^1 = Me; **6** R = Et, R^1 = Me; **7** R = *i*-Pr, R^1 = CH_2Ph

The torsion angles 1-2-3-4 (τ_1), 2-3-4-5 (τ_2), and 3-4-5-6 (τ_3) were used as reaction coordinates for the inversion process. They were changed (scanned) in units of 10°. With the MM+ method using the molecule of ester **1** it was observed that scanning of τ_1 caused only a deformation of the ring: *sofa* → *distorted chair* → *flexible forms*, but there was no inversion. In contrast, changes in τ_2 or τ_3 caused a chain of consecutive conformational transitions: *sofa* (S), *semichair* (SC), *1,4-twist* (1,4-T), *unsymmetrical bath* (UB), *2,5-twist* (2,5-T) (maximum) – after which the system is transformed discontinuously into the inverted *sofa* (S').

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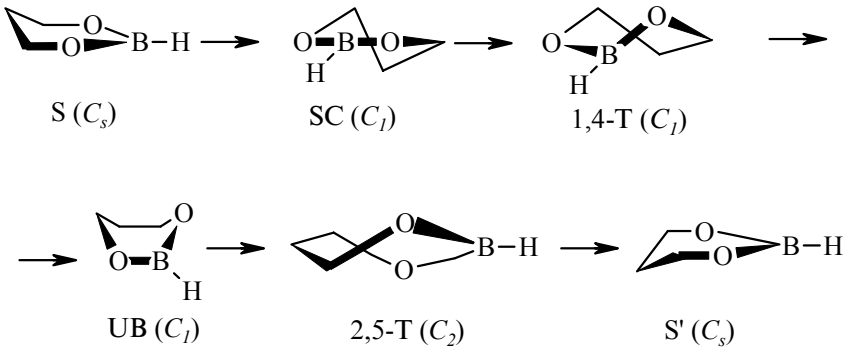

All of the interconversions noted are symmetry allowed [6] (C_s, C_1, and C_2) and thus correspond to one likely routes for the interconversion of the molecules of 1,3,2-dioxaborinanes *via* the 2,5-*twist* transition state. The similarity in the energy changes of the molecule of ester **1** on scanning torsion angles τ_2 and τ_3 (Fig. 1) indicates that the two routes to pseudorotation of the ring are practically equally probable.

Within the frames of quantum-mechanical methods to choose the cross-over point we used the eigen value and reaction map regimes [5]. The experimental ($\Delta G^{\neq}$) [4, 7] and calculated ($\Delta E^{\neq}$) values for the potential barrier for the interconversion of the molecules of compounds **1-7** are given in Table 1. The conformation properties of the equilibrium form, or *sofa*, and the transition state are described *via* folding parameters (S – degree of folding, θ and ψ – polar angles characteristic of the type of conformation [8]) based on AM1 optimal geometry. All of the methods used to choose the transition state led unambiguously to the 2,5-*twist* conformation; its folding parameters are quite close to the canonical *flexible form* [8]. According to the quantum-chemical data the stability of the *sofa* relative to the transition state is achieved *via* advantageous electronic energy in comparison with the nuclear skeleton. In all cases the calculated dipole moment of the transition state is 0.08-0.27 D smaller than that of the *sofa;* this indicates that the value of $\Delta G^{\neq}$ should increase in polar solvents.

It was shown using compounds **5-7** as examples that the best agreement with experimental results were obtained from the MM+ and *ab initio* (HF/6-31G) methods. On the other hand, data from AM1 clearly decreased $\Delta E^{\neq}$. Because of the low coalescence temperature in the ^{1}H NMR spectrum of ester **3** (below -100°C) only the probable upper limit of $\Delta G^{\neq}$ of this molecule (< 9.0 kcal/mol) was succeeded to estimate using the temperature dependence of the half width of the middle line of the signal of the CH_2O protons [9]. The results obtained provide a reason for expecting that the value of $\Delta G^{\neq}$ for the unstable compounds **1** and **2** [10, 11] and also ester **3** lies in the range 7.0-7.3 kcal/mol. Hence the nature of the substituent on the boron atom (H, OMe,

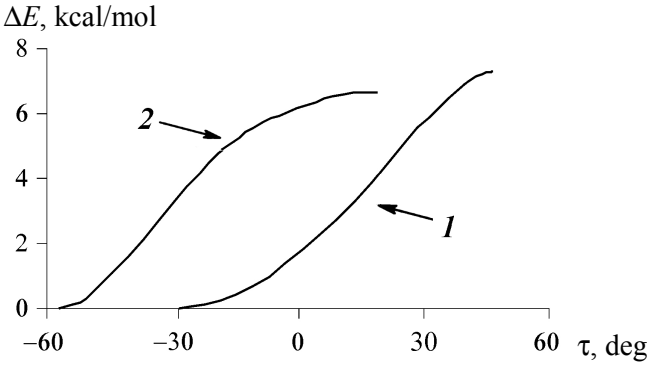

Fig. 1. Changes in energy of the ester molecule **1** on scanning the torsion angles τ_2 (*1*) and τ_3 (*2*).

TABLE 1. Inversion Barriers (kcal/mol) and Folding Parameters of the Equilibrium and Transition Forms of the Molecules of 1,3,2-Dioxaborinanes **1-7***

Com-pound	Method of calculating geometry	Method of choice of TS	$\Delta E^{\neq}$	$\Delta G^{\neq}$*[2]	Folding parameters*[3]			Confor-mation
					S	θ	ψ	
1	MM+	2-3-4-5	7.3	—	0.68	36.9	0	S
		3-4-5-6	6.9		0.41	90.1	30.1	2,5-T
	AM 1	EV, RM	3.4					
	HF/STO-3G	RM	6.7					
	HF/3-21G	RM	8.1					
	HF/6-31G	RM	7.8					
	HF/6-31G*	RM	7.7					
	HF/6-31G**	RM	7.6					
2	MM+	2-3-4-5	7.3	—	0.71	34.5	2.4	S
		3-4-5-6	6.9		0.60	88.0	28.4	2,5-T
	AM1	RM	2.8					
3	MM+	2-3-4-5	7.2	<9.0	0.69	36.5	0.2	S
		3-4-5-6	6.9		0.54	90.1	29.8	2,5-T
	AM1	EV	3.2					
4	MM+	2-3-4-5	8.0	—	0.68	36.2	0	S
		3-4-5-6	7.7		0.52	89.6	29.8	2,5-T
	AM1	EV, RM	3.6					
5	MM+	2-3-4-5	7.9	7.0 [7]	0.71	33.5	2.6	S
		3-4-5-6	7.7		0.65	92.0	28.8	2,5-T
	AM1	EV, RM	2.8					
6	MM+	2-3-4-5	8.1	8.0 [7]	0.68	36.7	0.2	S
		3-4-5-6	7.7		0.63	90.8	29.6	2,5-T
	AM1	EV, RM	3.0					
	HF/STO-3G	RM	7.4					
	HF/3-21G	RM	9.1					
	HF/6-31G	RM	8.3					
7	MM+	2-3-4-5	9.8	9.7 [4]	0.72	36.0	4.8	S
		3-4-5-6	9.5		0.68	91.5	28.3	2,5-T
	AM1	EV	5.0					

* TS – transition state, EV – eigen values, RM – reaction map.
*[2] Solvents : CS_2 (compound **3**) and CF_2Cl_2 (compounds **5-7**).
*[3] For the ideal *sofa* θ = 45°, ψ = 0°, for the ideal *flexible form* θ = 90°, ψ = 30° [8].

i-Pr – compounds **1-3**) has practically no effect on the value for the barrier of inversion for the ring. At the same time the larger values of $\Delta G^{\neq}$ for similar non-boron analogs: 1,3-dioxane and its 5,5-dimethyl derivative (9.7-11.2 kcal/mol [12, 13]) – indicates the principal difference between the inversion pathways for the rings of cyclic formals [12] and 1,3,2-dioxaborinanes. The principal reason for this is the higher conformational flexibilty of the molecules of the cyclic boron esters, caused by the decrease in the number of intramolecular independent interactions resulting from the planar configuration of the trigonal boron atom.

EXPERIMENTAL

The ^{1}H NMR spectrum of 2-isopropyl-1,3,2-dioxaborinane (**3**), described in paper [14] was measured at temperatures from +20 to -100°C with a Tesla BS-497 machine using 20% solutions in CS_2 relatively to TMS (external standard).

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