ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 5, pp. 936–939. © Pleiades Publishing, Ltd., 2010.
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Conformational Analysis of 2-Methyl-5-Alkyl- and 5-Aryl-1,3,2-Dioxaborinanes

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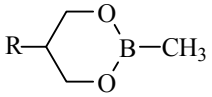
Received September 21, 2009

Abstract—Quantum chemical study of conformational isomerization of 2-methyl-5-alkyl- and 5-aryl-1,3,2-dioxaborinanes using RHF/6-31G(d) method led to the conclusion that the equilibrium between equatorial and axial sofa conformers is shifted to the latter form. Based on the experimental and theoretically calculated vicinal coupling constants J_{HH} the quantitative conformational composition and the values of ΔG^0 for substituents at the C^5 ring atom were established.

DOI: 10.1134/S1070363210050129

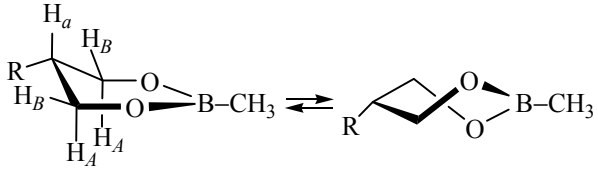
Interest to 1,3,2-dioxaborinanes is caused by ever-increasing importance of these compounds in fine organic synthesis (synthesis of enantiomeric alcohols and polyenes), a complex of practically useful properties (biologically active compounds, inhibitors of corrosion, components of polymer and lubricating materials), as well as their specific structure (electronic and steric intramolecular interactions) [1–11]. Earlier [1, 5], based on the NMR spectroscopy data, it was shown that in conformational equilibrium of 2,5-dialkyl-1,3,2-dioxaborinanes the equatorial conformer predominates. By the use of empiric and semiempiric calculations it was found that the potential energy surface (PES) of the molecules of the studied compounds contained the equatorial and axial *sofa* conformers (*Ce* и *Ca*), which are interconverted via the transition state of the 2,5-*twist*-form (2,5-*T*) [12]. The goal of this work was to study the conformational isomerization and to determine quantitatively the conformational composition of 2-methyl-5-alkyl- and 5-aryl-1,3,2-dioxaborinanes (**I–IX**) using the non-empirical approximation RHF/6-31G(d) as implemented in the HyperChem softwar [13], as well as the ^{1}H NMR spectroscopy data.



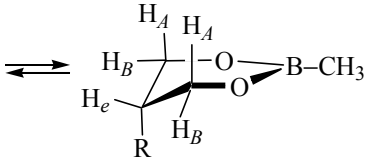
I–IX

R = Me (**I**), Et (**II**), *i*-Pr (**III**), allyl (**IV**), Bu (**V**), *i*-Bu (**VI**), *t*-Bu (**VII**), Ph (**VIII**), Bz (**IX**).

The calculated parameters for the conformational equilibrium of the studied compounds are given in Table 1.



Ce 2,5-*T*



Ca

According to the obtained results, the differences in energy between the *Ce* and *Ca* forms (ΔE) are from 0.6 to 3.4 kcal mol^{-1}, being minimal for the benzyl group. Alkyl substituents, except for *t*-Bu, are characterized by the ΔE value of 1.2–1.3 kcal mol^{-1}. Introduction of an olefinic fragment (allyl group) slightly decreases this value, while for the phenyl group it is maximal. At

the same time, the relative energy of the transition state ($\Delta E^{\neq}$) is less sensitive to the nature of the substituent at the C^5 atom of the ring and for the majority of the studied cyclic boron esters falls within the interval 7.8–8.2 kcal mol^{-1}, that practically coincides with the known values of the experimental barriers of interconversion for compounds of this class [14, 15]. Only 5-tert-butyl- and 5-benzyl-substituted analogs have lower values of $\Delta E^{\neq}$.

The relative content of the conformers and the values ΔG^0 of conformational equilibrium for esters **I–IX** were estimated by the use of the experimental (from the ^{1}H NMR spectra: $^3J_{AX}$, $^3J_{BX}$) and theoretical (J_{Aa}, J_{Ba}, J_{Ae}, J_{Be}) vicinal spin-spin coupling constants of the conformers with the relative content of N and 1-N, respectively [16]:

$$^3J_{AX} + {}^3J_{BX} = N(J_{Aa} + J_{Ba}) + (1 - N)(J_{Ae} + J_{Be}),$$

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

Theoretical coupling constants, in turn, can be determined from the modified Carplus equation [17], using the torsional angles between the corresponding protons in the conformers involved in the binary equilibrium (φ_{Aa}, φ_{Ba}, φ_{Ae}, φ_{Be} for the optimized geometry). For esters **II–IX**, because of asymmetry of substituent R with respect to the methylene protons at the C^4 and C^6 atoms of the ring, these angles are

Table 1. Energy (kcal mol^{-1}) parameters of conformational equilibrium for esters **I–IX** and torsional angles between the ring protons in the equatorial and axial conformers (deg)

Comp. no.	R	ΔE	$\Delta E^{\neq}$	φ_{Aa}	φ_{Ba}	φ_{Ae}	φ_{Be}
I	CH_3	1.2	8.1	174.3	55.2	48.1	71.1
II	C_2H_5	1.2	7.9	174.1	55.2	48.2	71.0
				174.2	54.8	49.0	70.2
III	*i*-C_3H_7	1.3	8.2	173.0	53.6	47.6	71.9
				173.0	53.6	52.2	66.7
IV	CH_2–CH=CH_2	0.9	7.8	173.8	54.8	49.8	69.2
				173.7	54.2	48.2	71.0
V	*n*-C_4H_9	1.2	8.0	174.0	55.1	48.5	70.7
				174.0	54.6	48.4	70.8
VI	*i*-C_4H_9	1.3	8.2	175.0	56.0	49.1	70.0
				174.5	55.1	47.3	71.9
VII	*t*-C_4H_9	2.2	6.9	178.1	57.9	45.6	72.6
				178.1	57.9	40.3	78.2
VIII	C_6H_5	3.4	7.8	175.5	56.2	41.6	77.0
				175.5	56.2	41.5	77.1
IX	CH_2–C_6H_5	0.6	6.3	174.1	55.1	48.1	71.1
				174.3	54.9	49.5	69.8

Table 2. Calculated and experimental spin–spin coupling constants (Hz), constant of conformational equilibrium and energy parameters of substituents at the C^5 atom of the ring (kcal mol^{-1})

Comp. no.	R	Calculated spin-spin coupling constants				Experimental coupling constants		N	ΔG^0	1,3-Dioxanes	
		$^3J_{Aa}$	$^3J_{Ba}$	$^3J_{Ae}$	$^3J_{Be}$	$^3J_{AX}$	$^3J_{BX}$			ΔH	ΔG^0
I	CH_3	11.6	4.8	3.4	2.6	10.0	4.8	0.85	1.0	0.8–1.1	0.6–1.0
II	C_2H_5	11.7	4.8	3.4	2.6	10.3	4.3	0.82	0.9	0.7–0.8	0.7–0.8
		11.7	4.9	3.3	2.7						
III	*i*-C_3H_7	11.7	5.1	3.5	2.5	10.0	4.5	0.79	0.8	1.0–1.2	1.1
		11.7	5.1	2.9	3.2						
IV	CH_2–CH=CH_2	11.7	4.9	3.2	2.8	10.2	3.8	0.75	0.7	–	–
		11.7	5.0	3.4	2.6						
V	*n*-C_4H_9	11.7	4.9	3.4	2.7	10.2	4.3	0.80	0.8	–	–
		11.7	4.9	3.4	2.6						
VI	*i*-C_4H_9	11.7	4.7	3.3	2.7	10.7	3.7	0.80	0.8	–	–
		11.7	4.9	3.6	2.5						
VII	*t*-C_4H_9	11.6	4.4	3.8	2.4	10.9	4.1	0.9	1.3	1.4–2.3	1.4–1.8
		11.6	4.4	4.6	1.9						
VIII	C_6H_5	11.7	4.7	4.4	2.0	10.1	4.9	0.86	1.1	–	1.0
IX	CH_2–C_6H_5	11.7	4.9	3.4	2.6	10.8	4.5	0.88	1.2	–	–
		11.6	4.9	3.2	2.8						

somewhat different (Table 1); in this case additional terms were introduced to the right part of the equation for calculation of N, and the sum of the experimental coupling in the left part was doubled.

The obtained results (Table 2) show that the value of ΔG^0 for the majority of the alkyl substituents at the C^5 in 1,3,2-dioxaborinanes vary within 0.8–1.0 kcal mol^{-1}, and for the Ph and *t*-Bu groups is equal to 1.1 and 1.3 kcal mol^{-1}, respectively. These data are very close to the observed values of ΔH and ΔG^0 in the similarly substituted nonboron analogs, 1,3-dioxanes [18]. The lowest value of the free conformational energy is observed for the 5-allyl derivative (ester **IV**). It should be noted that according to the ^{1}H and ^{13}C NMR analysis, 2-oxy-5-methyl-1,3,2-dioxaborinane is characterized by a lower concentration of the equatorial form (75%) [2]. This is in agreement with a lower, as compared to the present work, value of ΔG^0 for methyl group (~0.7 kcal mol^{-1}, 298 K). Nevertheless, the obtained data allow to conclude that the character of interaction of the substituents at the C^5 atom with the heteroatom fragment of the ring is identical both in 1,3-dioxanes and in 1,3,2-dioxaborinanes. The main difference between these two classes of heterocyclic compounds consists in a larger conformational flexibility of the molecules of the six-membered cyclic boron esters due to the absence of steric interactions in the heteroatomic fragment of the ring [1, 10, 15].

EXPERIMENTAL

Boron-*i*-Pr and boron-*i*-Bu analogs of esters **I–IX** are described in [19], and some ^{1}H NMR spectra – in refs. [5, 12]. NMR spectra for esters **II** and **VIII** were registered on a AM-250 Bruker spectrometer with working frequency 250 MHz for 10% solutions in $CDCl_3$ with TMS as an external standard.

Simulation of conformational isomerization was performed by optimization of geometry of the molecules of esters **I–IX** with variation of the endocyclic torsional angle OCCC within ±50°. The route of interconversion and the values of potential barriers were found using the procedure for search of transition states as implemented in the HyperChem software [13]. The stationary points on the PES as transition states (form 2,5-*T*) were confirmed by the presence of one imaginary frequency of the Hessian matrix.

The modified Carplus equation has the form [17]:

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

where $\Delta\chi_i$ is the difference of electronegativities between the substituents of the corresponding ethane fragment and hydrogen, φ is the calculated torsional angle between the interacting protons, ξ_i is equal to ±1 depending on the orientation of the substituents at the carbon atoms of the ethane fragment, P_1–P_6 are parameters depending on the degree of substitution in the fragment. For its solution the numerical values of parameters P_1–P_6 for fragments with three substituents were used: P_1 = 13.22, P_2 = –0.99, P_3 = 0, P_4 = 0.87, P_5 = –2.46, P_6=19.9°, as well as the values of electronegativities from [20]. The ΔG^0 value was determined for temperature 298 K, at which the ^{1}H NMR spectra were registered.

REFERENCES

1. Gren', A.I. and Kuznetsov, V.V., *Khimiya tsiklicheskikh efirov bornykh kislot* (Chemistry of Tricycles Esters of Boron Acids), Kiev: Naukova Dumka, 1988.
2. Rossi, K. and Pihlaya, K., *Acta Chem. Scand. B.*, 1985, vol. 39, no. 8, p. 671.
3. Matteson, D.S., *J. Organometal. Chem*., 1999, vol. 581, no. 1, p. 51.
4. Kuznetsov, V.V., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 1, p. 71.
5. Kuznetsov, V.V., Zakharov, K.S., Petrovskii, I.V., and Gren', A.I., *Chem. Heterocycl. Comp*., 1990, vol. 26, no. 8, p. 927.
6. Kliegel, W., Preu, L., Rettig, S.J., and Trotter, J., *Can. J. Chem*., 1986, vol. 64, no. 9, p. 1855.
7. Kuznetsov, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 2005, vol. 54, no. 7, p. 1543.
8. Valiakhmetova, O.Yu., Bochkor, S.A., and Kuznetsov, V.V., *Sovremennye Naukoemkie Tekhnologii*, 2006, no. 2, p. 72.
9. Valiakhmetova, O.Yu., Bochkor, S.A., and Kuznetsov, V.V., *Bash. Khim. Zh*., 2004, vol. 11, no. 12, p. 79.
10. Kuznetsov, V.V., *Uspekhi organicheskogo kataliza i khimii geterotsiklov* (Succesfull of Organic Catalyst and Heterocyclic Chemistry), Moscow: Khimiya, 2006.
11. Valiakhmetova, O.Yu., Bochkor, S.A., and Kuznetsov, V.V., *Zh. Org. Khim.*, 2008, vol. 44, no. 5, p. 783.
12. Kuznetsov, V.V., Novikov, A.N., Rublev, I.S., and Markolenko, P.Yu., *Chem. Heterocycl. Comp*., 2003, vol. 39, no. 3, p. 379.
13. *HyperChem 7.01. Trial version. www.hyper.com*.

14. Carton, D., Pontier, A., Ponet, M., Soulie, J., and Cadiot, P., *Tetrahedron Lett*., 1975, no. 28, p. 2333.
15. Kuznetsov, V.V., Valiakhmetova, O.Yu., and Bochkor, S.A., *Chem. Heterocycl. Comp*., 2007, vol. 43, no. 12, p. 1577.
16. Zefirov, N.S., Blagoveshchenskii, V.S., Kazimirchik, I.V., and Yakovleva, O.P., *Zh. Org. Khim*., 1971, vol. 7, no. 3, p. 594.
17. Haasnoot, C.A.G., de Leeuw, F.A.A.M., and Altona, C., *Tetrahedron*, 1980, vol. 36, no. 19, p. 2783.
18. *Internal Rotation in Molecules*, Orville-Thomas, W.J., Ed., London: Wiley, 1974.
19. Kuznetsov, V.V., *Dep. VINITI*, Moscow, 1983, no. 5646-83.
20. Huggins, M.L., J. *Am. Chem. Soc*., 1953, vol. 75, no. 17, p. 4123.