STEREOCHEMISTRY OF HETEROCYCLES

XLIX.* INVESTIGATION OF THE CONFORMATION OF ALKYL-1,3,2-DIOXABORINANES BY PMR SPECTROSCOPY

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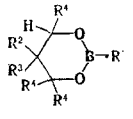
A number of previously undescribed alkyl-1,3,2-dioxaborinanes were synthesized by condensation of substituted 1,3-diols with alkylboron dichlorides or dibutyl isopropylborate. It was shown by PMR spectroscopy that the 2,5-dialkyl-1,3,2-dioxaborinane molecules are conformationally homogeneous and do not contain an axial substituent in the 5 position, whereas the 2-isopropyl-5,5-dimethyl-1,3,2-dioxaborinane molecules exist in a state of rapid ring inversion, and introduction of methyl substituents in the 4, 4, and 6 positions of the 1,3,2-dioxaborinane ring leads to distortion of the ring conformation and conformational heterogeneity of the investigated sample. The observed regularities are explained from the position of intensive "oxygen–boron" electron exchange in the heteroring. It is concluded that the 2,5-dialkyl-1,3,2-dioxaborinane molecules have primarily a conformation with a semiplanar form.

Systematic studies with respect to the conformational analysis of 1,3-dioxanes and 1,3-dithianes [2, 3] have made it possible to establish a number of principles resulting from the presence of 1,3-nonbonding interactions in the ring. Taking the results of these studies into account, we undertook the synthesis of a number of alkyl-1,3,2-dioxaborinanes (I-V) in order to study their stereochemical peculiarities. We expected that because of the planar configuration of the boron atom, the number of nonbonding 1,3 interactions would be different than in 1,3-dioxanes. The synthesis of compounds of this type is also of interest from a practical point of view, since 1,3,2-dioxaborinanes are extremely promising as additives for gasolines and hydrocarbon lubricants [4].

From the few available studies devoted to the stereochemistry of individual representatives of this series [5-8] it is known that the methyl group in 2-phenyl-5-methyl-1,3,2-dioxaborinane is equatorially oriented [5]. The introduction of a second methyl group in the 5 position of the dioxaborinane ring leads to rapid ring inversion with a rather low barrier of 7-8 kcal/mole [5, 6]. The molecules of 2-substituted 4,4,6-trimethyl-

TABLE 1



Compound	R¹	R²	R³	R⁴	bp, °C (mm)	d_4^{20}	n_D^{20}	Empirical formula	B, % found	B, % calc.	Yield, %
I	*i*-C_3H_7	*i*-C_3H_7	H	H	72 (5)	0,8937	1,4317	$C_9H_{19}BO_2$	6,2	6,5	30
II	*i*-C_3H_7	C_6H_{13}	H	H	102 (3)	0,8951	1,4360	$C_{12}H_{25}BO_2$	4,8	5,2	42
III	*i*-C_3H_7	CH_3	CH_3	H	58—59 (13)	0,8989	1,4218	$C_8H_{17}BO_2$	7,1	7,1	33
IV	*i*-C_3H_7	H	H	CH_3	38 (8)	0,8815	1,4265	$C_9H_{19}BO_2$	6,1	6,5	40
V	*t*-C_4H_9	H	H	CH_3	48 (10)	0,8423	1,4112	$C_{10}H_{21}BO_2$	5,6	6,0	62

*See [1] for communication XLVIII.

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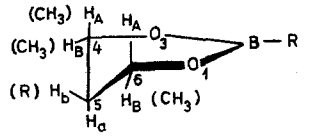
TABLE 2. Chemical Shifts and Spin–Spin Coupling Constants of Alkyl-1,3,2-dioxaborinanes



Compound	δ, ppm										J, Hz				
	2-R	4-H_A	4-H_B	4-$(CH_3)_2$	5-H_a	5-$(CH_3)_2$	5-H_b	6-H_A	6-H_B	6-CH_3	$^2J_{AB}$	$^3J_{Aa}$	$^3J_{Ba}$	$^3J_{Ab}$	$^3J_{Aa}$
I	1,00	3,50	3,80	—	1,30	—	—	3,50	3,80	—	−10,0	10,0	4,5	—	10,0
II	1,20	3,77	4,27	—	1,56	—	—	3,77	4,27	—	−10,0	10,0	4,0	—	10,0
III	1,01	3,46		—	—	0,86	—	3,46		—	—	—	—	—	—
IV	1,11	—	—	1,57	1,84	—	1,84	3,75 4,35	—	1,48	—	—	—	4,0	8,0
V	1,19	—	—	1,55	1,85	—	1,85	3,75 4,38	—	1,50	—	—	—	4,0	8,0

1,3,2-dioxaborinanes are conformationally less labile than 1,3-dioxane molecules [7, 8], although ring inversion evidently also occurs for them [6].

However, the lack of systematic studies of the stereochemistry of compounds of this type does not make it possible to estimate the effect of substituents on the primary conformation of the 1,3,2-dioxaborinane ring. The reasons responsible for the realization of only the 5e conformer of 2-substituted 5-methyl-1,3,2-dioxaborinane or inversion of the ring of 2-substituted 5,5-dimethyl- and 4,4,6-trimethyl-1,3,2-dioxaborinanes are not examined in the papers cited above.

Alkyl-1,3,2-dioxaborinanes I-V (Table 1) were synthesized by the methods in [9, 10].

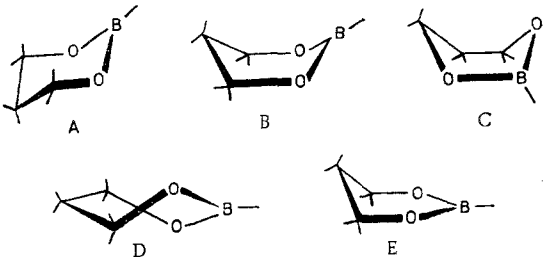
The IR spectra of all of the synthesized compounds contain an intense band at 1335-1345 cm^{-1}, which corresponds to the stretching vibrations of the B–O bond, an intense band at 1300 cm^{-1}, which is characteristic for the stretching vibrations of the B–C bond [11], and a number of bands of variable intensity at 980-1180 cm^{-1}, which correspond to the vibrations of the C–O bond.

The $^3J_{4,5}$ values and the magnetic nonequivalence of the ring methylene protons (Table 2) in the PMR spectra of I and II indicate the absence of ring inversion and the realization of only one primary conformation with an equatorial alkyl group attached to 5-C. It is characteristic that this sort of conformational homogeneity is not observed in the case of 5-isopropyl-1,3-dioxanes and 1,3-dithianes [2, 3].

In conformity with the data in [5, 6], the PMR spectrum of III contains singlet resonance signals of ring methylene protons and gem-dimethyl groups attached to the 5-C atom. This character of the signals constitutes evidence in favor of ring inversion.

To explain the observed regularities we assume practically complete sp^2 hybridization of the ring oxygen atoms and, as a consequence of this, the presence of stronger (than in 1,3-dioxanes) 1,3-nonbonding interactions of the "alkyl–unshared electron pairs of the ring heteroatoms" type, which hinder realization of a conformation with an axial orientation of the alkyl group attached to 5-C. In fact, the considerable p-electron exchange [4, 11] between the oxygen and boron atoms should lead to a change in the spatial orientation of the orbitals of the unshared electron pairs of the ring oxygen atoms and to reinforcement of the p character of the latter. The COB valence angle in 1,3,2-dioxaborinane, which, according to the results of x-ray diffraction measurements [12], is 120°, a value that speaks in favor of an sp^2-hybridized oxygen atom, may serve as a confirmation of this conclusion; the p orbital of the free electron pair is perpendicular to the plane passing through the nucleus of the oxygen atom and two of its bonds. On the other hand, the presence of a considerable barrier to rotation about the B–O bond, which, according to the data in [13], is 9-12 kcal/mole, should somewhat stabilize a conformation whose geometry allows parallel character of the orbitals of the unshared electron pairs of the oxygen atoms and a vacant $2p_Z$ orbital of the boron atom; i.e., in other words, it should create conditions for maximum "oxygen–boron" electron exchange. Analysis of the Dreiding models of the possible conformations of 1,3,2-dioxaborinanes provides evidence that the conformation of the half-chair form (E) is the most favorable in this sense.

Data from x-ray diffraction analysis of 2-hydroxy-4,6-dimethyl-1,3,2-dioxaborinane [12] also provide evidence in favor of the E conformation; the value of the dihedral angle formed by the O_1, B, O_3 and C_4, C_5, and C_6 planes calculated from these data is 132°.



It follows from the above material that the "preferred" conformation for 2,5-dialkyl-1,3,2-dioxaborinane molecules is the semiplanar form or a very strongly compressed (in the heteroatomic portion of the ring) chair and that the nature of the 1,3-nonbonding interactions evidently consists in mutual repulsion of the axial substituent attached to 5-C and the electron pairs of the oxygen atoms perpendicular to the plane of the heteroatomic portion of the molecule. The same reason is one of the major reasons for ring inversion of III.

The "oxygen–boron" electron exchange probably also changes the resonance conditions of the protons of the isopropyl substituent attached to the boron atom in I-IV (Table 2), which shows up in the spectrum in the form of an anomalous singlet instead of a doublet. Data on an anomaly of this type are not available in the literature. This anomaly may be due to a change in the shielding constant of the methylidyne proton of the isopropyl group, evidently under the influence of the magnetic anisotropy of the B–O bond, as a result of which it becomes practically magnetically equivalent to the protons of the methyl groups of the isopropyl group.

One's attention is directed to the character of the resonance band of the methylene protons attached to the 5-C atom and the proton attached to 6-C in the PMR spectra of IV and V. The former give a multiplet centered at δ 1.85 ppm, while the latter give a low-intensity triplet at 3.75 ppm ($^3J = 8.0$ Hz) and a complex multiplet centered at 4.38 ppm. All of this provides a basis for the assumption that IV and V are conformationally heterogeneous mixtures containing flexible form D. This conclusion is in good agreement with the above-noted change in the spatial orientation of the unshared electron pairs of the oxygen atoms, which causes an increase in the conformational ring strain because of a "4-CH_3–electron pair" shielded interaction in the semiplanar chair conformation. Transition to the D conformation weakens this interaction, as well as the 1,3 interaction of the axial CH_3 group with the 6-H proton, although it also leads to a certain amount of disruption of the p-electron exchange between oxygen and boron.

Thus the results obtained in this research make it possible to assume that the realization of one "preferred" conformation with a 5e orientation of the alkyl group of inversion and conformational heterogeneity of the 1,3,2-dioxaborinane ring are determined mainly by the peculiarities of the "alkyl–unshared electron pairs of the ring oxygen atoms" nonbonding interaction.

To obtain additional data on the "preferred" conformation we calculated the dipole moments for the A-E conformations of 2,5-dialkyl-1,3,2-dioxaborinane (Table 3). The "preferableness" of the conformation of the semiplanar form for a number of 5-nitro-5-alkyl-2-phenyl-1,3,2-dioxaborinanes was previously proved [14] by this method. However, our data constitute evidence for the low degree of suitability of the dipole-moment method for the conformational analysis of 2,5-dialkyl-1,3,2-dioxaborinanes in view of the small differences in the dipole moments calculated for the various conformations.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in chloroform and carbon tetrachloride were measured with an RS-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of solutions in carbon tetrachloride were recorded with a UR-20 spectrometer. The starting data for the calculation of the dipole moments were: angles OBO 123°48', COB 119°57', CCO 109°54', and CCC 111°54'; bond lengths B–O 1.362, C–O 1.459, and C–C 1.510 Å [12]; dipole moments B←O ~ 0.40, B→C ~ 0.25, C→O ~ 0.86, and C←H ~ 0.30 D [14].

TABLE 3. Calculated and Experimental Dipole Moments of the Conformers of 2,5-Diisopropyl-1,3,2-dioxaborinane

Conformer	A	B	C	D	E
μ_{calc}, D	2,49	2.49	2,36	2,36	2,49
μ_{exp}, D	2,46				

The μ_{exp} value was determined from the experimental dielectric permeabilities measured with a Tangens apparatus.

The individuality of the investigated substances was monitored by gas-liquid chromatography with LKhM-7M and LKhM-8M chromatographs; the detector was a catharometer, the phases were E-301, SKTFT-50, and Carbowax-20M, the column temperature was 125-135°C, and the carrier-gas (helium) flow rate was 3.5 ml/min.

1,3,2-Dioxaborinanes I and III [9]. A mixture of equimolar amounts of 2,2-dimethyl- [15] or 2-isopropyl-1,3-propanediol [16] and dibutyl isopropylborate [17] was refluxed in a nitrogen atmosphere for 5 h, after which it was subjected to vacuum distillation.

1,3,2-Dioxaborinanes II, IV, and V [10]. A solution of 0.05 mole of 2-hexyl-1,3-propanediol (obtained by reduction of the corresponding malonic ester by the method in [16]) or 2-methyl-2,4-pentanediol (synthesized by reduction of diacetone alcohol with sodium borohydride by the general method in [19]) in 50 ml of methylene chloride was added dropwise with stirring to a cooled (to 0°C) solution of 0.05 mole of alkylboron dichloride [18] in 70 ml of methylene chloride in a nitrogen atmosphere, after which the mixture was heated at 40°C until hydrogen chloride evolution ceased completely (~3 h). The methylene chloride was then removed by distillation, and the residue was fractionated in vacuo.

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