CONFORMATIONAL BEHAVIOR OF 2-, 2,3-, 2,5-, AND 2,3,5-ALKYL-SUBSTITUTED 1,3,2-OXAZABORINANES

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The molecules of 2- and 2,3-substituted 1,3,2-oxazaborinanes exist in a state of interconversion of the heterocycle that is rapid on the NMR time scale; the molecules of 2,5- and 2,3,5-substituted 1,3,2-oxazaborinanes exist primarily in the sofa conformation.

The conformational properties of molecules of 1,3,2-dioxaborinanes are determined to a great degree by the boron–heteroatom partial double bond [1, 2]. Here we are reporting on an investigation of the conformational behavior of 2-, 2,3-, 2,5-, and 2,3,5-substituted 1,3,2-oxazaborinanes, using ^1H and ^{13}C NMR spectroscopy.

The spectra of the 2-substituted 1,3,2-oxazaborinanes I-III (Table 1) contain signals of the 4-H–6-H protons with vicinal SSCC $^3J = 5.5$-5.8 Hz. This is evidence in favor of heterocycle interconversion, rapid on the NMR time scale, between two energetically equivalent forms, with simultaneous inversion of the nitrogen atom.

Variation of the substituent on the boron atom does not affect the character of the spectrum. Here we must note the upfield shift (in comparison with monotypical substituted 1,3,2-dioxaborinanes [1]) of the signals of the 4-H protons, amounting to about 0.7 ppm, this shift being related to redistribution of electron density in the heteroatomic part of the ring as a consequence of replacement of one of the oxygen atoms by a nitrogen atom.

In the NMR spectra of the 2,3-substituted 1,3,2-oxazaborinanes IV-IX, the character of the signals from the protons in the carbon part of the ring and the values of the vicinal SSCC also indicate heterocycle interconversion that is rapid on the NMR time scale. We were not able to determine the interconversion barrier, owing to the low temperature of coalescence (below –85°C).

In the spectra of the 2,5-substituted 1,3,2-oxazaborinanes X and XI, the protons on the N and $C_{(4)}C_{(6)}$ atoms form an ABCDMX spin system (Table 1). The values of the vicinal SSCC provide unambiguous evidence of equatorial orientation of the substituents on the $C_{(5)}$ atom. The constants $^3J_{ANH}$ and $^3J_{BNH}$ indicate equatorial orientation of the N–H proton and hence an axial position of the n-electron pair. The hybrid state of the nitrogen atom bound to the boron atom approaches sp^2. According to data obtained by electron diffraction and x-ray structural measurements, the structure of the nitrogen atom in aminoboranes is almost planar [3-6], and the experimental barrier to rotation around the B–N bond is estimated at 20 kcal/mole [7, 8]. All of this provides grounds for believing that the predominant conformation of the molecules of 2,5-substituted 1,3,2-oxazaborinanes is the sofa, which allows maximum electron exchange between the vacant orbital of the boron atom and the coplanar n-electron pairs of the nitrogen and oxygen atoms. It is known that this sort of conjugation stabilizes planar conformations of organoboron compounds containing at least two boron–heteroatom bonds [1], in particular the sofa conformation for 2,5-substituted 1,3,2-dioxaborinanes [2].

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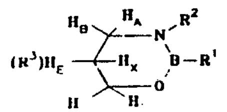
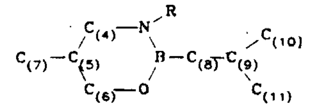
TABLE 1. Parameters of ^{1}H NMR Spectra of Substituted 1,3,2-Oxazaborinanes



Compound	R^1	R^2	R^3	H_A	H_B, m	H_X, m	H_E	H_C, t	H_D	R^1	R^2	J, Hz				
												$^3J_{AX}$	$^3J_{BX}$	$^3J_{CX}$	$^3J_{DX}$	other J
I	C_2H_5	H	H	3,1 m		1,54 q		3,84 t		0.54	3,1	5,8		5,5		—
II	C_3H_7	H	H	3,04 m		1,63 q		3,82 t		0,62	3.05	5,8		5,5		—
III	i-C_4H_9	H	H	3,26 m		1,73 q		3,65 t		0,46	2,95	5,8		5,5		—
IV	C_2H_5	t-C_4H_9	H	2,68 t		1,72 m		3,91 t		0,78	1,13	5,5		5,5		—
V	C_3H_7	t-C_4H_9	H	2,71 t		1,68 m		3,92 t		0,75	1,15	5,5		6,5		—
VI	C_2H_5	C_6H_{11}	H	2,85 t		1,98 m		3,95 t		0,72	—	5,5		5,5		—
VII	C_3H_7	C_6H_{11}	H	2,84 t		1,78 m		4,28 t		0,71	—	5,5		5,5		—
VIII	C_2H_5	C_6H_5	H	2,91 t		1,51 m		3,83 m		0,65	6.5	5,5		6,5		—
IX	C_2H_5	$CH_2C_6H_5$	H	2,78 m		1,83 m		3,91 t		0,78	4,11	5,5		5,5		—
X	i-C_4H_9	H	$CH_2C_6H_5$	2,73 m	2,97	2,15	—	3,69	4,05	0,65	3.10	8,3	4,4	10,2	4,6	$^3J_{ANH}=1,6$; $^3J_{BNH}=4,4$
XI	C_2H_5	H	C_6H_{13}	2,67 t	3,06	2,00	—	3,30	4,01	0,75	3,12	9,8	4,8	10,4	4,4	$^3J_{BNH}=4,8$
XII	C_2H_5	C_6H_{11}	CH_3	2,47 t	2,89	1,90	—	3,41	3,83 m	0,75	—	9,8	4,6	10,2	4,2	$^2J_{AB}=-10,0$
XIII	C_3H_7	C_6H_{11}	CH_3	2,45 t	2,91	1,85	—	3,43	3,75 m	0,72	—	9,8	4,6	10,2	4,2	$^2J_{AB}=-10,0$
XIV	C_2H_5	$CH_2C_6H_5$	CH_3	2,51 t	2,70	2,02	—	3,48	3,89 m	0,95	7,25	10,2	5,2	10,5	4,6	
XV	C_3H_7	$CH_2C_6H_5$	CH_3	2,58 t	2,78	2,10	—	3,55	3,95 m	1,05	7.35	10,2	5,2	10,5	4,6	$^2J_{AB}=-10,8$

TABLE 2. Parameters of ^{13}C NMR Spectra of Substituted 1,3,2-Oxazaborinane



Compound	δ, ppm								
	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	C—N
III	38,5	28,4	62,4	—	27,0	25,5	25,7		—
V	37,9	31,0	60,0	—	17,1	15,7	15,1	—	48,3
VI	38,1	27,5	62,0	—	8,8		—	—	55,5
VII	38,4	27,7	62,1	—	17,0	18,5	17,1	—	55,6
VIII	41,5	31,0	61,7	—	8,6		—	—	148,3
IX	45,1	28,5	62,8	—	10,0		—	—	54,9
X	43,5	36,3	66,2	38,2	25,5	24,8	25,4		—
XIII	34,3	26,3	68,0	14,7	8,8		—	—	56,7
XV	51,7	31,3	68,0	14,6	8,7		—	—	53,4

The values of the vicinal SSCC in the spectra of the 2,3,5-substituted 1,3,2-oxazaborinanes XII-XV indicate the absence of any distortion of the carbon fragment of the molecule, as well as a predominantly equatorial orientation of the substituent on the $C_{(5)}$ atom. For the molecules of these compounds, quite apparently, the sofa conformation with equatorial orientation of the substituent on the nitrogen atom is also characteristic.

A study of the ^{13}C NMR spectra of individual compounds (III, V-X, XIII, XV) showed that when the change is made from the 2-substituted derivative to the 2,3-substituted derivative with an N-cyclohexyl group (compounds III, VI, and VII), the chemical shifts of the ring carbon atoms remain practically unchanged (Table 2). However, in the spectrum of the N-tert-butyl analog V, we observe a downfield shift of the $C_{(5)}$ signal ($\Delta\delta$ = 3.5-2.6 ppm) and an upfield shift of the signals of the $C_{(4)}$ atom ($\Delta\delta$ = 0.6-0.2 ppm) and the $C_{(6)}$ atom ($\Delta\delta$ = 2.4-2.0 ppm). The identity of the conformational behavior of the molecules of compounds III and V-VII at room temperature suggests that the observed differences are due mainly to the paramagnetic contribution [9]. For compounds VIII and IX, which contain aryl groups on the nitrogen atom, there is also a significant influence from the magnetically anisotropic component of the chemical shift. Its contribution can also be observed upon comparing the spectra of the conformationally similar compounds X, XIII, and XV.

EXPERIMENTAL

The substituted 1,3,2-oxazaborinanes have been described in [10]. The ^{1}H NMR spectra were measured in an AM-250 instrument (250 MHz) for 20% solutions in $CDCl_3$, relative to TMS (internal standard). The low-temperature investigations using ^{1}H NMR were performed in a BS-597 instrument (100 MHz) for 20% solutions of compounds IV-XI in C_6D_6 and toluene (TMS standard) at temperatures of 0, −30, −50, −70, and −85°C. The ^{13}C NMR spectra of 40-50% solutions of the test compounds in $CDCl_3$ were measured with natural content of ^{13}C isotope in an AM-250 instrument (62.89 MHz) and in a BS-597 instrument (25.14 MHz) (compound V) in the Fourier transform mode with complete and incomplete proton decoupling. Internal standard TMS.

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