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CONFORMATION OF 2,5-SUBSTITUTED 1,3,2-DIOXABORINANES STUDIED BY NMR

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UDC 547.87'841'244:541.63:543.422.25

The conformation of a series of 2,5-substituted 1,3,2-dioxaborinanes is studied by PMR. The preferred conformation for the majority of compounds has an equatorial group on atom $C_{(5)}$. The 5-nitroderivative exists in the conformation with an axial nitro group.

The conformations of 1,3,2-dioxaborinanes are largely determined by the electronic interactions in the B–O bonds. Thus, the majority of these molecules have a preferred half-planar shape [1-3]. Quantum chemical calculations confirm the suitability of this conformation [4]. The present work reports an NMR study of the conformation of 2,5-substituted 1,3,2-dioxaborinanes with different substituents on atom $C_{(5)}$ (Table 1).

It has already been noted that the heteroatomic fragment increases (in comparison to the analogs without boron, 1,3-dioxanes) the conformational energy of the alkyl substituent on $C_{(5)}$ [3]. For a methyl group, the experimental values are ΔG^0 = 3.3-4.2 kJ/mole for 1,3-dioxanes [9] and at least 10.5 kJ/mole for 1,3,2-dioxaborinanes. The latter values were obtained from data for the configurational isomerization of 2-isopropyl-4,5-dimethyl-1,3,2-dioxaborinane [10]. It seemed interesting to measure the energy by an independent method using averaged and standard SSCC and the equation [11]

$$^3J_{AX}+{}^3J_{BX}=N(J_{aa}+J_{ae})+(1-N)(J_{ea}+J_{ee}),$$

where N is the fraction of equatorial conformer, $^3J_{AX}$ and $^3J_{BX}$ are the observed (averaged) SSCC in the molecule studied, and J_{ae}, J_{ee}, J_{aa}, and J_{ea} are the standard SSCC. Using the constants from the spectra of cis- and trans-2-isopropyl-4,5-dimethyl-1,3,2-dioxaborinane (J_{aa} = 10.5, J_{ae} = 4.4, J_{ea} = 7.4, J_{ee} = 4.2 Hz [3]), we find that N = 0.97 for compound I. This means that at room temperature in the equilibrium system

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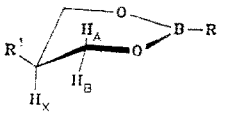
0009-3122/90/2608-0927$12.50

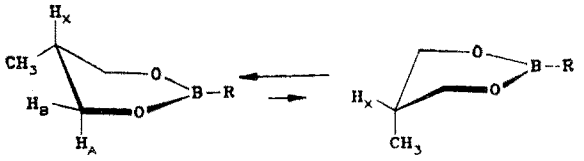
TABLE 1. PMR Spectra of 2,5-Substituted 1,3,2-Dioxaborinanes*



Compound**	R'	δ, ppm			J, Hz		
		H_A	H_B	H_X	$^3J_{AX}$	$^3J_{BX}$	$^2J_{AB}$
I	CH_3	3,58	3.91	1,47	10,0	4,8	10,8
II	i-C_3H_7	3,43	3,83	1,30	10,0	4,5	10,0
III	i-C_4H_9	3,42	3,85	1,54	10,8	4,3	11,0
IV	t-C_4H_9	3,45	3,73	1,59	10,9	4,1	10,6
V	C_6H_{13}	3,63	4,03	2,00	10,3	4,4	10,8
VI	C_7H_{15}	3,52	3,92	1,92	9,8	4,4	11,0
VII	C_6H_5	3,40	3,58	2,45	10,0	4,9	10,0
VIII	$C_6H_5CH_2$	3,86	4,16	2,42	10,8	4,5	10,5
IX	CH_2=CH—CH_2	3,42	3,83	1,58	10,2	3,8	10,8
X	NO_2	4,54	4,86	4,98	2,9	1,9	11,8

*The PMR spectrum of compounds I-VI and VIII-X were recorded in CCl_4; compound VII, in C_6H_6.

**For I-V and VII-X, R = i-C_3H_7; for VI, R = i-C_4H_9.



K = 32.3 and ΔG^0 = 8.4 kJ/mole. Thus, our data correlate approximately with the result of the configurational method [10]. The amount of axial conformer at room temperature for 5-methyl-1,3-dioxane determined from the corresponding equilibrium constants [9] is ~16-20%. The substantial difference from 5-methyl-1,3,2-dioxaborinanes indicates a qualitative stereochemical uniqueness for the latter due to structural features of the heteroatomic fragment.

The AB part of the spectrum of the 5-phenyl derivative of VII in CCl_4 has a high order due to the small $\Delta\delta$ value of the ring methylene protons (<0.01 ppm). Using benzene as solvent increases $\Delta\delta$ to 0.18 ppm and makes possible first-order analysis.

In contrast to other 2,5-substituted 1,3,2-dioxaborinanes, the substituent on $C_{(5)}$ is primarily axial for compound X. Changing solvent (CCl_4, nitrobenzene) does not change the nature of the spectrum (with the exception of the large difference in chemical shifts of protons H_B and H_X in nitrobenzene). The preference for the axial conformer of the 5-nitro-1,3,2-dioxaborinanes is also supported by dipole moment measurements [6]. In a series of substituted cyclohexanes, the nitro group is primarily equatorial (ΔG^0 = –4.6 kJ/mole), whereas in 5-nitro-1,3-dioxane it occupies the axial position (ΔG^0 = 1.6 kJ/mole in CCl_4) [12]. The similarity in conformational behavior of 5-nitro derivatives of 1,3,2-dioxaborinanes and 1,3-dioxanes in all probability is due to "internal solvation" of the oxygen atom p-electron pairs by the axial nitro group through interaction with the heteroatomic part of the molecule. Due to this, 1,3-dioxanes gain 6.3 kJ/mole. This type of electronic effect is impossible for the equatorial conformer for steric reasons [12].

EXPERIMENTAL

PMR spectra were measured on a BS-497 spectrometer for 15-20% solutions in CCl_4, benzene, and nitrobenzene (TMS internal standard). The compounds I-X have been described earlier [13].

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NONAROMATIC ISOXAZOLINEDIAZONIUM SALTS

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UDC 547.786.1.04:542.958.-3:543.422

Diazotization of 3-aminoisoxazolines has given stable, nonaromatic 2-isoxazoline-3-diazonium salts which undergo the azo-coupling reaction. The electronic structures of these diazo- and azo-compounds are discussed.

Direct diazotization of the appropriate amines in aqueous media has given the nonaromatic 2-pyrazoline-3-diazonium [1, 2] and 1,3,4-thiadiazoline-5-diazonium salts [3] (the reactivity of which is comparable with that of aromatic salts). Continuing these investigations, we have examined the possibility of obtaining 2-isoxazoline-3-diazonium salts by diazotizing 3-amino-2-isoxazolines.

Treatment of the 3-amino-2-isoxazolines (I) with sodium nitrite in acetic, hydrochloric, phosphoric, or nitrosylsulfuric acid in acetic acid gives the 2-isoxazoline-3-diazonium salts (II), which are intermediate in terms of stability in aqueous solution between pyrazoline- and thiadiazolinediazonium salts. Pyrazolinediazonium salts are stable in aqueous hydrochloric acid at 20-25°C for several days [2], and thiadiazolinediazonium salts for a few seconds [3], while the cations (II) decompose under these conditions within 2-3 h.

5-Phenylisoxazolinediazonium fluoroborate (IIb) can be isolated in the solid state but, since it is less stable than pyrazolinediazonium salts, not in an analytically pure state. Its IR spectrum shows stretching vibrations for the diazonium group at 2280 cm^{-1}, i.e., in the range usual for aromatic diazonium salts (2290 cm^{-1} for benzenediazonium chloride [4]). In the case of pyrazolinediazonium cations, diazonium group absorption is seen, depending on the substituent X attached to $N_{(1)}$, between 2125 cm^{-1} when X = Ph and 2265 cm^{-1} when X = $PhSO_2$ [2]. It is therefore apparent that the tendency of the lone pair on oxygen in the isoxazolinediazonium cation (IIb) to conjugate with the C=N double bond and the diazonium group is less than that of the nitrogen in the 1-phenylpyrazolinediazonium cation, which is in accordance with a decreased contribution of the diazo-structure (II') as compared with its contribution in its pyrazoline analog.

Research Institute for Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1110-1112, August, 1990. Original article submitted January 2, 1989; revision submitted June 27, 1989.

0009-3122/90/2608-0929$12.50