FEATURES OF SIGNALS FROM PROTONS OF ALKYL GROUP ON BORON ATOM IN PMR SPECTRA OF 1,3,2-OXAZABORINANES

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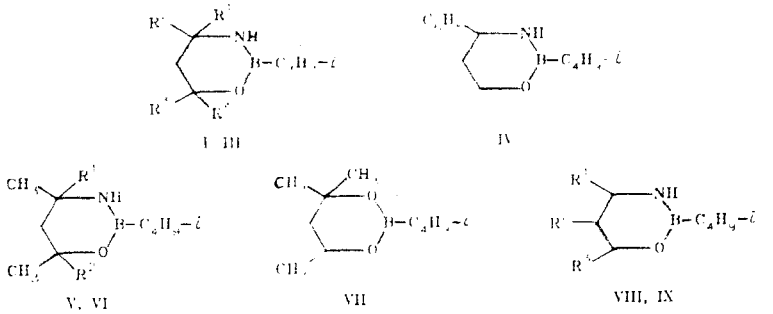
It has been shown that the signal from isopropyl-group protons in the PMR spectra of 2-isopropyl-1,3,2-oxazaborinanes degenerates into a singlet; but the protons of the gem-dimethyl groups and the methylene link in an isobutyl substituent on the boron atom, where a chiral center is present in the molecule, may manifest anisochronicity. In the latter case, $\Delta\delta$ is determined by the character of the solvent, the temperature, and the contribution of the conformation with a flexible form.

It had been shown previously [1, 2] that the signal from isopropyl-group protons in the PMR spectra of cyclic and acyclic esters of isopropylboric acid degenerates into a singlet, owing to superposition of the region of resonance of the methine group and protons of the *gem*-dimethyl groups under the influence of anisotropy of diamagnetic susceptibility of the B—O bond. Here we are reporting on an investigation of the character of the proton signals from isopropyl and isobutyl groups on the boron atom in the PMR spectra of a number of substituted 1,3,2-oxazaborinanes:



I, III

IV

V, VI

VII

VIII, IX

I $R^1=R^2=R^3=R^4=H$; II $R^1=R^2=R^3=CH_3$, $R^4=H$; III $R^1=H$, $R^2=R^3=R^4=CH_3$; V $R^1=CH_3$, $R^2=H$; VI $R^1=H$; $R^2=CH_3$; VIII $R^1=R^2=CH_3$, $R^3=H$; IX $R^1=H$, $R^2=R^3=CH_3$

In the PMR spectra of compounds I-III, the signal from the isopropyl-group protons has the form of a singlet that includes all seven protons, according to integration data. This effect does not depend on the solvent ($CDCl_3$ or C_6D_6), and it is probably due to factors analogous to those that are operative for 1,3,2-dioxaborinanes [2]. From a comparison of the half-width of the experimental signal with values calculated by the use of the PANIC program, it follows that the constant $^3J_{HCH_3}$ is 0.7 Hz. Thus, the observed phenomenon is quite general in character, and it pertains to all compounds containing an i-$C_3H_7BO_2$ or i-C_3H_7BON fragment.

Another interesting feature of the PMR spectra of certain substituted 1,3,2-oxazaborinanes with a chiral center in the molecule is the anisochronicity of protons of an isobutyl group on the boron atom.

The value of $\Delta\delta$ depends on the temperature and the solvent, and also on the type of substitution and the character of the substituents. In the spectrum of compound IV, which contains an aromatic substituent on the chiral center, i.e., on the $C_{(4)}$ atom, the value of $\Delta\delta$ is equal to zero, both for the methylene link and for the *gem*-dimethyl groups. For the 2,4,4,6-substituted derivative V the anisochronicity of the protons in question is quite small; for the methylene link at room temperature it is o greater than 0.012 ppm in C_6D_6 (see Table 1). When the temperature is

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TABLE 1. Anisochronicity of Protons of Isobutyl Group on Boron Atom in PMR Spectra of Substituted 1,3,2-Oxazaborinanes (20°C)

Compound	Solvent	Δδ, ppm	
		CH_2	$(CH_3)_2$
V	$CDCl_3$	0	0
	C_6D_6	0,012	0
	CD_2Cl_2	0,001	0,004
	$C_6D_5NO_2$	0	0,003
	$(CD_3)_2SO$	0,004	0
VI	$CDCl_3$	0,030	0,006
	C_6D_6	0,047	0
	CD_2Cl_2	0,030	0,007
	$C_6D_5NO_2$	0,054	0,002
	$(CD_3)_2SO$	0,035	0,006
VII	$CDCl_3$	0,003	0,006
	C_6D_6	0,017	0,009
cis-VIII	$CDCl_3$	0	0
	C_6D_6	0,028	0
cis-IX	$CDCl_3$	0,013	0
	C_6D_6	0,033	0

TABLE 2. Temperature Dependence of Δδ of Diastereotopic Protons of Isobutyl Group in PMR Spectra of Compounds V and VI

Compound	T, °C	Δδ, ppm (CD_2Cl_2)	
		CH_2	$(CH_3)_2$
V	20	0,001	0,004
	0	0,008	0,006
	−20	0,012	0,007
	−40	0,077	0,008
	−60	0,086	0,009
	−80	0,096	0,013
VI	20	0,030	0,007
	0	0,087	0,008
	−20	0,094	0,010
	−40	0,101	0,012
	−60	0,112	0,015
	−80	0,127	0,019

raised to only 50°C (in DMSO-D_6), the anisochronicity becomes unobservable. In CD_2Cl_2 solution at 20°C the value of Δδ is close to zero, but it increases considerably when the temperature is lowered (so-called conformative anisochronicity [3], Table 2). Here, Δδ for the *gem*-dimethyl groups is smaller in most cases than for the methylene link.

An analogous picture is observed for the 2,4,6,6-substituted derivative (VI), but in this case Δδ increases (see Table 2). In the spectrum of the model compound 2-isobutyl-4,4,6-trimethyl-1,3,2-dioxaborinane (VII), Δδ assumes values in the interval between compounds V and VI (see Table 1).

The presence of two chiral centers in the molecules does not introduce any substantial changes. In the spectrum of the stereoisomeric 2,4,5- and 2,5,6-substituted derivatives (VIII and IX, respectively), the anisochronicity of the protons of the *gem*-dimethyl groups is unobservable; Δδ of the methylene link is nonzero only for the *cis* isomers, and is somewhat greater for compound IX (see Table 1).

Thus, we have not found any clear-cut dependence of Δδ on the distance of the diastereotopic protons from the chiral center or on the character of substitution of the 1,3,2-oxazaborinane ring. This indicates a complex character of formation of Δδ of the diastereotopic protons of the isobutyl group, owing to the action of several factors. We can only note at the present time that, apart from a lowering of temperature and the influence of an aromatic solvent, a significant role in increasing the value of Δδ is played by the character of the predominant conformation. Molecules of the *trans* isomers of compounds VIII and IX exist predominantly in the sofa conformation; for the *cis* isomers, the 2,5-twist form is characteristic [4]. Consequently, for alkyl-substituted 1,3,2-oxazaborinanes in a given solvent and at a given temperature, the value of Δδ of diastereotopic protons of an isobutyl group on the boron atom is greater when the flexible-form conformation predominates.

EXPERIMENTAL

The PMR spectra were measured in an AM-250 instrument (250 MHz) on 20% solutions in $CDCl_3$, C_6D_6, CD_2Cl_2, $C_5D_5NO_2$, and DMSO-D_6, relative to TMS (internal standard). The calculated spectra were obtained in the computer of the AM-250 instrument, using the PANIC program with modeling of the constant $^3J_{HCH_3}$ in the interval from 0 to 2 Hz with a step of 0.1 Hz. The substituted 1,3,2-oxazaborinanes have been described in [5], and the model 1,3,2-dioxaborinane in [6].

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INVESTIGATION OF ISOMERIC FORMS OF 2-AMINOBENZOTHIAZOLES BY ^{13}C NMR SPECTROSCOPY

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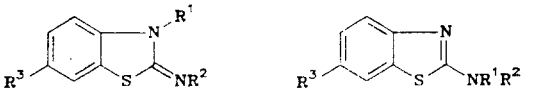
A method is presented for distinguishing the amino and imino isomers in a series of benzothiazoles by ^{13}C NMR. It is shown that this method is suitable for determination of the position of the side chain.

Isomeric 2-aminobenzothiazole derivatives are usually identified by IR, UV, PMR, and mass spectra [1, 2]. However, reliable data are obtained only for relatively simple structures. The presence of branched substituents containing more than one functional group levels the difference between the physicochemical characterizations of the isomers [3], because of which we undertook a study of the ^{13}C NMR spectra of a series of aminobenzothiazoles and iminobenzothiazolines:

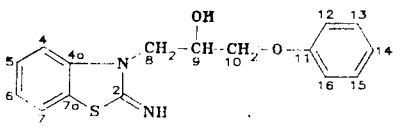


I–IX X–XIV

I $R^1=CH_3$, $R^2=H$; II $R^1=CH_2CH_2OH$, $R^2=H$; III $R^1=CH_2CH_2OH$, $R^2=H$; IV $R^1=CH_2CH(OH)CH_2OC_6H_5$, $R^2=H$; V $R^1=CH_2CH(OH)CH_2OC_6H_5$, $R^2=CH_3$; VI $R^1=CH_3$, $R^2=CH_2CH(OH)CH_2OC_6H_5$; VII $R^1=C_6H_5$, $R^2=CH_2CH(OH)CH_2OC_6H_5$; VIII $R^1=CH_2CH(OH)CH_2OC_6H_5$, $R^2=C_6H_5$; IX $R^1=R^2=CH_2CH(OH)CH_2OC_6H_5$; X $R^1=CH_3$, $R^2=H$; XI $R^1=CH_2CH_2OH$, $R^2=H$; XII $R^1=CH_2CH_2OH$, $R^2=H$; XIII $R^1=CH_2CH(OH)\times$ $\times CH_2OC_6H_5$, $R^2=H$; XIV $R^1=CH_2CH(OH)CH_2OC_6H_5$, $R^2=CH_3$; I, II, IV–XI, XIII, XIV $R^3=H$, III, XII $R^3=CH_3$

The peaks of the carbon atoms were assigned on the basis of spectral data (see Table 1) obtained with complete and incomplete (off-resonance) suppression of C—H interactions and also by comparison with published data of ^{13}C NMR spectra of structurally close thiazole derivatives [4-6] and by taking into account α, β, and γ contributions of substituents [7].

For substituted aminobenzothiazoles and iminobenzothiazolines, the following order of arrangement of the carbon atoms is accepted:



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