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PMR STUDY OF THE CONFORMATIONAL BEHAVIOR OF 2,5,5-TRISUBSTITUTED 1,3,2-DIOXABORINANES

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The conformational behavior of 2,5,5-trisubstituted 1,3,2-dioxaborinanes was studied by PMR spectroscopy. Molecules with similar substituents at $C_{(5)}$ are in a state of rapid ring inversion between two energetically equivalent forms. In the case of different substituents, the inversion proceeds between energetically inequivalent states with a shift in the equilibrium toward one of them.

The conformational freatures of 1,3,2-dioxaborinanes are a function of their substitution, the nature of the substituents in the carbon part of the ring and p,p-conjugation at the boron—oxygen bond [1-5]. In the present work, we studied the effect of the nature of the substituents at $C_{(5)}$ on the conformational behavior of 2,5,5-trisubstituted derivatives by PMR spectroscopy.

All the compounds studied (I-XXIV) fall into three groups relative to their conformational properties. The first group comprises compounds with substituents similar in nature and bulk at $C_{(5)}$, which leads to ring inversion between two energetically equivalent forms which is rapid on the NMR time scale (I-XIV, Table 1). This is indicated by the singlet nature of the signal for the ring methylene protons and the low-temperature PMR data. The magnitude of the inversion barrier for 5,5-dialkyl- and 5,5-diallyl-1,3,2-dioxaborinanes could not be determined due to the exceedingly low coalescence temperature (from —115 to —133°C for dimethyl analogs according to Carton et al. [3]). The coalescence temperature is —83°C for 2-isopropyl-5,5-dibenzyl-1,3,2-dioxaborinane corresponding to $\Delta G^{\neq} = 9.7$ kcal/mole, which hardly differs from the analogous value for 5,5-disubstituted 1,3-dioxanes [6]. The nature of the signal for the ring methylene protons at —100°C (Fig. 1a) indicates that cessation of ring inversion leads to an undistorted form. The x-ray structural [7-10] and dipole measurement data [11-13] indicate the predominance of a semiplanar or sofa form.

Analysis of the PMR spectra of analogs containing groups at $C_{(5)}$ differing in their bulk and electronic properties shows rapid ring inversion between two energetically inequivalent states. Compounds, for which the $\Delta\nu$ value for the ring methylene protons at room temperature for solutions in CCl_4 is not less than 0.09 ppm, belong to the second and third groups (the $\Delta\nu$ values for compounds in the first group do not exceed 0.02 ppm). In this case, the spectrum of these protons for compounds in the second group (XV-XIX) is a multiplet consisting of five lines with $\Delta\nu$ value from 0.09 to 0.17 ppm (Fig. 1b). With decreasing temperature, this multiplet degenerates into an AB system which, however, may also be a consequence not only of hindrance to inversion but also to a change in the chemical shifts of the protons at $C_{(4)}$ and $C_{(6)}$ with change in the temperature.

The signals for the ring methylene protons in the third group of compounds (XX-XXIV) at room temperature correspond to a usual AB system (Fig. 1c) with $\Delta\nu$ value in the range from 0.20 to 0.49 ppm (solutions in CCl_4).

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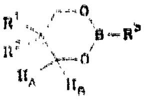
TABLE 1. PMR Spectral Parameters for 2,5,5,-Trisubstituted 1,3,2-Dioxaborinanes



Compound	R^1	R^2	δ, ppm			$-^2J_{AB}$, Hz
			H_A	H_B	$C_{(5)}-CH_3$ (s)	
I	CH_3	CH_3	3,63 (s)		1,01	—
II	CH_3	CH_3	3,44 (s)		0,86	—
III	C_2H_5	C_2H_5	3,86 (s)		—	—
IV	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	3,90 (s)		—	—
V	$C_6H_5CH_2$	$C_6H_5CH_2$	3,66 (s)		—	—
VI	C_6H_5	C_6H_5	4,47 (s)		—	—
VII†	C_6H_5O	C_6H_5O	3,96 (s)		—	—
VIII	$COOCH_3$	$COOCH_3$	4,06 (s)		—	—
IX	$COOC_2H_5$	$COOC_2H_5$	4,41 (s)		—	—
X	i-C_3H_7O	i-C_3H_7O	3,56 (s)		—	—
XI	$COOCH_3$	$COOCH_3$	4,20 (s)		—	—
XII	$COOCH_3$	$COOCH_3$	4,21 (s)		—	—
XIII	$COOC_2H_5$	$COCH_3$	4,21 (s)		—	—
XIV	$CH_2{=}CHCH_2$	$C_6H_5CH_2$	3,58 (s)		—	—
XV	CH_3	CH_3O	3,60 (m)		1,00	—
XVI	CH_3	CH_3O	3,68 (m)		1,03	—
XVII	CH_3	i-C_3H_7	3,60 (m)		0,81	—
XVIII	CH_3	$CH_2{=}CHCH_2$	3,50 (m)		0,78	—
XIX	i-C_3H_7	$CH_2{=}CHCH_2$	3,67 (m)		—	—
XX	CH_3	CH_3OCH_2	3,75 (e)	4,03 (e)	0,30	11,0
XXI	CH_3	C_6H_5	4,10 (e)	4,42 (e)	1,51	11,0
XXII	CH_3	C_6H_5O	3,97 (e)	4,22 (e)	1,39	11,0
XXIII	C_2H_5	CH_3OCH_2	3,89 (e)	4,10 (e)	—	11,0
XXIV	Br	NO_2	4,15 (e)	4,64 (e)	—	12,0

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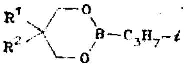
*I R^3 = OH; II–X, XIII–XV, XVII–XXIV, R^3 = i-C_3H_7; XI R^3 = C_2H_5; XII R = i-C_4H_9; XVI R^3 = C_3H_7O.

†The spectrum was taken in benzene, while CCl_4 was the solvent for the other compounds.

TABLE 2. Temperature Dependence of the Difference in the Chemical Shifts of the Protons of the AB Segment of the PMR Spectra of Several 2,5,5-Trisubstituted 1,3,2-Dioxaborinanes



R^1	R^2	Temperature, °C	Δν, Hz	ΔΔν, Hz (for maximum temperature range)
$C_6H_5CH_2$	$C_6H_5CH_2$	Room	<2,0	>11,8
		−100;	13,8	
i-C_3H_7	$CH_2{=}CHCH_2$	Room	10,2	2,8
		0	10,7	
		−50	11,8	
		−70	13,0	
C_2H_5	CH_3OCH_2	Room	20,1	1,6
		0	20,4	
		−20	20,6	
		−40	21,2	
		−60	21,4	
		−80	21,7	
Br	NO_2	Room	47,3	1,0
		0	47,8	
		−20	47,9	
		−40	48,3	
		−60	48,3	

The spectra of compounds in the second and third groups show a definite similarity due to the presence of a prochiral center at the ring $C_{(5)}$ atom which gives rise to diastereotopic CH_2 protons at $C_{(4)}$ and $C_{(6)}$. However, there is also a significant difference between these

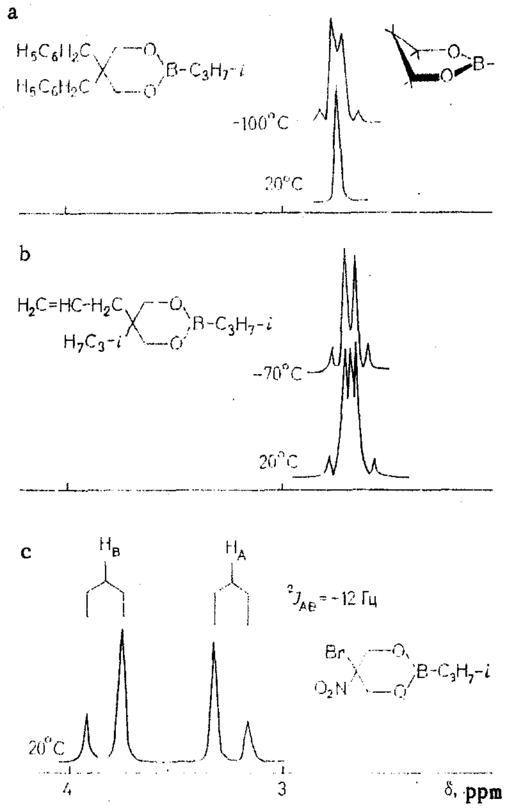


Fig. 1. PMR spectra for ring methylene protons of a) 5,5-dibenzyl-2-isopropyl-1,3,2-dioxaborinane, b) 5-allyl-5-isopropyl-1,3,2-dioxaborinane, and c) 5-bromo-5-nitro-1,3,2-dioxaborinane.

two groups of compounds related to the different change in the internal shift between these two protons with decreasing temperature evident upon comparing the low-temperature spectra of XIX, on one hand, with those for XXIII and XXIV, on the other (Table 2). The lower $\Delta\Delta\nu$ values for XXIII and XXIV relative to XIX indicates a greater shift of the conformation equilibrium toward one form at room temperature for compounds of the third group which is sufficient to distinguish a predominant conformation by analogy to 5,5-disubstituted 1,3-dioxanes [6]. The $^2J_{AB}$ coupling constants for compounds in the third group do not differ from the $^2J_{AB}$ values of the corresponding 1,3-dioxanes [14]. In our previous work [4], we noted similar nature for the coupling in the carbon part of 1,3-dioxanes and 1,3,2-dioxaborinanes. Thus, this similarity in the coupling constants indicates the lack of distortion in the carbon fragment of XX-XXIV which exist in the predominant semiplanar conformational form.

The PMR data for compounds of the third group do not guarantee unequivocal conclusions concerning the spatial orientation of the substituents at $C_{(5)}$ in the predominant conformation. The major reason for this lies in the considerable differences in the shielding constants of the substituent protons due to interaction of these groups. In particular, the chemical shift of the known equatorial methyl group in the spectrum of 2-isopropyl-5-methyl-1,3,2-dioxaborinane is 0.95 ppm (in CCl_4) [4], while δ_{CH_3} for XX-XXII varies from 0.30 to 1.51 ppm. Thus, determination of the relative orientation of the methyl group on the basis of the δ values is difficult. We may only note that the orientation of the nitro group in 5-bromo-2-isopropyl-5-nitro-1,3,2-dioxaborinane is predominantly axial. This is indicated by the dipole measurements for 5-alkyl-5-nitro-1,3,2-dioxaborinanes [11, 12] and the nature of the PMR spectrum of 2-isopropyl-5-nitro-1,3,2-dioxaborinane [4].

Thus, the introduction of two substituents at $C_{(5)}$ in the 1,3,2-dioxaborinane ring leads to the appearance of rapidly inverting systems with different extents of displacement of the conformational equilibrium determined by the nature of the substituents at $C_{(5)}$.

EXPERIMENTAL

The PMR spectra were taken on a BS-497 spectrometer at 100 MHz for 15% solutions of the compounds studied in CCl_4 and benzene with TMS as the internal standard. Freon-12 was used for the low-temperature spectra of V and carbon disulfide was used for the low-temperature spectra of XIX, XXIII, and XXIV . The inversion barrier was determined according to a standard procedure [15] while the $\Delta\nu$ value was determined from the experimental spectra according to Emsley et al. [16].

2,5,5-Trisubstituted 1,3,2-dioxaborinanes I-XXIV were described in our previous work [17].

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