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CONFORMATIONAL ANALYSIS OF 3-BORABICYCLO[3.3.1]NONANE DERIVATIVES

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Summary

Conformations of 3-borabicyclo[3.3.1]nonane derivatives have been studied by means of ^1H and ^{13}C NMR spectroscopy. With the aid of the coupling constants $^3J(HH)$ and ^{13}C chemical shifts it has been shown that all the derivatives of 3-borabicyclo[3.3.1]nonane with the trigonal boron atom studied are in a flattened double-chair conformation. In 3-borabicyclo[3.3.1]nonane derivatives with the tetra-coordinated boron atom and substituents at the 7α-position, the chair-boat conformation predominates, the boat conformation being characteristic of the cyclohexane ring; exceptions are the compounds with the internal donor—acceptor bond between the boron atom and 7α-substituent.

Study of the derivatives and hetero-analogues of bicyclo[3.3.1]nonane is of great importance for solving a number of theoretical organic chemistry problems. This is a reason for the intensification of the studies in both the synthetic field [1] and conformational analysis [2] of these compounds. By the use of ^1H and ^{13}C NMR techniques, it was shown that bicyclo[3.3.1]nonane itself (A) and its 3β (7β) substituted derivatives are in a flattened double-chair conformation, for the substituted ring and, moreover, two bulky substituents at 3α- and 7α-positions are able to induce the boat-boat conformation [3—6]. Analogous behaviour is observed in the series of 3-oxa- [7] and 3-azabicyclo[3.3.1]nonanes [8].

Introduction of a trigonal atom into the bicyclo[3.3.1]nonane skeleton at the 3 position substantially alters the non-bonding interactions in the molecule, so this factor should affect the conformational regularities in such compounds.

Data on the problem published so far have a fragmentary character. Otherwise the compounds of the 3-borabicyclo[3.3.1]nonane series (B) are excellent

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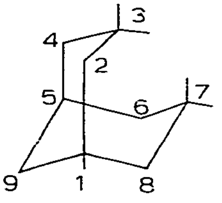
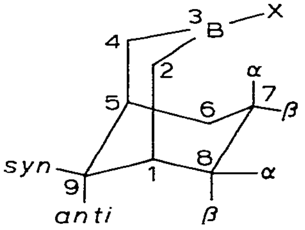
models for conformational researches of such kind.

During the last years, a great deal of experimental data on the chemistry of 3-borabicyclo[3.3.1]nonane derivatives has been obtained [9,10], but the question on the spatial structures of these bicyclic compounds was left open. In this report the results of conformational analysis of various 3-borabicyclo[3.3.1]nonane derivatives, involving both the tri- and tetra-coordinated boron atom, are discussed.



(A)



(B)

3-Borabicyclo[3.3.1]nonane derivatives with tetra-coordinated boron atom

The compounds of the 3-borabicyclo[3.3.1]nonane series with an sp^3-hybridized boron atom have very similar conformations to their carbon analogues. This is due to the same atom hybridization and, hence, similar valence angles and spatial location of the substituents. In this series one may utilize as a model system a compound whose conformation is well defined. By means of X-ray analysis it was found that the dimeric 4-oxa-3-borahomoadamantane (I) possesses the double-chair conformation [11]. In addition, by the use of ^{11}B NMR spectra, 7α-methoxymethyl-3-methyl-3-borabicyclo[3.3.1]nonane (II) was shown to be an intra-complex compound thus confirming the chair-chair (CC) conformation of this bicycle too. Other compounds studied were β-diketonates of 7α-substituted derivatives of 3-borabicyclo[3.3.1]nonane, readily obtained from the corresponding 3-methoxy derivatives.

In the whole series of compounds chosen, atoms C(9) and C(1,5) have comparable ^{13}C chemical shifts indicating their considerable dependence on the bicycle conformation [4,7] and their insignificant dependence on the substituents at the boron and C(7) atoms (because of their considerable remoteness). In the case of bicyclo[3.3.1]nonane systems it was shown that the transition from the double chair conformation to the chair-boat (CB) one is followed by an upfield shift for both C(1,5) (~2 ppm) and C(9) (~6 ppm) [4,7]. Chemical shifts of other carbon atoms, especially C(7) and C(6,8), also change, however, in this case the alterations are possibly affected by the substituents inductive influence, so chemical shifts of C(6,8) and C(7) will be discussed below. Returning to the consideration of C(9) and C(1,5) chemicals shifts it should be noted that all the compounds under question may be divided into two groups (Table 1). The first involves, beside compound I which was proved to have the double chair conformation, also compound II, 3-borabicyclo[3.3.1]nonyl- (III), and 7-methylene-3-borabicyclo[3.3.1]nonyl-acetylacetonate (IV). In this series, chemical shifts of C(9) are in the range 35.5—37.5 ppm, and of C(1,5) from 28—30 ppm. This suggests that all the compounds related to the first group possess an identical conformation, namely the chair-chair one.

The second group of bicycles is represented by the compounds V—VIII. In this group, the C(9) and C(1,5) signals are shifted upfield. It is natural to assume that such a range, similarly to the bicyclo[3.3.1]nonane series, is connected with an alteration of the conformation from double-chair to chair-boat. The question which of the cycles alters conformation from chair to boat is solved by consideration of the NMR spectra of these compounds. In all the series of compounds V—VIII the coupling constant values $J(12\alpha)$ ($J(54\alpha)$) and $J(12\beta)$ ($J(54\beta)$) do not exceed 6 Hz, whereas the conformation alteration from chair to boat has to be followed by an appearance of a large coupling constant between H(1) and H(2β) (H(5) and H(4β)) for which case the dihedral angle is close to 0°. Having suggested the conformational preference of the boron-containing cycle for one compound of the second series, 7-phenyl-3-borabicyclo[3.3.1]nonyl-benzoylacetophenonate (VI), we may find direct evidence in favor of alteration of the cyclohexane ring conformation. As shown in Table 2, the coupling constant $^3J(6\alpha7\beta)(^3J(8\alpha7\beta))$ is equal to 13 Hz, indicating the boat conformation. It will be shown below that coupling constants $^3J(6\alpha7\beta)(^3J(8\alpha7\beta))$ and $^3J(6\beta7\beta)(^3J(8\beta7\beta))$ for the chair conformation of the carbon cycle are essentially lower in value.

Thus, the combined analysis of ^{13}C and ^{1}H NMR spectra allows us to assign to the compounds I—IV predominantly the chair-chair, conformation and compounds V—VIII the chair-boat.

^{13}C chemical shifts of compounds I, II and 7-methoxymethyl-3-borabicyclo-[3.3.1]nonyl-acetylacetonate (V) are worth a more detailed discussion. Of these I and II relate to the first series (chair-chair), and V to the second one (chair-boat), while the substituents at C(7) are have similar structure and inductive influence.

For the latter three compounds all the differences in ^{13}C chemical shifts may be accounted for by the variations in conformation of these compounds. Indeed, in I and II the chemical shifts of all ring carbon atoms are very similar (Table 1). At the same time, distinct differences are observed in chemical shifts of I and II, on the one hand, and those of V, on the other. Besides the difference in C(9) and C(1,5) chemical shifts considerable differences in C(6,8) chemical shifts are seen. Analogous to the derivatives of bicyclo[3.3.1]nonane [4,7], the upfield shift for C(9) when progressing from the double chair conformation (I, II) to the chair-boat (V) is possibly connected with the spatial interaction of $H(9)_{anti}$ and H(7), similar variations in C(1,5) and C(6,8) chemical shifts are probably conditioned by shielding H(1,5) and H(6β, 8β) atoms.

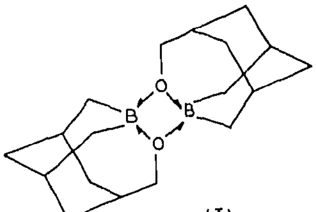
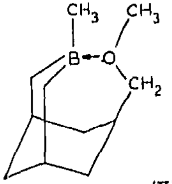
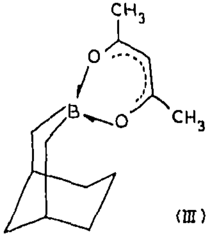
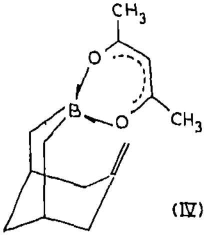
In conclusion, to complete the discussion of 3-borabicyclo[3.3.1]nonane compounds with a tetra-coordinated boron atom, one can note the conformation dependence of these compounds on the presence of a substituent at the 7α-position, as observed in the bicyclo[3.3.1]nonane series. However, the analogy is not absolute, because the organoboron compounds are able to form intra-complexed compound I, II leading to the double chair conformation even in the presence of 7-*endo*-substituents.

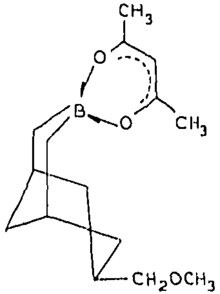
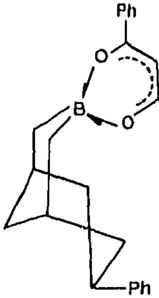
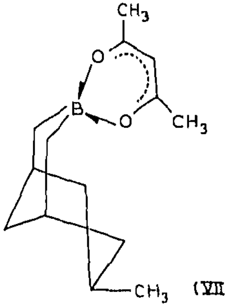
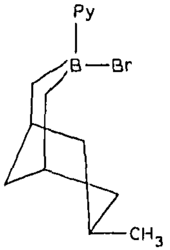
In addition, we have not discovered any alteration of the borinane cycle conformation from chair to boat, this fact probably being connected with the absence of hydrogen atoms at the α-atom of the substituent at B in the β-diketonates. It is also possible that the boron-containing cycle is rather flattened.

(Continued on p. 176)

TABLE 1

^{13}C CHEMICAL SHIFTS OF 3-BORABICYCLO[3.3.1]NONANE DERIVATIVES WITH A TETRACOORDINATED BORON ATOM (in $CDCl_3$)

Compound	Conformation	Temperature (°C)	Chemical shifts (ppm) C(1,5)	C(2,4)	C(6,8)	C(7)	C(9)	CH_3—C	Remainder	Method
[d]  (I)	CC [a]	0	29.2		36.85	32.05	36.85		69.9 (CH_2O)	[13]
		−50	28.85	25.4	36.4	31.3	36.4		69.75	
 (II)	CC	+100 [b]	27.7		36.9	32.9	36.9		83.05 (CH_2O), 59.5 (CH_3O)	This work
		0	28.0		37.45	32.8	36.8		84.9, 60.9	
		−70	27.9	28.8	37.45	32.4	36.7		85.4, 61.4, 11.3 (CH_3B)	
 (III)	CC	0	28.9		34.6	17.4	36.1		190.6, 189.5, 100.35, 24.5	This work
		−50	28.65	26.5	34.2	17.25	35.95		190.4, 189.2, 100.88 24.6	
		−60	28.6	26.35	34.05	17.25	35.9		190.3, 189.3, 101.00, 24.6, 24.5	
 (IV)	CC	0	30.1		42.75	146.2	35.3		109.3, 189.6, 189.4, 100.4, 24.2	This work
		−50	29.9	25.6	42.4	146.3	35.1		109.2, 190.0, 189.5, 100.9, 24.3	

 (V)	CB [c]	0	26.1		32.3	31.1	31.45		190.6, 189.4, 100.09, 80.0, 58.65, 24.3	This work
		−50	25.7	28.05	31.75	30.8	31.2		190.45, 189.55, 100.04, 79.8, 58.8, 24.5	
 (VI)	CB	50	27.3	29	37.1	37.1	31.5		148.9, 137.7, 128.8, 128.5, 128.2, 128.0, 127.53, 125.4, 92.65	This work
 (VII)	CB	0	26.7		37.5	25.5	31.2	23.0	190.3, 189.7, 100.65, 24.5	This work
		−50	26.4	28.2	37.1	25.4	31.0	23.0	190.45, 189.5, 100.2, 24.5	
 (VIII)	CB	0	27.0		35.4	25.25	30.8	22.35	145.2, 127.6, 126.4,	
		−50	27.0		34.7	25.5	31.5	22.5	144.85, 127.55, 126.2	

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[a] CC = chair-chair. [b] Without a solvent. [c] CB = chair-boat. [d] The compound was synthesized by L.S. Vasil'ev and V.V. Veselovsky. Arrows with half-heads represent semi-coordinate bonds [14].

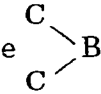
TABLE 2

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 7-PHENYL-3-BORABICYCLO[3.3.1]NONYLBENZOYLACETOPHENONATE (VI) (100 MHz, $CDCl_3$ sol., TMS)

δ (ppm)		J (Hz)	
H(1)	2.31	$^2J(2\alpha 2\beta)$	13.4
H(2α)	1.05	$^2J(6\alpha 6\beta)$	12.5
H(2β)	0.59	$^2J(9_{syn}9_{anti})$	13.0
H(6α)	1.64	$^3J(12\beta)$	5.3
H(6β)	2.04	$^3J(18\alpha)$	3.5
H(7β)	2.84	$^3J(18\beta)$	~12
$H(9_{syn})$	1.21	$^3J(6\alpha 7\beta)$	13
$H(9_{anti})$	2.12	$^3J(6\beta 7\beta)$	4.9
		$^3J(19_{syn})$	2

In the *AB* part of the *ABX* spectrum of compounds II and V—VIII where the protons H(2α,2β)(H(4α,4β)) make up the *AB* part, a clear doublet splitting with the coupling constant for one pair of protons (H(2β,4β) is seen, whereas the other pair only reveals a doublet components broadening. These differences of the constants evidence flattening of the borinane cycle.

3-Borabicyclo[3.3.1]nonane derivatives with tri-coordinated boron atom

The planarity of the  $C_2B{-}X$ fragment in 3-borabicyclo[3.3.1]nonane compounds containing a trigonal boron atom leads to a decrease of the 3—7 interaction which is characteristic of the bicyclo[3.3.1]nonane structure in the chair-boat conformation. Therefore substitution of the 3-methylene group by a trigonal boron atom can promote stabilization the double chair form even in the presence of 7α-substituents.

The ^{13}C chemical shifts of 3-borabicyclo[3.3.1]nonane derivatives are listed in Table 3. Chemical shifts of the C(9) and C(1,5) atoms for the compounds IX—XVI lie within the region 33.9—35.6 and 27.1—31.8 ppm, respectively. The range of C(9) chemical shifts of compounds IX—XVI is partially overlapped by that of I—IV which were proved to be in the chair-chair conformation (see above). At the same time, the former range does not reach the C(9) chemical shift range of compounds V—VIII which are in the chair-boat conformation. In this case the shifts of C(1,5) are less characteristic, though here one can observe better coincidence of the C(1,5) chemical shifts values for the series I—IV and IX—XVI than for V—VIII and IX—XVI. Thus, the comparison of the characteristic chemical shifts of C(1,5) and C(9) in compounds I—XVI indicates a predominant double-chair conformation for the series IX—XVI. However, there are two factors which make one regard this deduction carefully. Firstly, consideration of molecular models of compounds IX—XVI shows that *endo*-substituents at C(7) must interact sterically with the substituent at the boron atom and with the α-protons at C(2,4), despite the lack of *endo*-substituents and flattening of the cycle. Secondly, for 3,7α-dimethyl-3-borabicyclo[3.3.1]-nonane (XI), 3-methoxy-7α-methyl-3-borabicyclo[3.3.1]nonane (XII), 3-t-butyl-7α-methyl-3-borabicyclo[3.3.1]nonane (XIV), and 3-bromo-7α-methyl-

3-borabicyclo[3.3.1]nonane (XV) containing a methyl group at C(7), the chemical shift of the latter changes from 24.25 to 24.7 ppm i.e. downfield as compared with the chemical shift of the methyl group in 7-methyl-3-borabicyclo[3.3.1]nonyl-acetylacetonate (VII), pyridine-3-bromo-7α-methyl-3-borabicyclo[3.3.1]nonane (VIII), and 3-methylbicyclo[3.3.1]nonane [6] which are found to be in the chair-chair conformation.

These facts mean that additional evidence is required for the determination of the conformations of compounds IX—XVI, pointing again to ^{1}H NMR spectra of some representatives of this series. Of all the series, only 3-methoxy-7-phenyl-3-borabicyclo[3.3.1]nonane (XVI) has an interpretable spectrum when recorded on a 100 MHz spectrometer (Table 4). Spectra of compounds XI—XIII were recorded on a 360 MHz instrument, however, even in this case we were unsuccessful in avoiding superposition of some resonance lines for 3,7-dimethyl-3-borabicyclo[3.3.1]nonane (XI) and 3-methoxy-7α-methyl-3-borabicyclo[3.3.1]-nonane (XII). Nevertheless the structure of the H(6β,8β) lines is seen well enough in all the spectra which permits us to determine the conformational preference of the cyclohexane ring (Fig. 1). Indeed, if there is the double-chair conformation, the signals of H(6β,8β) should have a doublet shape with a large heminal coupling constant ($^2J(6\alpha 6\beta)$ or $^2J(8\alpha 8\beta)$, and each of the doublet components must be split or broadened owing to interaction between H(8β)-(H(6β)) and H(1), H(7), H(2β) (H(5), H(7), H(4β). The constants $^3J(18\beta)$ and $^3J(78\beta)$ are affected by a dihedral angle close to 60°, and consequently are substantially less than the heminal constant $^2J(8\alpha 8\beta)$. The constant $^4J(2\beta 8\beta)$ does not usually exceed 1—3 Hz. For the chair-boat conformation, the shape of the spectrum of the H(6β8β) protons differs essentially from the spectrum characteristic of the double-chair conformation due to the appearance of the

(Continued on p. 180)

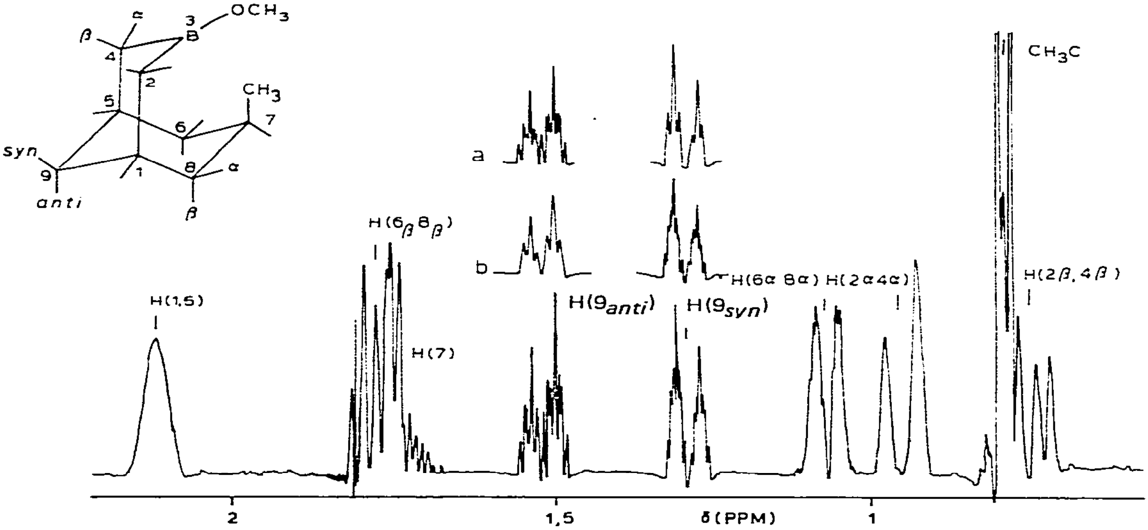
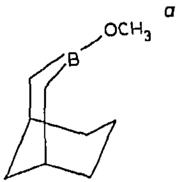
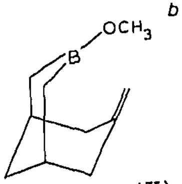
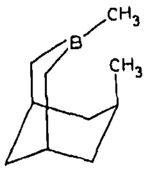
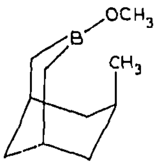
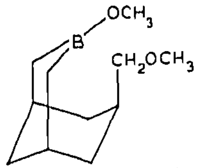
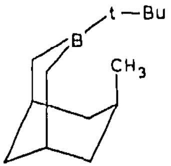
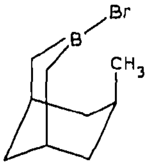
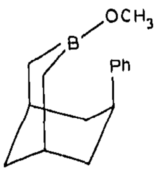


Fig. 1. ^{1}H NMR spectrum (360 MHz) of 3-methoxy-7-methyl-3-borabicyclo[3.3.1]nonane (XII). At the top: the proton signals H(9_{syn}) and H(9_{anti}), (a) signals of H(6α,8α) decoupled, (b) signals of H(2α,4α) decoupled.

TABLE 3

^{13}C CHEMICAL SHIFTS OF 3-BORABICYCLO[3.3.1]NONANE DERIVATIVES WITH A TRIGONAL BORON ATOM (in CH_2Cl_2)

Compound	Conformation	Temperature (°C)	Chemical shifts (ppm) C(1,5)	C(2,4)	C(6,8)	C(7)	C(9)	CH_3—C	Remainder	Method
 (IX) [a]	CC	0	29.5		34.2	17.7	35.7		53.3 ($BOCH_3$)	
		−50	29.3		34.0	17.7	35.45	53.5	53.5	[15]
		−90	29.3	25.7	34.0	17.6	35.2		53.6	
			29.1	22.5						
 (X) [b]	CC	0	32.0		43.9	145.4	35.15		52.95, 112.3 (CH_2=C)	
		−50	31.8	24.5	43.7	145.5	34.85		53.1, 112.4	[16]
		−90	32.05	22.95	43.8	145.7	34.6		53.4, 112.5	
			31.5	26.2	43.35					
 (XI)	CC	0	27.1		38.6	26.05	35.45	24.8		This work
		−70	26.8	35.4	37.95	26.0	35.4	25.0	~12 (B—CH_3)	
		−90	26.7	35.6	37.8	25.9	35.3	25.1	12.0	
 (XII)	CC	0	27.6		39.3	25.9	34.7	24.65	53.0	
		−50	27.45		38.85	25.9	34.85	25.0	53.2	[17]
		−90	27.45	24.8	38.55	25.8	34.9	25.25	53.4	
			27.2	27	38.25					

 (XIII)	CC	0	27.1	25.7	34.4	31.8	35.2		52.9 ($BOCH_3$), 58.6 (OCH_3), 79.2 (OCH_2)	This work
		–50	26.9	25.8	34.2	31.75	35.2		53.1, 58.7, 79.2	
		–80	26.8	25.5	33.9	31.75	35.2		53.2, 58.8, 79.2	
 (XIV)	CC	0	26.7		39.0	26.3	34.4	24.7	27.75 ($(CH_3)_3C$)	This work
		–70	26.5	30.8	38.25	26.3	35.0	24.95	28.0	
 (XV)[c]	CC	0	27.6	38.4	37.3	25.5	34.1	24.9		[13]
		–70	27.7	38.4	37.3	25.7	34.3	25.4		
 (XVI)[b]	CC	0	27.7	29	36.9	34.85	34.4		52.8, 145.2, 128.3, 127.7, 125.7	
		–50	27.75	28 25.5	35.15	36.15	33.9		52.8, 144.9, 128.2, 127.8, 125.6	[18]
	CB⇌CC	–60	27.8	28 25.4	35.4	35.4	33.8		52.9, 144.8, 128.2, 127.8, 125.6	
		–70	27.8 27.9	28 25.1	35.1	35.5	33.6		52.9, 144.6, 128.2, 127.8, 125.55	
		–80	27.9, 27.75	27.5 24.95	34.85	35.6	33.4		52.9, 144.44, 128.1, 127.8, 125.5	
		–90	27.95 27.8	27.5 24.8	34.6	35.8	33.3		52.95, 144.25, 128.1, 127.9, 125.5	

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[a] Synthesized by Yu.N. Bubnov and M.Sh. Grigorian. [b] Prepared by K.L. Cherkasova. [c] Prepared by L.S. Vasil'ev and V.V. Veselovsky.

TABLE 4

CHEMICAL SHIFTS (δ, ppm) AND ABSOLUTE VALUES OF COUPLING CONSTANTS J (Hz) FOR COMPOUNDS XI—XIII (360 MHz) AND XVI (100 MHz) ($CDCl_3$, TMS)

	XI	XII	XIII	XVI
H(1)	2.10	2.10	2.14	2.25
H(2α)	1.66	0.98	0.93	0.95
H(2β)	1.10	0.78	0.84	0.71
H(6α)	1.32	1.08	1.38	1.75
H(6β)	~1.85	~1.79	1.76	2.02
H(7β)	~1.90	~1.73	1.90	2.85
H(9_{syn})	1.47	1.28	1.38	1.29
H(9_{anti})	1.64	1.52	1.58	~1.8
^2J(22)	17.8	17.0	17.5	16.0
^2J(66)	12.4	13.0	14.5	13.5
^2J(99)	12.3	12.3	13.2	13.4
^3J(12α)		<2	<2	
^3J(12β)	6.8	6.8	7.2	6.4
^3J(18α)		3		3.0
^3J(18β)	5.2	6.2	6.4	6.7
^3J(6α7β)	<4	3.0	1.8	
^3J(6β7β)		6.0	7.1	6.4
^3J(19_{syn})		3.0	3.5	
^3J(19_{anti})		3.7	~3	
^4J($6\alpha 9_{syn}$)		1.6		
^4J($2\alpha 9_{anti}$)		2.5	~2	

large coupling constant $^3J(18\beta)(^3J(56\beta))$ affected by a dihedral angle H(1)—C(1)—C(8)—H(8β) which is equal to 0°, the main splitting of the line must have a doublet of doublets structure with the constant greater than 10 Hz or a triplet (equality of the ^2J and ^3J constants). Of course, the shape of the H(7), H(1,5) and H(6) proton spectrum changes in progressing from the chair-chair conformation to the boat-chair one. So H(7) has a large constant with H(6α)(H(8α)) (13 Hz) in the spectrum of VI, whereas in the spectra of XII and XVI the largest of the constants observed for this proton does not exceed 7 Hz. The results of the PMR spectra analysis of compounds XI—XIII and XVI are listed in Table 4. These results demonstrate clearly that compounds XI—XIII and XVI are in the chair-chair conformation. This conformation is confirmed also by large values of ^4J constants from the distant spin-spin interaction of H(6α) with H(9_{syn}) as well as H(2α) with H(9_{anti}), since only in the case of the double chair do these proton pairs form a flat W-type structure.

The same conformation should be attributed to all compounds of the series IX—XVI with trigonal boron atoms judging from the similarity of the characteristic carbon atoms ^{13}C chemical shifts. As to the unusual downfield shift of the CH_3 group carbon atom at C(7) in bicycles XI, XII, XIV, XV, this phenomenon may be explained by δ-interaction of the CH_3 group with α-protons at C(2) and C(4); e.g. in polymethylcyclohexanes, this interaction is displayed as a downfield shift of the resonance of the carbon of the CH_3 groups, which are in 1,3-interaction with other axial CH_3 groups, by a value of several ppm in comparison with compounds not revealing such interaction [12].

Thus in all the studied compounds of the 3-borabicyclo[3.3.1]nonane series with trigonal boron atoms, including compounds with 7α-substituent in the cyclohexane ring, XI—XVI, double-chair conformations are observed. However, the chair-boat conformation should not be excluded at all, bearing in mind the limited number of C(7)-substituents utilized in the work.

It should be noted also that flattening of the framework of the bicyclo[3.3.1]nonane compounds in the double-chair conformation [3,5—7] is also observed in the series of 3-borabicyclo[3.3.1]nonane compounds. Substantial differences in $^3J(18\alpha)$ and $^3J(18\beta)$ values as well as in $^3J(78\alpha)$ and $^3J(78\beta)$ indicate flattening of the cyclohexane ring, while the differences for XI—XIII and XVI demonstrate the dependence of the degree flattening on the substituents at C(7) and B (Table 4). An additional flattening of the borinane ring is beyond doubt (a difference in $^3J(12\alpha)$ and $^3J(12\beta)$ even bearing in mind the sp^2-hybridization of the boron atom.

Low-temperature spectra of 3-borabicyclo[3.3.1]nonane compounds

Analysis of the spectra recorded over a narrow temperature range does not allow one to determine whether a proved conformation of compounds I—XVI is stable or one ought to speak of a dynamic equilibrium of different conformational forms. In studying ^{13}C spectra over a wide temperature range (Tables 1, 3) it was found that the proved conformation for most of the compounds may be considered either to be stable or the dynamic equilibrium is shifted almost completely to the conformational form shown in Tables 1 and 3. A weak variation of the ^{13}C chemical shift of C(1,5), C(6,8), and C(7) with temperature decrease evidences in favour of such conclusion. Compounds IX, X, XII and XVI, containing the $B{-}OCH_3$ group, are exceptions: on temperature decrease splitting of some signals into doublets with an intensity ratio 1 : 1 (Fig. 2) is observed in their ^{13}C spectra. The greatest splitting (2.5—3 ppm)

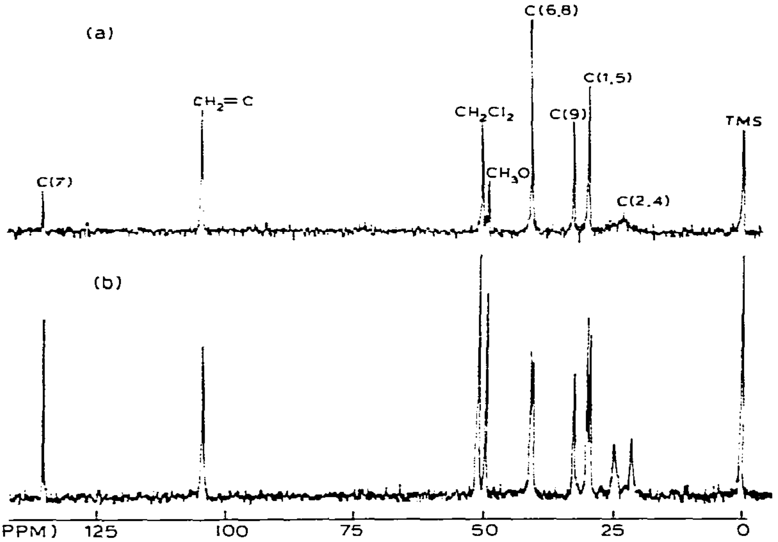
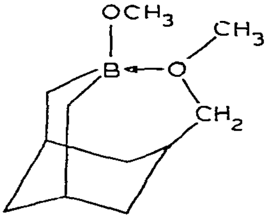


Fig. 2. ^{13}C NMR spectra of 3-methoxy-7-methylene-3-borabicyclo[3.3.1]nonane (X) in CH_2Cl_2: a) —40°C, b) —88°C.

is observed for C(2,4), a rather appreciable one (up to 0.9 ppm) for C(1,5), and the least up to 0.5 ppm) for C(6.8). This suggests a possibility of formation, of dimeric or trimeric associates of the compounds or a hindered rotation about the B—O bond. In this case the greatest alteration of chemical shift as a result of spatial interaction will be observed for C(2,4) atoms and, to a lesser degree, for more the distant C(1,5) and C(6,8) because of the asymmetrical location of the substituents at the boron atom with respect to the 3-borabicyclo[3.3.1]nonane framework.

The small difference in chemical shift of all doublet signals except for C(2,4) gives the possibility of excluding freezing of different conformations in the equilibrium CC ⇌ CB as a cause of the spectrum complication. In addition, such an assumption contradicts the lack of peak splitting in compounds XI, XV, and XVI. 3-Methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]nonane (XIII) also does not reveal any tendency for oligomer structure formation, probably because of possible formation of the intra-molecular complex XIIIa at low temperature.



(XIIIa)

As for the equilibrium CC ⇌ CB, its shift to one side or another with temperature change would first of all affect the C(6,8), C(9), and C(7) chemical shifts. Such a signal shift is distinctly observed only in 3-methoxy-7-phenyl-3-borabicyclo[3.3.1]nonane (XVI). In the latter case we are probably observing a dynamic process of the CC ⇌ CB equilibrium which is displaced to CB with temperature decrease. The latter fact suggests that for the series of 3-borabicyclo[3.3.1]nonane with a trigonal boron atom (see above), such a combination of the substituents at B and C(7) which will condition the chair-boat conformation for the 3-borabicyclo[3.3.1]nonane system even at temperatures close to room temperature.

^{11}B NMR spectra

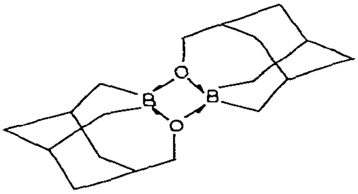
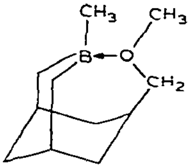
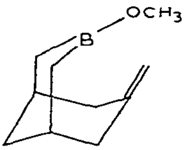
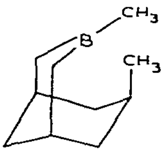
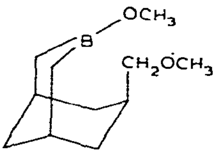
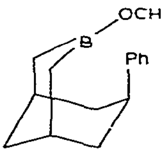
^{11}B NMR spectra of the borabicyclic compounds were recorded at room temperature (Table 5). As seen from data of Table 5, compounds X and XIII show normal chemical shifts for dialkylborinates not revealing any dimerization at 20°C. On the contrary, alteration of the chemical shift from the —80 ppm characteristic of trialkylboranes to the —35.9 ppm for 7-methoxymethyl-3-methyl-3-borabicyclo[3.3.1]nonane (II) evidences intra-molecular coordination.

Experimental

The complex VIII was obtained by mixing equimolar amounts of 3-bromo-7-methyl-3-borabicyclo[3.3.1]nonane (XV) and pyridine in $CDCl_3$.

TABLE 5

^{11}B NMR CHEMICAL SHIFTS OF SOME DERIVATIVES OF 3-BORABICYCLO[3.3.1]NONANE

Compound	X	Solvent	Chemical shift [a] (δ, ppm)
	I	C_6H_6	—17.5 [b]
	II	CH_2Cl_2	—35.9
	X	Et_3N	—52.5
	XI	without solv.	—82.9
	XIII	CH_2Cl_2	—53.2
	XVI	CH_2Cl_2	—53.5

[a] Relative to $BF_3 \cdot OEt_2$. [b] Data from ref. 13.

PMR spectra were recorded on BS-497 (100 MHz) and Bruker WH-360 (360 MHz) instruments. ^{13}C NMR spectra were recorded on a Bruker WP-60 spectrometer with a working carbon frequency of 15.08 MHz providing full carbon—proton decoupling. Chemical shifts were measured relative to internal TMS. Assignment of the spectral lines were carried out with the use of off-resonance, relative peak intensity and comparison with spectra for a number of related compounds including literature data on ^{13}C NMR chemical shifts of the bicyclo[3.3.1]nonane [4,6] and 3-oxabicyclo[3.3.1]nonane series [7]. Spectra of various compounds recorded in different solvents and over a broad temperature range showed a weak dependence of ^{13}C chemical shift on these factors. ^{11}B NMR spectra were recorded on a Bruker 4/100-IS instrument. Chemical shifts are given relative to external $BF_3 \cdot OEt_2$.

3,7-Dimethyl-3-borabicyclo[3.3.1]nonane (XI), 3-t-butyl-7-methyl-3-borabicyclo[3.3.1]nonane (XIV), and 7-methoxymethyl-3-methyl-3-borabicyclo-[3.3.1]nonane (II) were obtained by the action of methylmagnesium iodide or t-butylmagnesium chloride on the corresponding methoxyderivatives XII and XIII. XI: b.p. 80—81°C (20 torr), n_D^{20} 1.4775; XIV: b.p. 81—83°C (1 torr), n_D^{22}1.4790; II: b.p. 62—63°C (2 torr).

3-Methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]nonane was obtained by hydrogenation of 3-methoxy-3-borabicyclo[3.3.1]non-6-ene over nickel boride. B.p. 85—86°C (3 torr), n_D^{20} 1.4805 (see ref. 13).

β-Diketonates III—VII were synthesized by interaction of equimolar amounts of 7-substituted derivatives of 3-methoxy-3-borabicyclo[3.3.1]nonane with acetylacetone or dibenzoylmethane. All chelate compounds obtained are yellow (acetylacetonates) or orange (benzoylacetophenonates) crystals. They were recrystallized from hexane. M.p.: III, 65—75°C; IV, 54—60°C; V, 95—96°C; VI, 180—183°C; VII, 104—108°C.

Elemental analyses of all the compounds obtained were satisfactory.

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