Unique stereochemistry of 3-borabicyclo[3.3.1]nonane derivatives

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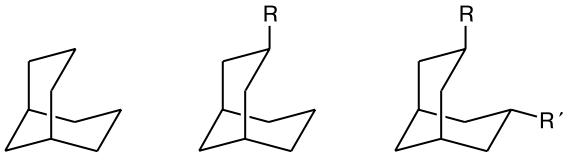
The conformational equilibrium in solution was examined by NMR spectroscopy for a series of 7α-phenyl-3-borabicyclo[3.3.1]nonane derivatives containing various substituents at the boron atom. The structures of these derivatives were studied in the crystalline state (X-ray diffraction analysis) and by quantum-chemical calculations (B3Pw91/6-31G*). The B...Ph transannular interactions corresponding to charge transfer from the π system of the phenyl group to the vacant p-orbital of the B atom were demonstrated to be responsible for unique stability of the chair—chair conformation of these derivatives.

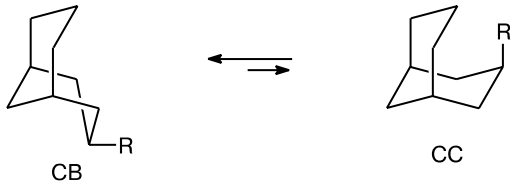
Key words: 3-borabicyclo[3.3.1]nonane derivatives, conformational analysis, dynamic NMR spectroscopy, transannular interactions, X-ray diffraction data, quantum-chemical calculations.

The chemistry of compounds of the bicyclo[3.3.1]nonane series, including those containing heteroatoms, have attracted the attention of researchers[1—3] because of their unusual stereochemical properties, due to which they serve as unique models for the development of theories and concepts of stereochemistry. Compounds of this type also find wide use in the synthesis, for example, of adamantane derivatives.[4—6] In addition, azabicyclo[3.3.1]nonane is a component of several alkaloids.[7—9]

According to the classical concepts of conformational analysis,[1] bicyclo[3.3.1]nonane can adopt three conformations free of angle strain, *viz.*, chair—chair (CC), chair—boat (CB), and boat—boat (BB). The chair—chair conformation is strongly destabilized due to repulsion between the 3- and 7-*endo*-hydrogen atoms. As a result, the starting bicyclo[3.3.1]nonane and its 3-*exo* and 3-*exo*-7-*exo* derivatives exist predominantly in the flattened chair—chair conformation.

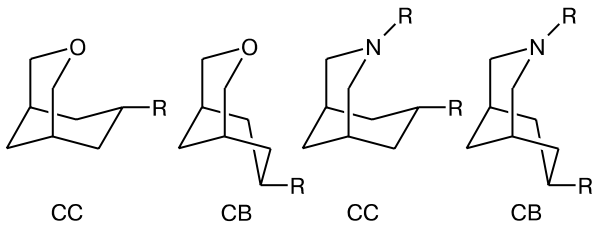


In the presence of substituents at the 3-*endo* or 7-*endo* position equivalent to the axial (α-) position in cyclohexane, this fragment assumes a boat conformation.



The general character of these regularities was demonstrated for a large number of bicyclo[3.3.1]nonanes containing various substituents.[1,10—12]

The replacement of the 3-methylene group in the bicyclo[3.3.1]nonane structure by the oxygen or nitrogen atom leads to weakening of the intramolecular 3,7 interactions in the chair—chair conformation. Nevertheless, the conformational behavior of 3-oxa- and 3-azabicyclo[3.3.1]nonanes obeys the same stereochemical rules as their carbocyclic analogs.[13,14]



The presence of the trigonal carbon atom at position 3 (for example, in the case of the exo methylene group) also leads to weakening of repulsion between the 3,7-*endo*-H atoms, which is thus favorable for stabilization of the

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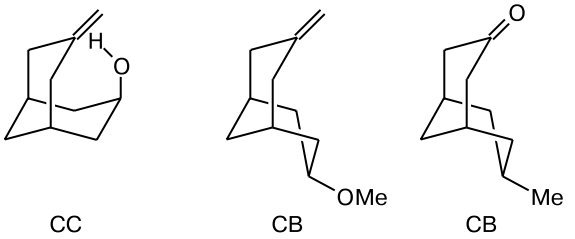
chair—chair conformation.[1] Earlier, it has been reported[11] that 7-*endo*-hydroxy-3-methylidenebicyclo[3.3.1]nonane adopts the chair—chair conformation due to the interaction between the OH group and the π orbital of the double bond. On the contrary, the chair—boat conformation is more favorable for 7-methylidene-3-*endo*-methoxybicyclo[3.3.1]nonane and 7-*endo*-methyl-3-oxobicyclo[3.3.1]nonane.[11,15]



CC CB CB

Investigations of compounds with the three-coordinate boron atom demonstrated that their conformational behavior in solution is inconsistent with the above-mentioned stereochemical features.[16—18] In particular, many 3-substituted 3-borabicyclo[3.3.1]nonanes possess unique stereochemical properties. These compounds containing the three-coordinate boron atom and the 7-α substituent are characterized by unpredictable and unusual stability of the chair—chair conformation. Unfortunately, quantitative data on relative stabilities of the conformations have previously been unavailable. The scope and the nature of this new stereochemical effect have not been studied either.

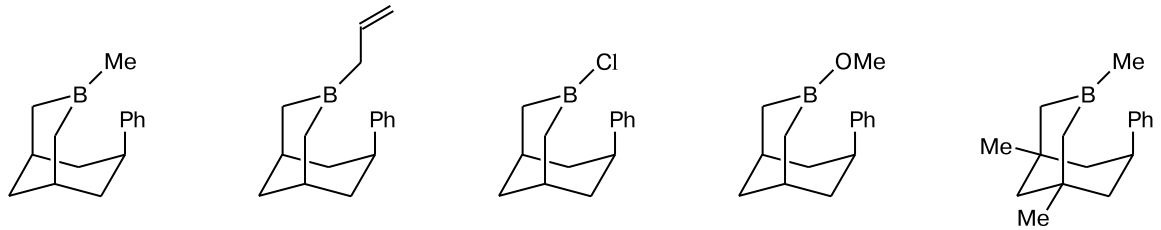
In recent years, considerable progress in the development of dynamic NMR spectroscopy and low-temperature X-ray diffraction techniques have provided new possibilities for studying the unique stereochemical properties of 3-borabicyclo[3.3.1]nonane derivatives in detail. Recent preliminary studies of these compounds revealed molecular dynamics associated with hindered rotation about the B—O bond and/or the conformational equilibrium between the CC and CB conformations.[18] A series of 7α-substituted 3-borabicyclo[3.3.1]nonane derivatives have been studied by X-ray diffraction analysis,[19,20] which provided direct evidence that the chair—chair conformation with an axial orientation of the 7-*endo* substituent is more favorable.

In this connection, we performed investigation of the structures of a series of bicyclic boron compounds, *viz.*, 7α-phenyl-3-borabicyclo[3.3.1]nonane derivatives containing various substituents at the boron atom (**1**—**10**), both in solution (by NMR spectroscopy) and in the solid state (by X-ray diffraction analysis).

Our aim was to obtain additional data on the characteristic structural features of bicyclic organoboranes and make conclusions about the causes of stability of the chair—chair conformation, although the available data indicate that it is the unoccupied orbital of the boron atom that is responsible for the unique stereochemical properties of 3-borabicyclo[3.3.1]nonanes, in particular, direct transannular contacts between the atoms at positions 3 and 7.

Analysis of NMR spectra

The use of ^{1}H NMR spectroscopy in the conformational analysis of bicyclo[3.3.1]nonane derivatives is based on the known dependence of the vicinal coupling constants $^3J_{H,H}$ on the dihedral angle (the Karplus equation).[21] The ^{1}H NMR spectra of most of the compounds under investigation are rather compex even when they are



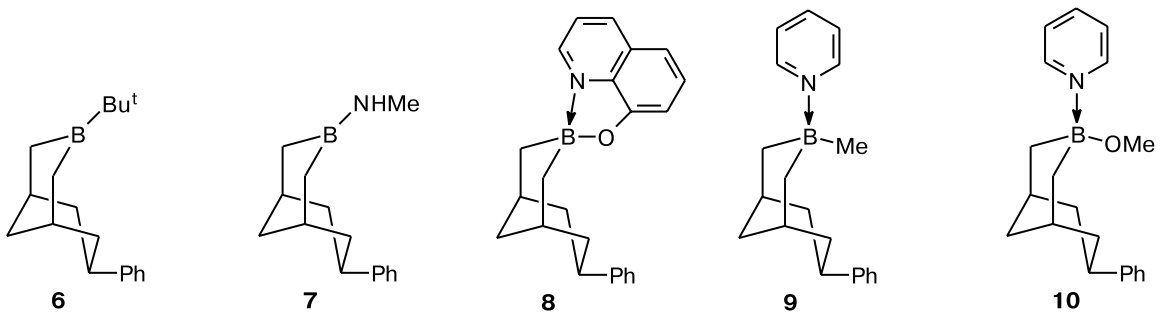


Table 1. Chemical shifts (δ) in the ^{1}H NMR spectra of compounds **1—10**

Compound	$\delta_{H(1)}$, $\delta_{H(5)}$	$\delta_{H(4\alpha)}$, $\delta_{H(2\alpha)}$	$\delta_{H(4\beta)}$, $\delta_{H(2\beta)}$	$\delta_{H(6\alpha)}$, $\delta_{H(8\alpha)}$	$\delta_{H(6\beta)}$, $\delta_{H(8\beta)}$	$\delta_{H(7)}$	$\delta_{H_{anti}(9)}$	$\delta_{H_{syn}(9)}$
1[a]	2.32	1.63	0.95	2.39	2.12	3.10	1.92	1.58
2[b]	2.15	1.49	0.72	2.22	1.87	2.84	1.71	1.41
3[a]	2.36	1.57	1.11	2.15	2.09	3.03	1.89	1.47
4[a]	2.35	1.1	0.8	1.82	2.08	2.88	1.8	1.4
5[a]	1.05	1.42	0.39	2.32	1.59	3.15	1.28	1.16
6[b]	2.33	1.72	1.02	1.27	2.16	2.83	1.98	1.23
7[b]	2.30 and 2.36	0.71 and 1.15—1.21	0.77 and 0.89	1.15—1.21	2.11	2.77	1.89	1.26
8[a]	2.42	0.88	0.54	1.95—2.07	1.95—2.07	2.87	2.12	1.32
9[c]	2.45	1.08	0.79	1.69	2.03	2.89	1.95	1.15
10[c]	2.55	1.22	2.15	0.68	2.11	2.99	2.11	1.39

[a] $CDCl_3$.
[b] Toluene-d_8.
[c] Py-d_5.

Table 2. Absolute values of the coupling constants (J/Hz) for compounds **1—10**

Compound	$^2J_{H(2\alpha),H(2\beta)}$	$^2J_{H(4\alpha),H(4\beta)}$	$^2J_{H(6\alpha),H(6\beta)}$	$^2J_{H_{syn}(9),H_{anti}(9)}$	$^3J_{H(6\alpha),H(7\beta)}$	$^3J_{H(6\beta),H(7\beta)}$	$^3J_{H(2\beta),H(1)}$	$^3J_{H(6\alpha),H(5)}$	$^3J_{H(6\beta),H(5)}$
1[a]	—	17.67	14.25	12.6	5.4	5.06	—	—	—
2[b]	—	17.41	13.98	12.37	5.96	—	5.5	—	—
3[a]	—	18.02	14.42	13.01	5.61	5.6	6.01	—	—
4[a]	—	17.32	13.8	12.76	6.5	6.5	—	—	—
5[a]	—	17.15	13.97	12.35	5.4	—	—	—	—
6[b]	—	18.03	14.05	12.95	9.9	5.5	5.61	3.52	8.61
7[b]	15.62	15.22	—	12.82	11.61	5.21	6.01	—	—
8[a]	—	13.21	13.62	12.81	12.82	5.6	4.8	—	—
9[c]	—	13.07	13.51	12.73	13.1	5.6	5.65	3.54	10.88
10[c]	—	16.78	13.7	12.6	11.8	5.7	2.09	3.2	—

[a] $CDCl_3$.
[b] Toluene-d_8.
[c] Py-d_5.

recorded at 400—500 MHz due to overlap of signals. However, the fine structure of the signals for H(7β) is observable in almost all spectra, which allows one to unambiguously establish the major conformation of the cyclohexane fragment. The chemical shifts and the coupling constants of the compounds under study are given in Tables 1 and 2, respectively. The assignment of the signals in the spectra was made using two-dimensional NMR techniques (^{1}H—^{1}H COSY and NOESY) and by comparing with the spectra of related compounds.[16—18]

The structures given in Tables 1 and 2 can be divided into two groups. For compounds **1—5**, the signal for the proton at C(7) appears as a broadened triplet of triplets with equal coupling constants ($^3J_{7\beta,6\alpha(8\alpha)} \approx {}^3J_{7\beta,6\beta(8\beta)} \leq$ ≤ 6.5 Hz) (Fig. 1).

These vicinal coupling constants correspond to the equatorial arrangement of the H(7) atom and the axial orientation of the phenyl group in the chair-like cyclohexane moiety of the bicyclic cage and, consequently, to the chair—chair conformation of the 3-borabicyclo[3.3.1]nonane derivatives of this group.*

The presence of the axial substituent is the most surprising structural feature of these compounds, which distinguishes them from other compounds of the bicyclo[3.3.1]nonane series, particularly taking into account the conformational energy of the phenyl group (according to different estimates, for phenylcyclohexane this energy varies from 11.29 to 12.29 kJ mol^{-1}).

The action of a complex-forming agent (pyridine) on bicyclic compounds **9** and **10** results in a substantial increase in the coupling constant $^3J_{6\alpha,7}$ from 6 to 11 Hz,

* A chair-like conformation of the borinane ring is evidenced by the coupling constants $^3J_{H(2\alpha),H(1)}$ ($^3J_{H(4\alpha),H(5)}$) and $^3J_{H(2\beta),H(1)}$ ($^3J_{H(4\beta),H(5)}$), which are ~6 Hz for all the compounds under study. If the borinane ring adopts a boat conformation, the ^{1}H NMR spectrum would have a larger coupling constant $^3J_{H(2\beta),H(1)}$ ($^3J_{H(4\beta),H(5)}$ >10 Hz), because the corresponding dihedral angle in this case is close to 0°.

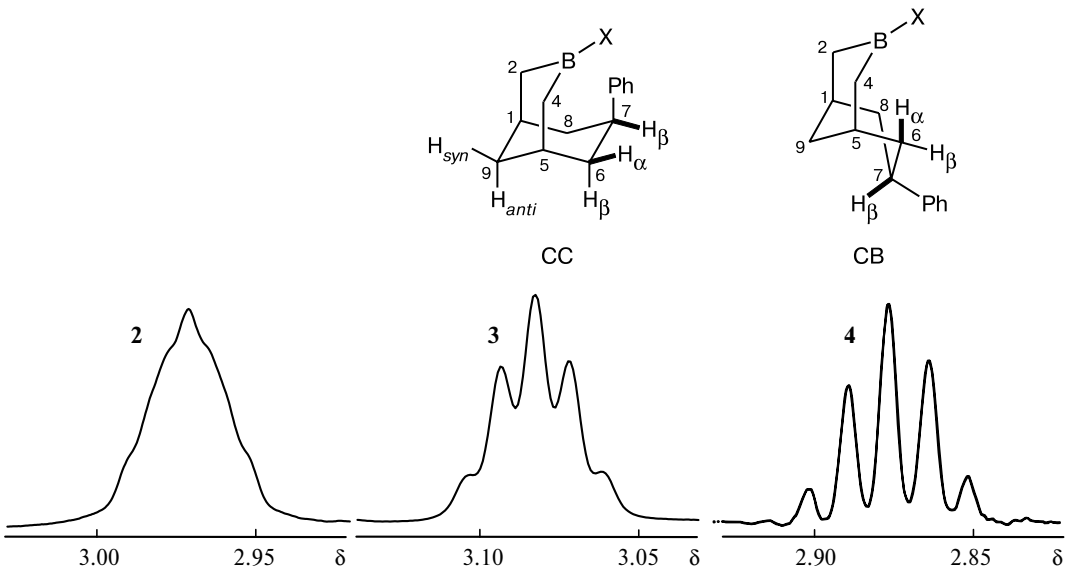
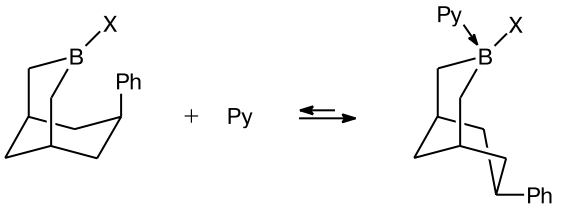


Fig. 1. Proton resonance region for H(7) in the ^{1}H NMR spectra of compounds **2—4**.

which suggests an increase in the content of the conformer with the axial H(7) atom, *i.e.*, the boat conformation of the cyclohexane ring (see Table 2).



The second group involves compounds **6—10** existing predominantly in the chair—boat conformation, as unambiguously evidenced by the large coupling constant (10—14 Hz) between H(7) and H(6α), *i.e.*, by the fact that the corresponding dihedral angle is close to 180° (Fig. 2).

This group includes primarily compounds containing the four-coordinate boron atom with the filled vacant orbital (3-methylamino-7α-phenyl-3-borabicyclo[3.3.1]nonane (**7**) is characterized by completely hindered rotation about the B—N bond). The conformational behavior of these compounds is very similar to that of the carbon analogs. 3-*tert*-Butyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (**6**) containing the bulky substituent at position 3 is the only representative of 7α-phenyl-3-borabicyclo[3.3.1]nonane derivatives with the three-coordinate boron atom, which exists predominantly in the chair—boat conformation.

According to the published data, the ^{13}C chemical shifts of the signals for the C(9) atom of the bicyclo[3.3.1]nonane system are characteristic for the determination of the prevailing conformation of the bicyclic fragment.[22] The transition from the CC to the CB conformation is accompanied by a substantial upfield shift of the signal for the C(9) atom. The ^{13}C chemical shifts for 3-borabicyclo[3.3.1]nonane derivatives are given in Table 3. The chemical shifts of the C(9) atoms for compounds **1—4** lie in a range of δ 34—37. In the spectra of compounds belonging to the second group (compounds **6—10**), the signals for C(9) are shifted upfield (δ 31—33). It is reasonable to assume that, by analogy with a number of bicyclo[3.3.1]nonanes, this is associated with a change in the conformation from CC to CB.

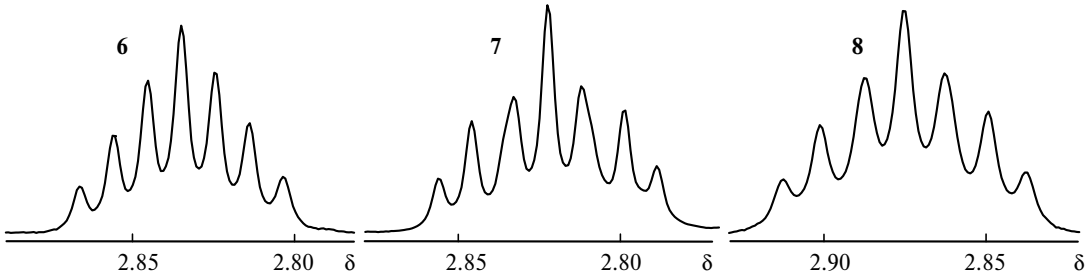


Fig. 2. Proton resonance region for H(7) in the ^{1}H NMR spectra of compounds **6—8**.

Table 3. Chemical shifts (δ) in the ^{13}C NMR spectra of compounds **1—10**

Compound	C(1), C(5)	C(2), C(4)	C(6), C(8)	C(7)	C(9)	Other
1[a]	28.7	37.1	35.8	34.5	37.1	129.06, 129.02, 126.38, 143.9, 11.37 (Me)
2[b]	28.74	35.31	35.31	34.35	37.55	126.92, 129.53, 129.60, 143.9, 5.31 (CH_2—CH=), 113.6 (CH=CH_2), 138.1 (—CH=)
3[a]	27.46	36.18	35.12	33.56	34.39	125.84, 127.2, 128.35, 142.63
4[a]	27.7	29.0	36.9	34.85	34.4	128.3, 127.7, 125.7, 145.2, 52.8
5[a]	32.2	42.4	40.2	34.85	51.9	8.9, 125.94, 128.53, 129.02, 140.4
6[b]	26.66	34.22	38.77	35.99	32.34	125.83, 127.34, 128.56, 146.72, 26.42
7[b]	28.55 and 28.53	26.84 and 30.87	39.81 and 40.15	30.01	33.23	37.75, 126.81, 128.50, 129.37, 148.53
8[a]	27.13	33.5	36.43	37.96	31.61	108.67, 110.50, 122.36, 125.34, 127.75, 128.02, 128.36, 132.60, 137.10, 137.23, 137.64, 149.41, 159.09
9[c]	27.8	33.27	36.23	37.76	31.54	124.93, 127.03, 127.72,
10[c]	28.28	29.09	36.44	38.11	33.22	123.99, 128.24, 128.72

[a] $CDCl_3$.
[b] Toluene-d_8.
[c] Py-d_5.

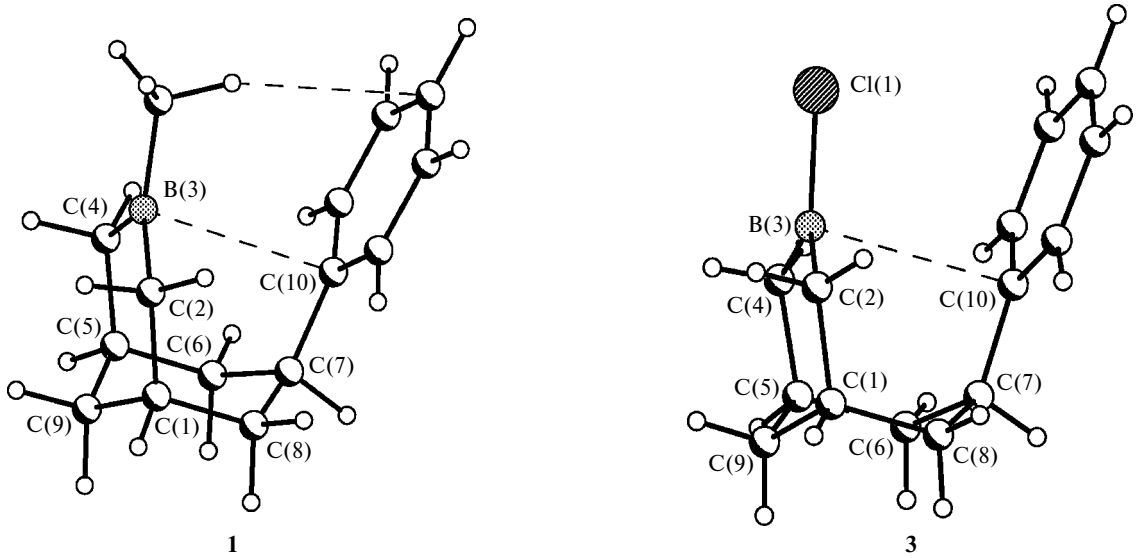
It is quite evident that the preponderance of the chair—chair conformation for compounds **1—6** reflects the energy compromise between the strain associated with steric repulsions of the 3,7-*endo*-H atoms and the specific intramolecular attractive interaction between the vacant 2p orbital of the boron atom and the substituent at the 7-*endo* position. The results of X-ray diffraction analysis considered below provide direct evidence for this interaction.

X-ray diffraction study and quantum-chemical calculations

To estimate the influence of the nature of the substituent at the boron atom on the conformation of 7α-phenyl-3-borabicyclo[3.3.1]nonane, we carried out X-ray diffraction studies of derivatives **2**, **4**, **7**, and **8**.

Earlier,[19,20] we have demonstrated that molecules **1** and **3** in crystals adopt the CC conformation stabilized by transannular B...Ph interactions (Fig. 3). This conclusion was made both based on analysis of the geometry and investigation of the electron density distribution[19,20] in terms of Bader's theory of Atoms in Molecules (AIM).[23]

Analysis of the geometry revealed the presence of rather short intramolecular B(3)...C(10) contacts in both structures and demonstrated that the phenyl substituent is virtually parallel to the C(2)B(3)C(4) plane. Shortening of the B...C contact is accompanied by substantial pyramidalization of the B atom, which deviates (d_B) from the plane passing through the atoms involved in its envi-



1 **3**

Fig. 3. Crystal structures of compounds **1** and **3**.

Table 4. Selected geometric parameters of the molecules in the crystalline and isolated states and the energy differences between the

Compound	Substituent (X) at atom B	Conformation	Method	Distance/Å			
				B(3)—C(2) (B(3)—C(4))	B(3)...C(10)	B—X	C(7)—C(10)
1	Me	CC	X-ray[f]	1.575(3)	2.983(1)	1.569(3)	1.538(3)
		CC	QCC[g]	1.581	3.026	1.576	1.535
		CB	QCC	1.581	—	1.576	1.519
2	All	CC	X-ray	1.598(4)	2.996(4)	1.594(5)	1.558(4)
3	Cl	CC	X-ray	1.559(1)	2.908(1)	1.782(1)	1.5322(8)
4	OMe	CB	X-ray	1.574(2)	—	1.358(2)	1.514(2)
		CB	QCC	1.585	—	1.363	1.516
		CC	QCC	1.585	3.179	1.363	1.531
7	NHMe	CB	X-ray	1.590(2)	—	1.391(2)	1.515(2)
		CB	QCC	1.591	—	1.409	1.519
		CC	QCC	1.593	3.113	1.409	1.538
8[h]	quin	CB	X-ray	1.598(3)	—	1.619(3) N(1) 1.550(3) O(1)	1.505(3)

[a] The angle between the B(3)...C(10) line and the plane of the phenyl ring.
[b] The deviation of the boron atom from the plane passing through the C(2), C(4), and X atoms.
[c] The deviation of the C(10) atom from the plane passing through the C(11), C(7), and C(15) atoms.
[d] The deviation of the B(3) atom from the C(1)C(2)C(4)C(5) plane.
[e] The deviation of the C(9) atom from the C(1)C(2)C(4)C(5) plane.
[f] Data from X-ray diffraction study.
[g] Results of quantum-chemical calculations.
[h] For compound **8**, the average values for three independent molecules are given.

ronment toward the phenyl substituent (Table 4). It should be noted that, on the contrary, the deviation of the *ipso*-C(10) atom of the phenyl ring (d_C) from the plane passing through the C(6), C(11) and C(15) atoms toward the B(3) atom decreases.

Since the geometric parameters serve only as indirect evidence for the specific interactions, we carried out topological analysis of the electron density distribution function $\rho(\mathbf{r})$, which was determined based on the results of quantum-chemical calculations without geometry optimization of **1**,[19] and the data from high-precision X-ray diffraction for compound **3**.[20] It was shown that the critical point (CP) (3, −1) in both molecules is localized in the region of the interatomic B(3)...C(10) contact. According to the AIM[23] theory, this critical point serves as the criterion of chemical bonding. The nature of this interaction was studied in detail using compound **3** as an example. Analysis of the deformation electron density distribution, the Laplacian of the electron density, and the electron localization function (ELF) demonstrated that this interaction corresponds to charge transfer from the π system of the phenyl fragment to the vacant orbital of the boron atom.[20] It should be noted that the critical point (3, −1) in compound **1** was revealed not only in the region of the B...C interaction but also in the region of the C—H...Ph contact[19] (see Fig. 3).

It was of interest to analyze the changes in the character and strength of the B(3)...C(10) interaction in the presence of substituents at the boron atom that can compete with the phenyl π-system and shield the vacant orbital of the boron atom, thus weakening the B(3)...C(10) dative interaction.

X-ray diffraction study of compounds **2**, **4**, and **7** demonstrated that the 3-borabicyclo[3.3.1]nonane fragment adopts the CC conformation only in **2** (Fig. 4), whereas the CB conformation is observed in **4** and **7** as well as in compound **8** containing the four-coordinate boron atom (Figs 4 and 5).

Taking into account that the preponderance of a particular conformation in the crystal can be associated with the crystal packing effects, we performed quantum-chemical calculations (B3PW91/6-31G(d)) for both conformations of compounds **1**, **4**, and **7**.

The functional and the basis set used in these calculations adequately reproduce the experimental geometry (see Table 4). Small elongation of the B...C contact agrees well with the known dependence of the dative interactions on the polarity of the environment. Earlier,[24,25] the lengths of dative contacts and, particularly, bond lengths in donor-acceptor boron complexes in the gaseous phase have been demonstrated to be systematically larger that the corresponding values in the crystalline state.

A comparison of the energies of the CC and CB conformations showed that the conformation of the bicyclic fragment observed in the crystals of compounds **1**, **4**,

conformations (ΔE) according to the results of B3PW91/6-31G(d) calculations

Angle/deg		d/Å				α^a /deg	ΔE /kJ mol^{-1}
C(11)—C(10)—C(15)	C(2)—B(3)—C(4)	$d_B{}^b$	$d_C{}^c$	$d_1{}^d$	$-d_2{}^e$		
116.9(2)	117.0(2)	0.076	0.052	0.299	0.75	73	—
116.7	117.4	0.0677	0.0521	0.273	0.75	80.2	0
117.9	117.8	0.032	0	0.3	0.76	—	1.0385
115.9(3)	116.8(3)	0.0684	0.0483	0.29	0.76	83	—
116.95(5)	121.21(5)	0.0921	0.0473	0.27	0.76	82	—
117.8(1)	120.3(1)	0.0425	0.0142	0.245	0.76	—	—
117.9	119	0.0334	0	0.38	0.76	—	0
117	119.4	0.0627	0.0432	0.26	0.76	64.3	2.4359
117.9(1)	117.2(1)	0.0142	0	0.45	0.75	—	—
117.9	117.2	0.009	0	0.48	0.76	—	—
116.9	118.4	0.0478	0.0476	0.3	0.76	79	8.74
117.7(3)	113.6(2)	—	0.018	0.51	0.75	—	—

and **7** corresponds to the energy minimum, although the energy difference between CC and CB in **1** and **4** is small.

The shortest B...C contact (2.908(1) Å) is observed in compound **3** (see Table 4), whereas the corresponding contacts in **4** and **7** (according to the results of calculations by the B3PW91/6-31G(d) method) are substantially longer (3.179 and 3.113 Å, respectively). Small elongation of the B(3)...C(10) contact in **2** compared to that in **1** is apparently associated with an increase in steric repulsion due to the allylic substituent.

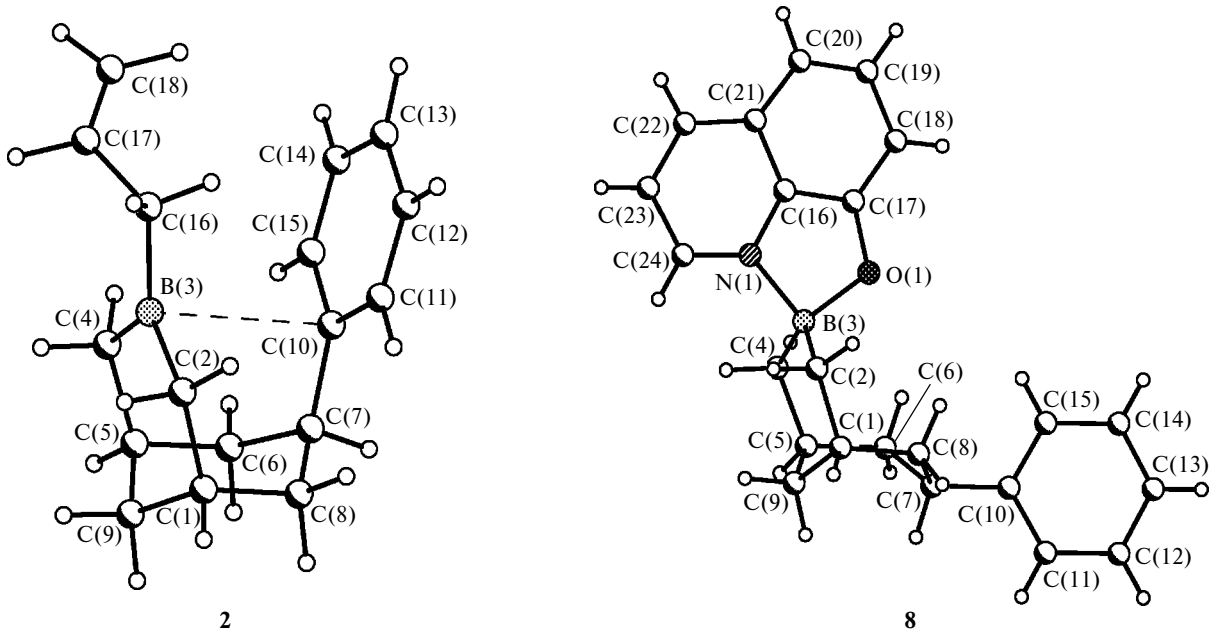


Fig. 4. Crystal structures of compounds **2** and **8**.

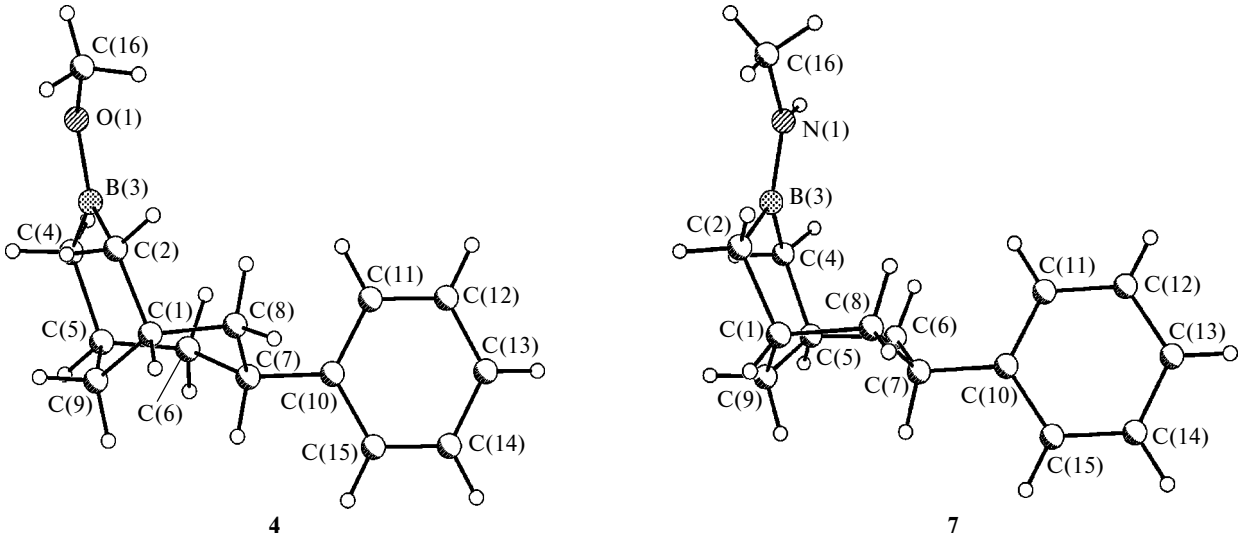


Fig. 5. Crystal structures of compounds **4** and **7**.

Topological analysis of $\rho(\mathbf{r})$ revealed charge transfer from the π system to the vacant orbital of B(3) in all compounds, including **4** and **7**, which exist in the CC conformation. However, the values of $\rho(\mathbf{r})$ (0.047—0.075 eÅ^{-3}) at the corresponding critical points (3, −1) in **4** and **7** are somewhat smaller. It should be noted that there are no C—H...π interactions in compounds **4** and **7** (see Fig. 3). Estimation of the energy of intramolecular interactions based on the potential energy densities at the critical points (3, −1)[26—28] demonstrated that the energy of interactions in **2** is virtually twice as high as that in **4** (7.94 and 4.18 kJ mol^{-1}, respectively).

Therefore, the replacement of the alkyl substituent at the boron atom in 7α-phenyl-3-borabicyclo[3.3.1]nonane by the methoxy or methylamino group leads to weakening of the B...Ph dative interaction, which appears to be sufficient for a decrease in the portion of the CC conformation in the CC $\rightleftharpoons$ CB equilibrium.

It should be noted that a substantial conjugation of the lone electron pair of the nitrogen atom with the vacant orbital of the B(3) atom in compound **7** follows also from the analysis of the geometry. The N(1) atom is characterized by a planar-trigonal configuration (the sum of the bond angles at the N(1) atom is 359.9°), and the B(3)—N(1) (1.391 Å) bond angle falls within a range of values typical of aminoboranes.[29]

A comparison of the geometry of 7α-phenyl-3-borabicyclo[3.3.1]nonane derivatives in the CC and CB conformations demonstrated that the B—X and B—C bond lengths, as well as the parameters describing distortions of the environment about the B atom, remain virtually unchanged. In particular, the degree of pyramidalization of the B(3) atom cannot be considered as a reliable criterion of the presence of transannular contacts, because pyramidalization is observed in the case of the chair—boat conformation as well (except for compound **7**).

On the contrary, the geometric parameters describing the phenyl substituent are more sensitive to the conformational changes. A weak B(3)...C(10) dative interaction in the CC conformation leads to substantial elongation of the C(7)—C(10) bond (1.532—1.538 Å) compared to that observed in the CB conformation (1.505—1.515 Å). Analogous differences are observed also for the *ipso*-C(11)C(7)C(15) angle and the distance d_C.

The conformation of the six-membered boron-containing ring is also rather sensitive to the nature of the substituent at the boron atom. The deviation of the boron atom from the C(1)C(2)C(4)C(5) (d_1) plane in **7** is as high as 0.45 Å and is virtually equal to the corresponding value in **8** (0.51 Å), whereas the boat conformation in the other structures is more flattened and d_1 varies within a rather narrow range of 0.24—0.30 Å.

Other bond lengths and bond angles in the bicycles are virtually independent of the nature of the substituent at the B(3) atom. In particular, the deviations of the C(9) and C(7) atoms from the C(1)C(5)C(6)C(8) plane in the compounds under study remain virtually constant (0.71, −0.62 Å and 0.68, 0.66 Å in the CC and CB conformations, respectively).

The geometric parameters in **8**, including the B(3)—N(1) and B(3)—O(1) bond lengths, are close to the corresponding values in 7α-methyl-3-borabicyclo[3.3.1]non-3-yl quinolin-8-olate.[30]

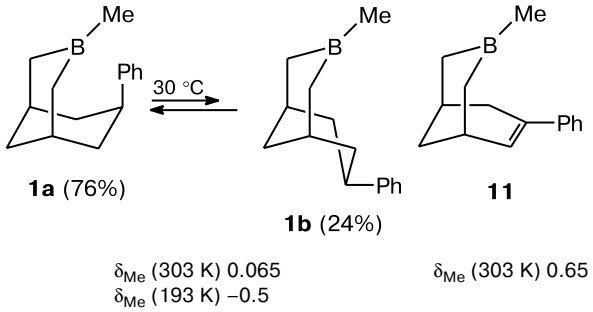
Analysis of the contacts in the crystal packings of **2**, **4**, **7**, and **8** showed that all intermolecular contacts correspond to usual van der Waals interactions, and no shortened intermolecular contacts are present even in the crystals of **7** containing the MeNH group.

Therefore, the X-ray diffraction studies and quantum-chemical calculations demonstrated that the chair—chair conformation in the series of 7α-phenyl-3-borabicyclo[3.3.1]nonane derivatives is stabilized owing to weak B...Ph dative interactions. The contribution of these interactions is determined primarily by the electrophilic characteristics of the boron atom (the occupancy of the vacant 2p orbital of the B atom) rather than by steric factors.

To obtain direct supproting evidence for the role of dative interactions, we performed calculations for two model compounds containing the methyl group at the boron atom and the *p*-aminophenyl or *p*-nitrophenyl substituent at position 7. Calculations by the B3Pw91/6-31G* method demonstrated that the B(3)...C(10) distances and the distances d_B in **1** and the model compounds are slightly different, the steric characteristics of the groups at positions 3 and 7 remaining unchanged. For example, the B(3)...C(10) distance in the 4-amino derivatives decreases to 2.983 Å, whereas deactivation of C(10) in the 4-nitro compound leads to elongation of the corresponding distance to 3.076 Å (for comparison, the corresponding distance in isolated molecule **1** is 3.026 Å).

Dynamic processes in 3-borabicyclo[3.3.1]nonane derivatives

1. Conformational equilibria. Bicycloboranes **1—6** possess high conformational lability, which is manifested in the equilibria characteristic of bicyclo[3.3.1]nonane derivatives.



In the ^{1}H NMR spectrum of compound **2** (303 K), the signal for the H(7) atom appears as a broadened triplet of triplets with the equal coupling constants $^3J_{7\beta,6\alpha} \approx {}^3J_{7\beta,6\beta} \approx$ 6 Hz, whereas the calculated coupling constants for the geometry determined from the X-ray diffraction data for the chair—chair conformation are $^3J_{7\beta,6\alpha}(72°) = 1.56$ Hz and $^3J_{7\beta,6\beta}(42°) = 5.71$ Hz. On the other hand, the corresponding experimental coupling constants for deuteriopyridine complex **9**, which adopts the chair—boat conformation, are $^3J_{7\beta,6\alpha} = 13.1$ Hz and $^3J_{7\beta,6\beta} = 5.6$ Hz.

Based on these data for the CC and CB conformations, one can estimate the fractions of the conformers in the conformational equilibrium.[31] At 303 K, the ratio between the CC and CB conformations of compound **1** is 76 : 24, which corresponds to $\Delta G° = 2.84$ kcal mol^{-1}.

Examination of the ^{13}C and ^{1}H NMR spectra in a wide temperature range (163—373 K) demonstrated that an increase in the temperature leads to a shift of this equilibrium toward the chair—chair conformation. This is manifested in the fact that the ^{1}H chemical shift of the the methyl group in the spectrum of compound **1** changes with temperature. In the CC conformation, the protons of the methyl group are located close to the center of the plane of the phenyl ring and should be strongly shielded due to magnetic anisotropy. At 303 K, δ_{CH_3} is 0.065, and this signal is shifted to δ –0.5 as the temperature decreases to 193 K. For 3-methyl-7-phenyl-3-borabicyclo[3.3.1]non-6-ene (**11**), in which the methyl group is virtually unaffected by ring currents of the phenyl group, $\delta_{CH_3} = 0.63$. The temperature dependence of the chemical shift of the protons of the methyl group of compound **1** (Fig. 6) is consistent with the theoretically expected exponential dependence due to the shift of the equilibrium and the inverse dependence on the cube of the distance to the plane of the phenyl ring.

Due to rapid exchange between the CC and CB conformations, the ^{1}H NMR spectrum has only one averaged signal of the methyl group, whose chemical shift (δ) depends on the equilibrium constant determined from the equation

$$K = (\delta_{CB} - \delta)/(\delta - \delta_{CC}). \quad (1)$$

Assuming that δ_{CC} and δ_{CB} are independent of the temperature in the temperature range used, these parameters were varied in such a way as to achieve the linear dependence of $\ln K$ on $1/T$, and then K was calculated by Eq. (1). The following values were obtained:

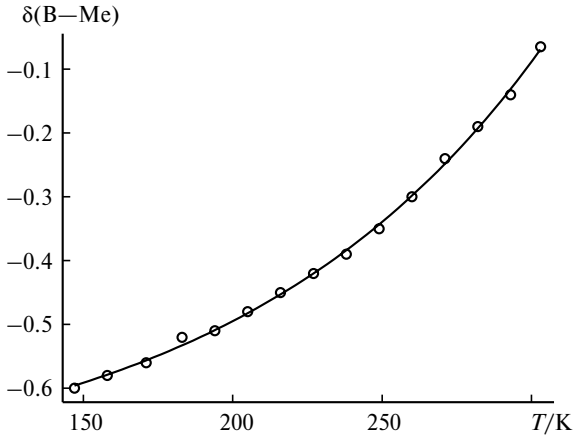
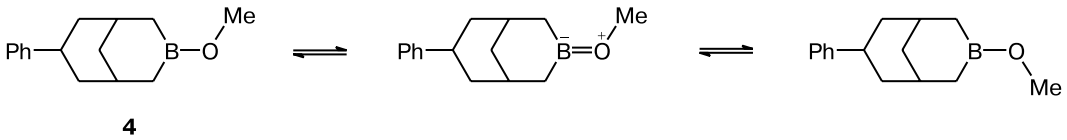


Fig. 6. Temperature dependence of the chemical shift of the protons of the methyl group in the ^{1}H NMR spectrum of compound **1**.



4

δ_{CC} = −0.625±0.005, δ_{CB} = 0.837±0.005, ΔH° = 7.9±0.2 kJ mol^{-1}, ΔS° = 20.4±0.5 J mol^{-1} K^{-1}.

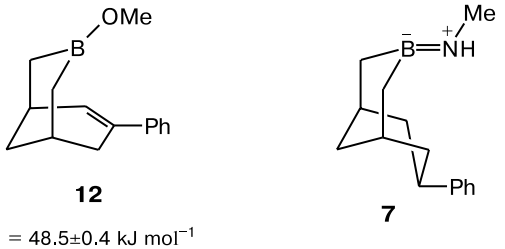
A decrease in the temperature leads to insignificant changes in the chemical shifts in the ^{11}B NMR spectra of these compounds. For example, cooling of a solution of compound **1** from 298 to 213 K results in Δδ of 1.3 ppm (δ changes from 82.0 to 80.7).

2. Hindered rotation about the B—O (or B—N) bond. Investigation of the ^{13}C NMR spectra of 3-methoxy-7α-phenyl-3-borabicyclo[3.3.1]nonane **4** in a wide temperature range revealed molecular dynamics associated with hindered rotation of the methoxy group about the B—O bond. This is clearly evident from the fact that certain carbon atoms (C(2), C(4); C(1), C(5); C(6), C(8)) become nonequivalent in the ^{13}C NMR spectra as the temperature decreases (a double set of signals in a ratio of 1 : 1) (Fig. 7).

The barrier to rotation about the B—O bond is attributable to π-bonding of the vacant 2p orbital of the boron atom with the lone electron pair of the oxygen atom.

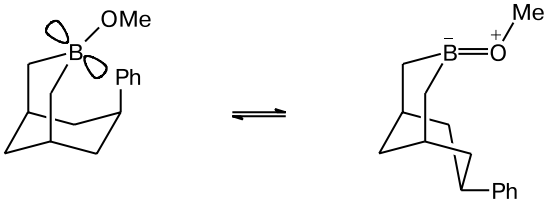
The activation parameters for this process, which were determined by analyzing the line shapes, are as follows: $\Delta H^{\#}$ = 56.6±0.9 kJ mol^{-1}; $\Delta S^{\#}$ = 19.7±4.3 kJ mol^{-1} K^{-1}; $\Delta G^{\#}_{298}$ = 50.8±0.9 kJ mol^{-1}. According to the published data,[32] the measured barriers to rotation about the B—O bond are in a range of 55.6—54.2 kJ mol^{-1}.

Interestingly, $\Delta H^{\#}$ for 3-methoxy-7-phenyl-3-borabicyclo[3.3.1]non-6-ene (**12**) characterized by weaker endocyclic interactions is also substantially lower.



12 **7**

$\Delta H^{\#}$ = 48.5±0.4 kJ mol^{-1}
$\Delta S^{\#}$ = −9.0±1.7 J mol^{-1} K^{-1}
$\Delta G^{\#}_{298}$ = 51.1±0.5 kJ mol^{-1}



4

For 3-methylamino-7α-phenyl-3-borabicyclo[3.3.1]nonane (**7**), complete inhibition of free rotation about the B—N single bond is observed at room temperature. This is clearly evident from the nonequivalence of certain carbon atoms (C(2), C(4); C(1), C(5); C(6), C(8)) in the ^{13}C NMR spectrum and the corresponding hydrogen atoms in the ^{1}H NMR spectrum (a double set of the signals in a ratio of 1 : 1). According to the published data,[33] the barrier to rotation about the B—N bond in (dimethylamino)methyl(phenyl)borane is 111.2 kJ mol^{-1}.

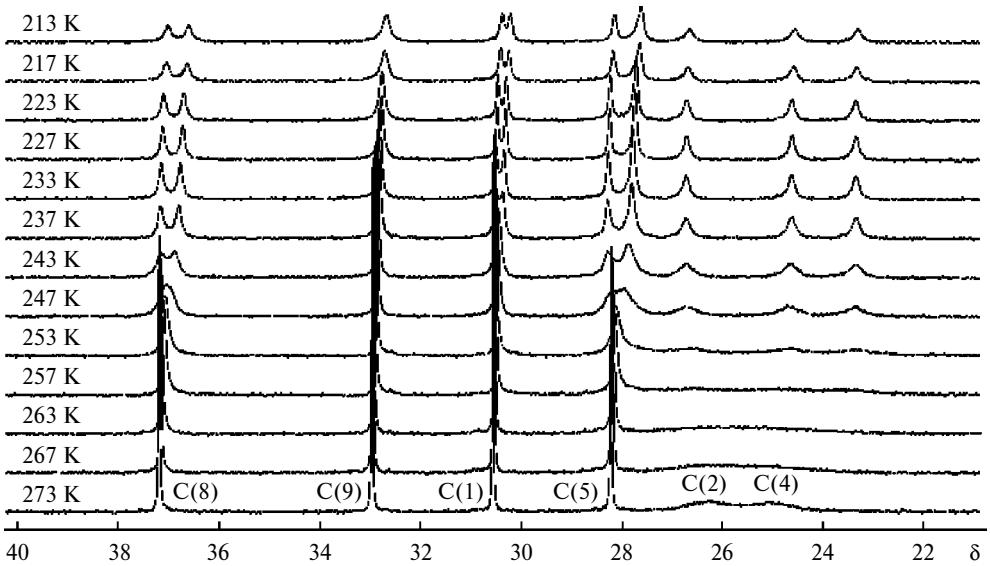
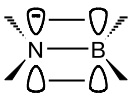
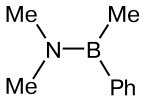


Fig. 7. Temperature dependence of the ^{13}C NMR spectra of 3-methoxy-7-phenyl-3-borabicyclo[3.3.1]non-6-ene (**12**).

These results provide an explanation for the X-ray diffraction data for compounds **4** and **7**. Overlap of the vacant 2p orbital of the boron atom with the electron pair of the oxygen or nitrogen atom leads to the disappearance of an interaction between boron and the 7-*endo* substituent and destabilization of the chair—chair conformation.

The results of the present study unambiguously show that the sterically hindered chair—chair conformations of 3,7-*endo*-disubstituted compounds of the 3-borabicyclo[3.3.1]nonane series can be stabilized due to the specific interaction between the vacant p orbital of the boron atom and the π electrons of the 7-*endo*-phenyl group.

3. Permanent allylic rearrangement. As in other allylboranes, the [1,3]-sigmatropic shift of boron, *viz.*, the permanent allylic rearrangement,[5] is observed in 7α-substituted 3-allyl-3-borabicyclo[3.3.1]nonane derivatives.

Stereochemical nonrigidity of these bicyclic compounds is responsible for a substantial influence of conformational equilibria on the thermodynamic parameters of the rearrangement. The activation parameters for 3-allyl-7α-methyl-3-borabicyclo[3.3.1]nonane (**13**) ($\Delta G^{\neq}_{298}$ = 73.7 kJ mol^{-1}) and 3-allyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (**2**) ($\Delta G^{\neq}_{298}$ = 72.6 kJ mol^{-1}) were measured using 2D NMR spectroscopy with chemical exchange[34] (2D ^{1}H—^{1}H ESXY). These values are the highest of all the known parameters for allylic triorganoboranes, except for allyldimesitylborane (**14**), in which the allylic rearrangement was not observed up to 140 °C.[36]

Hence, 3,7-disubstituted 3-borabicyclo[3.3.1]nonanes are unique models for studying transannular interactions in the chair—chair conformation, in particular, the interactions between the vacant p orbital of the boron atom and the substituent at position 7, the thermodynamic parameters of the CC ⇄ CB conformational equilibria, and the influence of these equilibria on other processes of molecular dynamics (hindered rotation about the B—O bond and the [1,3]-shift of boron in 3-allyl-3-borabicyclo[3.3.1]nonane derivatives).

Experimental

All operations with organoboron compounds were carried out under dry argon. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AC-200P (200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 64.21 MHz for ^{11}B), Bruker AMX-400 (400.13 MHz for ^{1}H and 100.13 MHz for ^{13}C), and Bruker DRX-500 (500.13 MHz for ^{1}H and 125.75 MHz for ^{13}C) instruments.

3-Methyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (**1**),[19] 3-methoxy-7-phenyl-3-borabicyclo[3.3.1]non-6-ene (**12**),[37] 3-chloro-7α-phenyl-3-borabicyclo[3.3.1]nonane (**3**),[37] 3-methoxy-7α-phenyl-3-borabicyclo[3.3.1]nonane (**4**),[37] and 3-methoxy-1,5-dimethyl-7α-phenyl-3-borabicyclo[3.3.1]nonane[18] were synthesized according to procedures described earlier.

The complexes of 3-methoxy- and 3-methyl-7α-phenyl-3-borabicyclo[3.3.1]nonane with pyridine-d_5 (**9** and **10**) were prepared by dissolution of the borabicyclic compounds in an excess of the ligand (Py-d_5).

X-ray diffraction study of compounds 2, 4, 7, and 8. Single crystals of compounds **2** and **7** suitable for X-ray diffraction study were grown by slow cooling of a melt. Single crystals of chelate compound **8** were prepared by recrystallization from diethyl ether. Bicyclic compound **4** crystallized spontaneously (after storage for 6 months).

The structures were solved by direct methods and refined against F^2_{hkl} by the least-squares method with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen

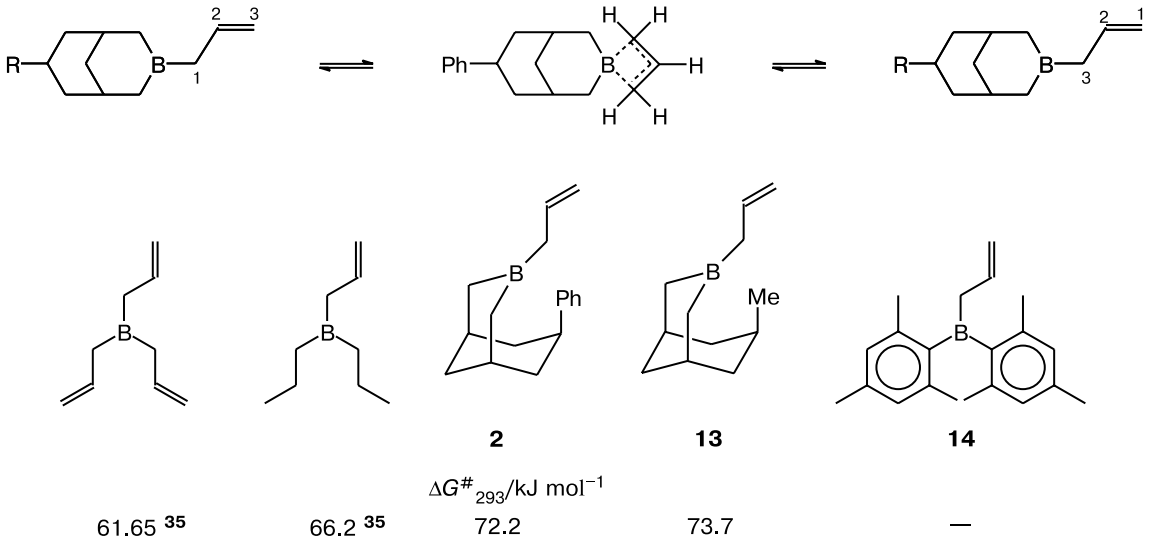


Table 5. Main crystallographic parameters and details of refinement

Parameter	**2**	**4**	**7**	**8**
Molecular formula	$C_{17}H_{23}B$	$C_{15}H_{21}BO$	$C_{15}H_{22}BN$	$C_{23}H_{24}BNO$
Molecular weight	238.16	228.13	227.15	341.24
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
T/K	120	110	120	298
Diffractometer	«SMART CCD»	«SMART CCD»	«SMART CCD»	«Siemens P3»
Z (Z')	2 (1)	4 (1)	4 (1)	6 (3)
a/Å	7.449(5)	7.761(3)	15.157(3)	10.445(2)
b/Å	9.544(7)	15.576(6)	7.318(2)	15.338(3)
c/Å	11.940(9)	10.726(4)	12.538(2)	19.037(4)
α/deg	69.44(2)	—	—	76.04(3)
β/deg	82.32(3)	96.741(9)	111.781(8)	77.67(3)
γ/deg	67.32(2)	—	—	78.13(3)
V/Å^3	733.4(9)	1287.8(8)	1291.4(4)	2853.0(10)
d_{calc}/g cm^{-3}	1.079	1.177	1.168	1.192
μ/cm^{-1}	0.59	0.70	0.66	0.71
F(000)	260	496	496	1092
Scanning mode	ω	ω	ω	ω
$2\theta_{max}$/deg	52	60	60	50
Number of measured reflections	4231	9919	7490	10016
Number of independent reflections	2728	3609	3666	9420
Number of reflections with $I > 2\sigma(I)$	1699	2889	2656	4825
R_{int} 0.0481	0.0312	0.0265	0.0383	
Number of parameters in refinement	255	250	242	703
GOOF	0.977	1.075	1.008	0.923
R_1	0.0741	0.0528	0.0597	0.0437
wR_2	0.1699	0.1298	0.1426	0.0978
Residual electron density/e·Å^{-3} (d_{min}/d_{max})	−0.19/0.20	0.37/−0.28	0.49/−0.21	0.24/−0.18

atoms in compounds **2**, **4**, and **7** were located from difference Fourier maps and refined isotropically. In compound **8**, the positions of the hydrogen atoms were calculated geometrically and refined using the riding model. The main crystallographic parameters and details of the refinement are given in Table 5. All calculations were carried out on an IBM-PC/AT using the SHELXTL PLUS program package.

Determination of the activation parameters for rotation of the methoxy group in 3-borabicyclo[3.3.1]nonane derivatives. The data from the NMR experiments were processed with the use of the standard Bruker software (DISNMR on ASPECT-3000 with the Adakos OS, XWINNMR on IBM-compatible personal computers with the Linux OS) and programs for recording and automatic processing the DNMR spectra (Global-DNMR) developed by us.

The full shapes of the resonance lines were analyzed using the DYNNMR program.[40] The cross-relaxation times were measured at each temperature point.

Quantum-chemical calculations were carried out using the Gaussian 98W program[38] with the B3PW91 hybrid functional and the 6-31G(d) basis set. Topological analysis of the theoretical (calculated) electron density distribution was performed with the use of the EXTREME program.[39]

3-Hexyloxy-7α-phenyl-3-borabicyclo[3.3.1]nonane (15). Hexyl alcohol (2.34 g, 23 mmol) was added with stirring to compound **7** (5.35 g, 23 mmol). The reaction mixture was heated at 100 °C for 1 h. Then methanol was distilled off *in vacuo* (15 Torr, 20 °C). Distillation of the residue afforded product **15** in a yield of 5.8 g (84.6%), b.p. 155—156 °C (1.5 Torr). Found (%): C, 80.54; H, 10.48; B, 3.62. $C_{20}H_{31}BO$. Calculated (%): C, 79.98; H, 10.45; B, 3.42. ^{1}H NMR ($CDCl_3$), δ: 0.8—0.91 (dd, 2 H, H(2β), H(4β), ^2J = 16.54 Hz); 0.91—1.00 (t, 3 H, (C$\underline{H}_3$), J = 6.61 Hz); 1.05—1.20 (d, 2 H, H(2α), H(4α), ^2J = 16.54 Hz); 1.40—1.55 (m, 9 H, H_{syn}(9), H(C$\underline{H}_2$)$_4$); 1.85—2.05 (m, 3 H, H_{anti}(9), H(6α), H(8α)); 2.10—2.30 (m, 2 H, H(6β), H(8β), ^2J = 13.97 Hz); 2.35—2.55 (m, 2 H, H(1), H(5)); 2.95—3.15 (m, 1 H, H(7)); 3.60—3.70 (t, 2 H, H(—O—C$\underline{H}_2$), ^2J = 6.61 Hz); 7.25—7.40 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 13.96 (C(Me)); 22.57 (C(5′)); 25.48 (C(4′)); 27.11 (C(1), C(5)); 27.74 (C(2), C(4)); 31.36 (C(9)); 31.58 (C(7)); 33.27 (C(3′)); 35.02 (C(2′)); 37.36 (C(6), C(8)); 65.18 (C(1′)); 125.35, 127.18, 127.93, 145.81 (Ph).

3-Allyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (2). A mixture of compound **15** (5.8 g, 19 mmol) and allyl bromide (2.35 g, 19 mmol) was added dropwise to a suspension of a Mg powder (0.449 g, 19 mmol) in Et_2O (20 mL). The reaction mixture was refluxed for 4 h. The diethyl ether was removed *in vacuo*. Hexane (90 mL) was added to the residue and the mixture was refluxed for 0.5 h. The solution was filtered and the solvent was removed. The residue was distilled and compound **2**

was obtained in a yield of 3.24 g (71.6%), b.p. 115—120 °C (1.5 Torr), m.p. 27—30 °C. Found (%): C, 85.73; H, 9.73; B, 4.54. $C_{17}H_{23}BO$. Calculated (%): C, 85.65; H, 9.71; B, 4.18. ^{1}H NMR (toluene-d_8), δ: 0.72 (dd, 2 H, H(2β), H(4β), $^2J_{H(2\beta),H(2\alpha)}$ = 17.41 Hz, $^3J_{H(2\beta),H(1)}$ = 5.5 Hz); 1.02 (d, 2 H, (C$\underline{H}_2$—CH), $^3J_{H(Y),H(X)}$ = 7.56 Hz); 1.41 (br.d, 1 H, H_{syn}(9), $^2J_{H_{syn}(9),H_{anti}(9)}$ = 12.37 Hz); 1.49 (d, 2 H, H(2α), H(4α), $^2J_{H(2\alpha),H(2\beta)}$ = 17.41 Hz); 1.71 (dm, 1 H, H_{anti}(9)); 1.87 (dt, 2 H, H(6β), H(8β), $^2J_{H(6\beta),H(6\alpha)}$ = 13.98 Hz, $^3J_{H(6\alpha),H(7)}$ = 5.96 Hz); 2.15 (m, 2 H, H(1), H(5)); 2.22 (br.d, 4 H, H(6α), H(8α), $^3J_{H(6\alpha),H(7)}$ = 5.96 Hz); 2.84 (m, 1 H, H(7), $^3J_{H(7),H(6\alpha)}$ = 5.96 Hz); 4.70 (dd, 2 H, (C$\underline{H}_2$=CH), $^3J_{H(A),H(X)}$ = 10.08 Hz, $^3J_{H(B),H(X)}$ = 17.06 Hz); 5.59 (ddt, 1 H, (C$\underline{H}$=CH_2), $^3J_{H(X),H(A)}$ = 10.08 Hz, $^3J_{H(X),H(B)}$ = 17.06 Hz, $^3J_{H(X),H(Y)}$ = 7.56 Hz); 6.93 (t, 1 H, (*p*-Ph), ^2J = 7.33 Hz); 7.05 (m, 2 H, (*m*-Ph)); 7.21 (d, 2 H, (*o*-Ph), ^2J = 7.56 Hz).

1,3,5-Trimethyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (5). Analogously to the synthesis of compound **2**, compound **5** was synthesized from MeMgI (prepared from Mg (0.47 g, 19.5 mmol) and MeI (2.8 g, 19 mmol)) and 3-methoxy-1,5-dimethyl-7-phenyl-3-borabicyclo[3.3.1]nonane (4.8 g, 18.7 mmol). The yield was 3.7 g (82%), b.p. 118—120 °C (1.5 Torr), m.p. 63 °C. Found (%): C, C, 85.00; H, 10.49; B, 4.50. $C_{17}H_{25}B$. Calculated (%): C, 85.16; H, 10.39; B, 4.36.

3-*tert*-Butyl-7α-phenyl-3-borabicyclo[3.3.1]nonane (6). The Grignard reagent prepared from Bu^tCl (5.4 g, 57 mmol) and Mg (1.4 g, 57.5 mmol) in Et_2O (25 mL) was added dropwise to a solution of compound **4** (6.52 g, 28 mmol) in pentane (25 mL). The reaction mixture was stirred for 3 h and filtered. The solvent was distilled off *in vacuo* and the residue was distilled. Compound **6** was prepared in a yield of 5.07 g (70%), b.p. 127—128 °C ($5\cdot10^{-2}$ Torr), n_D^{20} 1.5348. Found (%): C, 85.03; H, 10.70; B, 4.26. $C_{18}H_{27}B$. Calculated (%): C, 84.78; H, 10.61; B, 4.10. ^{1}H NMR ($CDCl_3$), δ: 0.79 (s, 9 H, Bu^t); 1.02 (dd, 2 H, H(2β), H(4β), $^2J_{H(2\beta),H(2\alpha)}$ = 18.03 Hz, $^3J_{H(2\beta),(H1)}$ = 5.61 Hz); 1.23 (br.d, 1 H, H_{syn}(9), $^2J_{H_{syn}(9),H_{anti}(9)}$ = 12.95 Hz); 1.27 (ddd, 2 H, H(6α), H(8α), $^2J_{H(6\alpha),H(6\beta)}$ = 14.05 Hz, $^3J_{H(6\alpha),H(5)}$ = 3.52 Hz, $^3J_{H(6\alpha),H(7)}$ = 9.9 Hz); 1.72 (dd, 2 H, H(2α), H(4α), $^2J_{H(2\alpha),H(2\beta)}$ = 18.03 Hz); 1.98 (dm, 1 H, H_{anti}(9)); 2.16 (ddd, 2 H, H(6β), H(8β), $^2J_{H(6\beta),H(6\alpha)}$ = 14.05 Hz, $^3J_{H(6\beta),H(7)}$ = 5.5 Hz, $^3J_{H(6\beta),H(5)}$ = 8.61 Hz); 2.33 (m, 2 H, H(1), H(5)); 2.83 (tt, 1 H, H(7)); 7.13 (t, 1 H, H(*p*-Ph), ^2J = 7.21 Hz); 7.19 (d, 2 H, H(*o*-Ph), ^2J = 7.21 Hz); 7.25 (t, 2 H, H(*m*-Ph), ^2J = 7.61 Hz).

3-Methylamino-7α-phenyl-3-borabicyclo[3.3.1]nonane (7). Gaseous $MeNH_2$ (1.06 g, 34.2 mmol) was introduced into a solution of compound **3** (1.47 g, 6.3 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 0.5 h, the solvent was distilled off, and the residue was distilled. Compound **7** was isolated in a yield of 0.74 g (51.7%), b.p. 125—126 °C (1.5 Torr), m.p. 59—60 °C. Found (%): C, 84.97; H, 10.25; B, 4.78. $C_{15}H_{22}BN$. Calculated (%): C, 84.27; H, 9.98; B, 4.32. ^{1}H NMR (toluene-d_8), δ: 0.71 (br.d, 1 H, H(4α), $^2J_{H(4\alpha),H(4\beta)}$ = 15.2 Hz); 0.77 (dd, 1 H, H(2β), $^2J_{H(2\beta),H(2\alpha)}$ = 15.62 Hz, $^3J_{H(2\beta),H(1)}$ = 6.01 Hz); 0.89 (dd, 1 H, H(4β), $^2J_{H(4\beta),H(4\alpha)}$ = 15.22 Hz, $^3J_{H(4\beta),(H5)}$ = 6.01 Hz); 1.15—1.21 (m, 3 H, H(6α), H(8α), H(2α)); 1.26 (dm, 1 H, H_{syn}(9), $^2J_{H_{syn}(9),H_{anti}(9)}$ = 12.8 Hz); 1.89 (dm, 1 H, H_{anti}(9), $^2J_{H_{anti}(9),H_{syn}(9)}$ = 12.81 Hz); 2.11 (m, 2 H, H(6β), H(8β)); 2.30 and 2.36 (both m, 2 H, H(1), H(5)); 2.61 (d, 3 H, CH_3, ^2J = 6.01 Hz); 2.77 (tt, 1 H, H(7), $^3J_{H(7),H(6\alpha)}$ = 11.61 Hz, $^3J_{H(7),H(6\beta)}$ = 5.21 Hz); 3.75 (br.s, 1 H, (NH)); 7.2—7.25 (m, 4 H, H(*o*-Ph), H(*m*-Ph)), 7.12 (t, 1 H, H(*p*-Ph), *J* = 7.2 Hz).

7α-Phenyl-3-borabicyclo[3.3.1]nonan-3-yl quinolin-8-olate (8). A solution of 8-hydroxyquinoline (1.38 g, 9.5 mmol) in Et_2O (20 mL) was added to a solution of compound **4** (2.17 g, 9.5 mmol) in Et_2O (10 mL). The reaction mixture was stirred for 1 h, the solvent was distilled off *in vacuo*, and the residue was recrystallized from Et_2O. Compound **8** was isolated in a yield of 3.10 g (95.6%), m.p. 146—148 °C. Found (%): C, 80.95; H, 7.09; B, 3.17. $C_{23}H_{24}BNO$. Calculated (%): C, 81.38; H, 7.05; B, 3.00. ^{1}H NMR ($CDCl_3$), δ: 0.54 (dd, 2 H, H(2β), H(4β), $^2J_{H(2\beta),H(2\alpha)}$ = 13.21 Hz, $^3J_{H(2\beta),H(1)}$ = 4.8 Hz); 0.88 (dd, 2 H, H(2α), H(4α), $^2J_{H(2\alpha),H(2\beta)}$ = 13.21 Hz); 1.32 (br.d, 1 H, H_{syn}(9), $^2J_{H_{syn}(9),H_{anti}(9)}$ = 12.81 Hz); 1.95—2.07 (m, 4 H, H(6α), H(8α), H(6β), H(8β)); 2.12 (dm, 1 H, H_{anti}(9), $^2J_{H_{anti}(9),H_{syn}(9)}$ = 12.81 Hz); 2.42 (m, 2 H, H(1), H(5)); 2.87 (tt, 1 H, H(7), $^3J_{H(7),H(6\alpha)}$ = 12.82 Hz, $^3J_{H(7),H(6\beta)}$ = 5.6 Hz); 7.03 (d, 1 H, H(7′), *J* = 7.61 Hz); 7.09 (d, 1 H, H(5′), *J* = 8.01 Hz); 7.18 (t, 1 H, H(*o*-Ph)); 7.33 (t, 1 H, H(*m*-Ph), *J* = 7.61 Hz); 7.49 (d, 2 H, H(*o*-Ph), *J* = 7.61 Hz); 7.51 (m, 1 H, H(3′)); 7.59 (t, 1 H, H(6′), *J* = 8.01 Hz); 8.24 (d, 1 H, H(4′), *J* = 8.01 Hz); 8.27 (d, 1 H, H(2′), *J* = 4.81 Hz).

3-Methyl-7-phenyl-3-borabicyclo[3.3.1]non-6-ene (11). A solution of compound **12** (7.96 g, 35.2 mmol) in Et_2O (20 mL) was added to a solution of MeMgI prepared from Mg (0.86 g, 35.3 mmol) and MeI (5 g, 35.3 mmol) in Et_2O (30 mL). The reaction mixture was refluxed for 3 h and then cooled. The diethyl ether was distilled off. The precipitate was washed with hexane and filtered off. The filtrate was concentrated *in vacuo* and the residue was distilled. Compound **11** was isolated in a yield of 3.48 g (47%), b.p. 126—127 °C (1.5 Torr), n_D^{20} 1.5615. Found (%): C, 85.73; H, 9.11; B, 5.15. $C_{15}H_{19}B$. Calculated (%): C, 85.66; H, 9.05; B, 5.11. ^{1}H NMR ($CDCl_3$), δ: 0.64 (s, 3 H, CH_3); 1.1, 1.2, 1.25, and 1.31 (all m, 2 H, H(2β), H(4β)); 1.50, 1.56, 1.61, and 1.68 (all m, 2 H, H(2α), H(4α)); 1.68, 1.72, 1.85, and 1.91 (all m, 2 H, H_{syn}(9), H_{anti}(9)); 2.15 (dd, 1 H, H(8α)); 2.52, 2.65 (m, 2 H, H(1), H(5)); 2.66, 2.75 (m, 1 H, H(8β)); 6.12 (m, 1 H, H(6)); 7.10—7.35 (m, 5 H, Ph).

3-Hexyloxy-7α-methyl-3-borabicyclo[3.3.1]nonane was prepared analogously to compound **15** from 3-methoxy-7α-methyl-3-borabicyclo[3.3.1]nonane (7.78 g, 46.9 mmol) and hexyl alcohol (4.79 g, 46.9 mmol). The yield was 9.1 g (82%), b.p. 120—123 °C (1.5 Torr). Found (%): C, 76.27; H, 12.38; B, 4.58. $C_{15}H_{29}BO$. Calculated (%): C, 76.01; H, 12.12; B, 3.98. ^{1}H NMR ($CDCl_3$), δ: 0.80—1.00 (m, 8 H, H(2β), H(4β), 2 C$\underline{H}_3$); 1.05—1.45 (m, 9 H, H(6α), H(8α), H_{syn}(9), (C$\underline{H}_2$)$_4$); 1.50—1.70 (m, 3 H, H(2α), H(4α), H_{anti}(9)); 1.75—2.0 (m, 3 H, H(6β), H(8β), H(7)); 2.15—2.2 (m, 2 H, H(1), H(5)); 3.75—3.90 (t, 2 H, H(—O—C$\underline{H}_2$)). ^{13}C NMR ($CDCl_3$), δ: 13.94 (C($CH_2\underline{C}H_3$)); 22.59 (C(5′)); 24.33 (C($CH\underline{C}H_3$)); 25.35 (C(4'); 25.52 (C(7)); 27.07 (C(1), C(5), C(2), C(4)); 31.42 (C(3′)); 31.58 (C(2′)); 34.09 (C(9)); 65.15 (C(1′)).

3-Allyl-7α-methyl-3-borabicyclo[3.3.1]nonane (13) was synthesized analogously to compound **2** from 3-hexyloxy-7α-methyl-3-borabicyclo[3.3.1]nonane (11.6 g, 39 mmol) and allylmagnesium bromide prepared from Mg (1.89 g, 77.8 mmol) and AllBr (4.72 g, 39 mmol) in Et_2O. Compound **13** was isolated in a yield of 7.79 g (84%), b.p. 115—120 °C (1.5 Torr). Found (%): C, 81.14; H, 11.92; B, 5.28. $C_{12}H_{21}B$. Calculated (%): C, 81.84; H, 12.02; B, 6.14. ^{1}H NMR (toluene-d_8), δ:

0.95 (d, 3 H, C<u>H</u>$_3$, ^2J = 7.34 Hz); 1.22 (dd, 2 H, H(2β), H(4β), $^2J_{H(2\beta),H(2\alpha)}$ = 18.1 Hz, $^3J_{H(2\beta),(H1)}$ = 6.12 Hz); 1.49 (br.d, 2 H, H(6α), H(8α), $^2J_{H(6\alpha),H(6\beta)}$ = 12.23 Hz); 1.65 (br.d, 1 H, H_{syn}(9), $^2J_{H_{syn}(9),H_{anti}(9)}$ = 12.71 Hz); 1.84—1.92 (m, 3 H, H_{anti}(9), H(2α), H(4α)); 2.03—2.06 (m, 3 H, H(6β), H(8β), H(7)); 2.18 (d, 2 H, (C<u>H</u>$_2$—CH), $^3J_{H(Y),H(X)}$ = 7.33 Hz); 2.32 (m, 2 H, H(1), H(5)); 5.1 (dd, 2 H, (C<u>H</u>$_2$=CH), $^3J_{H(A),H(X)}$ = 10.27 Hz, $^3J_{H(B),H(X)}$ = 16.87 Hz); 5.71 (m, 1 H, (C<u>H</u>=CH$_2$), $^3J_{H(X),H(A)}$ = 10.57 Hz, $^3J_{H(X),H(B)}$ = 16.87 Hz, $^3J_{H(X),H(Y)}$ = 7.33 Hz).

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