Transanular Interactions in Difunctional Medium Rings, 5[1]

Spectroscopic Investigations of Bicyclic Boraamines

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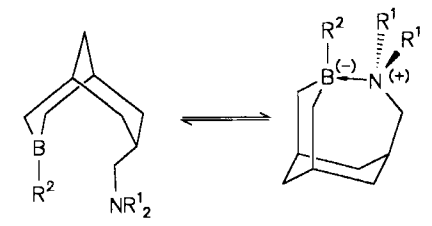
The *endo*-7-[(dialkylamino)methyl]-3-borabicyclo[3.3.1]nonanes **1** and **2** have been synthesized and their intramolecular complex formation of the corresponding 2-azonia-1-boratatricyclo[4.3.1.1^{4,8}]undecanes **3** and **4** has been studied in the gas phase by UV photoelectron spectroscopy and in solution by ^{11}B-NMR spectroscopy. Deviations of the characteristic spectral features from those of the monofunctional bicyclic boranes **5** and amines **6** and **7** indicate that in the gas phase the (dimethylamino)boranes with a *B*-alkyl substituent adopt the tricyclic form **3a–c** whereas the diethylamino and the *B*-methoxy derivatives **1e** and **2** prefer the bicyclic structure. In solution some deviations from this behavior are observed.

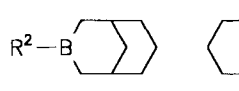
Boranes and organic boron compounds react with ammonia or amines to afford adducts[2]. The stability of such borane–amine complexes depends on the substituents. Brown and Johannesen[3] have determined the equilibrium constants of the reaction of amines with trimethylborane in one of the first quantitative analyses of non-bonded interactions. The dissociation enthalpy of the complex with trimethylamine for example is 72.7 kJ mol^{-1}. The formation of the B–N bond is only possible at the expense of repulsive interactions between the alkyl groups. We have studied the intramolecular complex formation and the corresponding bonding interaction between the empty $2p_z$ atomic orbital of the borane and the occupied n_N orbital of the amine by using the *endo*-7-[(dialkylamino)methyl]-3-borabicyclo-[3.3.1]nonanes **1** and **2** as examples. Formation of the adduct takes place only when the bicyclic system converts to the tricyclic system forming the alkyl-substituted 2-azonia-1-boratatricyclo[4.3.1.1^{4,8}]undecanes **3** and **4**. In addition, it also has to be expected that the substituents on the hetero atoms affect the formation and the stability of the adducts. If no adduct with a covalent B–N bond is formed, a donor/acceptor interaction by a through-space mechanism[4] might be possible. Since the two functional groups are separated by six σ bonds, it is likely that through-bond effects[4] are of little importance.

As experimental methods to study this isomerism and the relevant orbital interactions, UV photoelectron spectroscopy[5] and ^{11}B-NMR spectroscopy[6] have proved valuable. The mutual effects of the functional groups upon each other are investigated by a comparison of the spectra of the difunctional with those of the corresponding monofunctional compounds, which are the boranes **5** and the amines **6** and **7**. If there is no interaction we expect the spectra of the difunctional compounds **1** and **2** to result by addition of those of the monofunctional derivatives. Differences from additivity can be interpreted as indications of interaction.



1,2 3,4

		R^1	R^2
1,3,5	e	CH_3	OCH_3
	a		CH_3
	b		C_2H_5
	c		$CH(CH_3)_2$
	d		$C(CH_3)_3$
2,4	e	C_2H_5	OCH_3
	a		CH_3



5

	R^1
6	CH_3
7	C_2H_5

Synthesis of *endo*-7-[(Dialkylamino)methyl]-3-borabicyclo[3.3.1]nonanes

Reaction of chlorodiethylamine with the 1-boraadamantane–THF complex affords 3-chloro-7-[(diethylamino)methyl]-3-borabicyclo[3.3.1]nonane[7,8]. With sodium meth-

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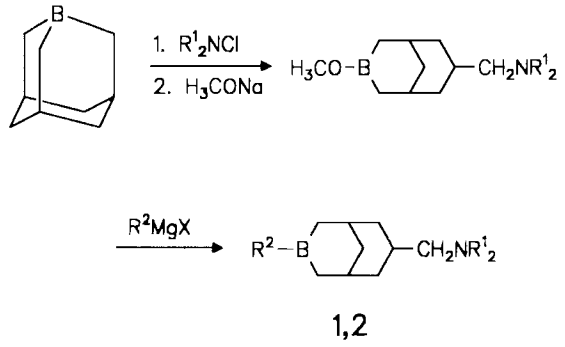


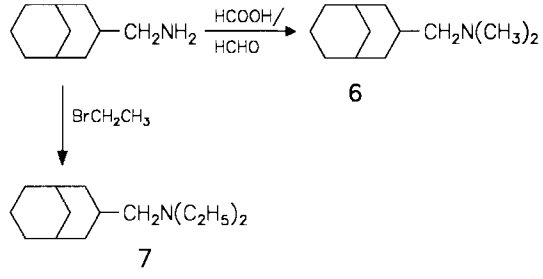
1,2

oxide 7-[(diethylamino)methyl]-3-methoxy-3-borabicyclo-[3.3.1]nonane (**2e**) is obtained.

In analogy to this method[7] we have synthesized 7-[(dimethylamino)methyl]-3-methoxy-3-borabicyclo[3.3.1]nonane (**1e**), from which the 3-alkyl-7-[(dialkylamino)methyl]-3-borabicyclo[3.3.1]nonanes **1a–c** are obtained by Grignard reaction. In the same way, **2e** has been transformed to **2a**.

The *tert*-butyl derivative **1d** could not be obtained although the solvent and the halogen in the Grignard reagent were varied. An attempt to synthesize it by treatment of 3-chloro-7-[(dimethylamino)methyl]-3-borabicyclo[3.3.1]-nonane with *tert*-butyllithium was not successful.

The monofunctional compounds *endo*-3-[(dimethylamino)methyl]bicyclo[3.3.1]nonane (**6**) and *endo*-3-[(diethylamino)methyl]bicyclo[3.3.1]nonane (**7**) were obtained from *endo*-3-(aminomethyl)bicyclo[3.3.1]nonane[9] by reductive methylation or reaction with bromoethane, respectively. Purification was performed by Hinsberg reaction.



6

7

The synthesis of the *B*-substituted 3-borabicyclo-[3.3.1]nonanes **5** has been described[1].

Results

Structures

In the difunctional compounds **1** and **2** the number of conformers is larger than that of the bicyclic skeleton[10] since different orientations of the *endo*-(dialkylamino)-methyl group are possible. We have studied the structure and the conformational properties of **1** and **2** and of the monofunctional bicyclic compounds **6** and **7** by molecular mechanics[11] (MMX) and by quantum-chemical (AM1[12]) calculations[13]. It was found that these methods are not well suited to investigate the problems studied here. Therefore, we retain from presenting the results en detail.

In Figure 1 the chair-chair (CC) and the chair-boat (CB) conformers with synclinal (sc) or anticlinal (ac) positions[14] of the *endo* substituent are shown for 7-[(dimethylamino)-methyl]-3-methyl-3-borabicyclo[3.3.1]nonane (**1a**). In the scCC form, which has a B–N distance of ca. 300 (MMX) or 320 pm (AM1), the functional groups have an optimal orientation for intramolecular interaction. However, this form is not found as favorable for **1** and **2**, its energy is clearly above the most stable conformers as determined by both methods (AM1 ca. 28, MMX 23–42 kJ mol^{-1}).

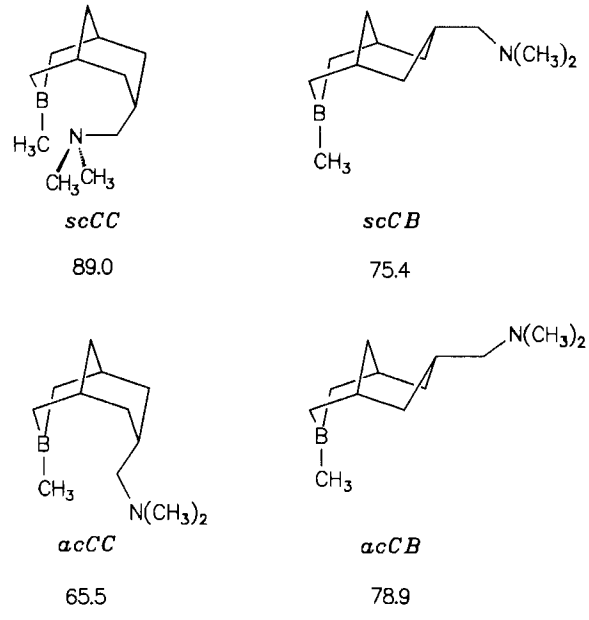


Figure 1. Conformers of *endo*-7-[(dimethylamino)methyl]-3-methyl-3-borabicyclo[3.3.1]nonane (**1a**) with MMX strain energies [kJ mol^{-1}]

Provided there is strong interaction of the donor/acceptor pair, intramolecular cyclization occurs, and a tricyclic system is formed, in which the former bicycle is fixed in the scCC form. The increase of strain may be compensated by the formation of the B–N bond (ca. 70 kJ mol^{-1}). According to MMX calculations the strain energy increases by ca. 30 kJ mol^{-1} in the transformation of **1a** to **3a**[13]. However, the AM1 method predicts an increase of the enthalpies of formation by 22.6 to 67.5 kJ mol^{-1} for the conversion of **1** and **2** to **3** and **4**, respectively[13]. Accordingly, only the bicyclic compounds should be found, which is not in accord with the experimental findings (vide infra).

Electronic Structures

In the compounds studied here, in the bicyclic form the orbital of the nitrogen lone pair, n_N, is the HOMO. The next two orbitals, HOMO-1 and HOMO-2, are MOs mainly of σ_{BC} character. If there is an interaction of the donor/acceptor pair, the n_N is stabilized. In Table 1 the energies of the three highest occupied MOs of the alkyl derivatives **1a–c** and **2a** as well as of the two highest occupied MOs of the methoxy derivatives **1e** and **2e**, as calculated by the AM1[12] method, are summarized. The small deviations of the n_N MOs of **1** and **2** relative to those of **6** and **7**

indicate that there are only small interactions of the functional groups.

Table 1. Orbital energies $-\varepsilon^{SCF}$ [eV] of the bicycles **1a–c**, **e**, **2a**, **e**, **6**, and **7** in the scCC form and of the tricycles **3a–c**, **e**, and **4a**, **e** (AM1 results)

	1a	**1b**	**1c**	**1e**	**2a**	**2e**		
n_N	8.97	9.01	9.02	8.93	8.82	8.82		
σ_{BC}	9.69	9.70	9.70		9.74			
σ_{BC}	10.18	10.02	9.89	9.69[a]	10.17	9.70[a]		
	3a	**3b**	**3c**	**3e**	**4a**	**4e**	**6**	**7**
n_N							9.06	8.84
σ_{BC}	9.09	9.09	9.10	9.16[a]	9.09	9.09[a]		
σ_{BC}	9.46	9.27	9.27		9.48			
σ_{BN}/σ_{CC}	10.33	10.31	10.31		10.27			

[a] $\sigma_{BC}/\sigma^*_{BO}$.

When the intramolecular borane–amine complexes **3** and **4** are formed, the nitrogen lone pair becomes the B–N σ bond, the n_N orbital being converted to the σ_{BN} orbital and clearly stabilized[15]. This orbital is found as HOMO-2, while HOMO and HOMO-1 are the two σ_{BC} MOs.

In Table 1 the calculated energies of the three highest occupied MOs are listed for the intramolecular adducts **3a–c** and **4a** and of the highest occupied MO of the 3-methoxy derivatives **3e** and **4e**. The orbitals are destabilized by 0.2–0.3 eV relative to the corresponding 3-alkyl-3-borabicycloalkanes[1] **5a–e**. The n_N orbital of the amino bicycles **6** and **7** is stabilized by 1.25–1.43 eV by the transformation to the σ_{BN} MO in **3** and **4**.

Photoelectron Spectra

If compounds **1** and **2** show strong intramolecular interactions or even form the adducts **3** and **4**, respectively, this should be obvious from their PE spectra. In the low-energy region of the spectra the n_N ionization of the bicyclic compounds should be found at about 8 eV. If this band is not present, a tricyclic structure has to be assumed. For a more accurate analysis, the spectra are compared with those of the bicyclic compounds **5**[1], **6**, and **7**.

In Figures 2 and 3 the spectra of compounds **1a**, **5a**, and **6** and of **2e**, **5e**, and **7**, respectively, are depicted as characteristic examples. The relevant ionization energies are summarized in Table 2.

Figure 2 clearly indicates strong intramolecular interaction of the donor/acceptor pair in 7-[(dimethylamino)methyl]-3-methyl-3-borabicyclo[3.3.1]-nonane (**1a**). Therefore, for this compound formula **3a** is correct. An n_N ionization is missing, and the first ionization band of **1a/3a** is rather broad and split like in **5a**[1]. Two σ_{BC} MOs are assigned to the first two IPs, and a MO with large σ_{BN} character is attributed to the third IP. Heating to 200°C does not change

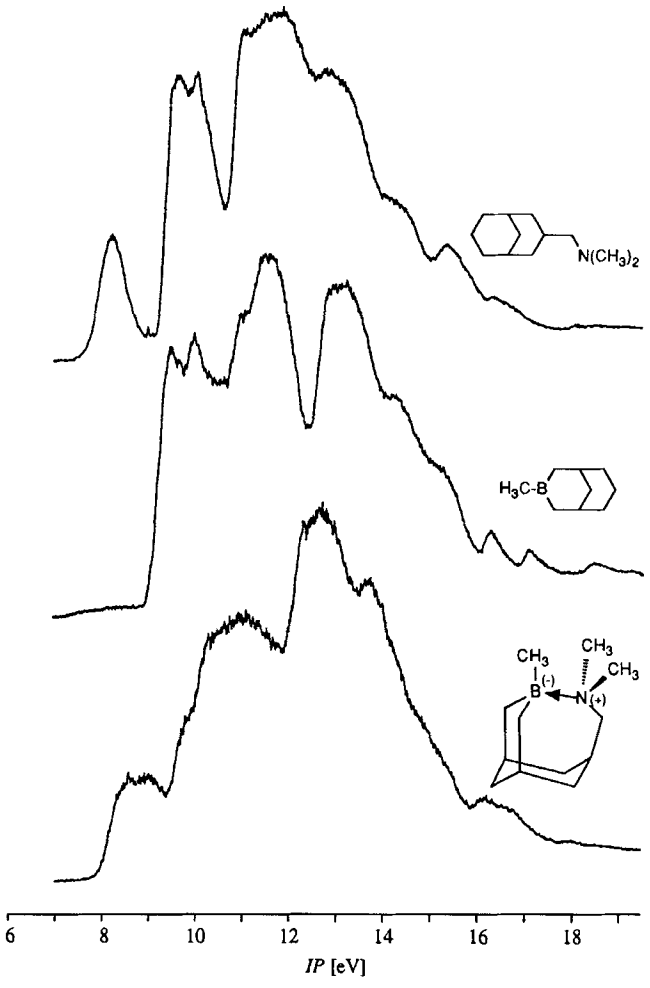


Figure 2. PE spectra of the difunctional compound **1a** (**3a**) and of the corresponding monofunctional compounds **5a** and **6**

the spectrum substantially indicating that **3a** is stable up to this temperature.

The same assignment as for **1a/3a** should be correct for the ethyl and the isopropyl derivatives **1b**, **c**, which also have tricyclic structures (**3b**, **c**). Also for these compounds the first ionization band is rather broad and no n_N ionization is found. On the other hand, in the spectrum of **2a** the characteristic n_N ionization is at the same place as in the amine **7**. This leads to the conclusion, that in this case there is no intramolecular interaction, and because of this the bicyclic and not the tricyclic structure is correct. The difunctional methoxy derivatives **1e** and **2e** (Figure 3) behave similarly to **2a**: The first IP is found very close to that of the bicyclic amines **6** and **7**. The second IP is shifted by only 0.03 eV relative to the first IP of 3-methoxy-3-borabicyclo[3.3.1]nonane[1] (**5e**). The spectra of the difunctional compounds are obtained in this region nearly additively from those of the monofunctional molecules, indicating the absence of intramolecular interactions of the donor/acceptor pairs. Accordingly, the first IP is assigned to the n_N and the second IP to a MO with large σ_{BC} and some σ^*_{BO} contributions.

The observed vertical ionization potentials are listed in Table 2 together with the assignments. On the assumption

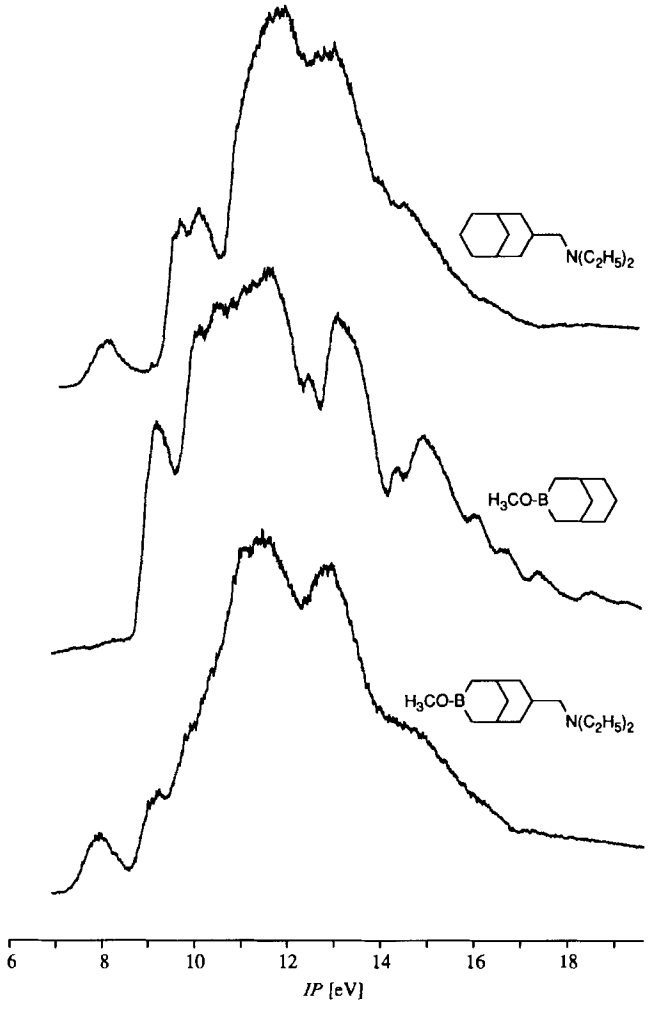


Figure 3. PE spectra of the difunctional compound **2e** and of the corresponding monofunctional compounds **5e** and **7**

Table 2. Vertical ionization potentials [eV] of compounds **1**, **2**, **6**, and **7**

	1a/3a	1b/3b	1c/3c	1e	2a	2e	6	7
n_N				8.06	7.94	7.88	8.18	7.96
σ_{BC}	8.51	8.54	8.44		9.36			
σ_{BC}	8.96	8.82	8.76		9.9			
σ_{BN}/σ_{CC}	9.86	9.72						
$\sigma_{BC}/\sigma^*_{BO}$				9.16		9.18		

that Koopmans theorem[16], $IP_i = -\varepsilon_i$, is valid, the calculated eigenvalues ε show the usual deviations up to 0.88 eV relative to the IP values of the tricyclic compounds **3a–c**.

^{11}B-NMR Spectra

The δ^{11}B values of the aminoborabicycles **1a–c**, **e**, **2a**, **e** are collected in Table 3. The high-field shifts of the difunctional compounds **1a–c**, **e**, and **2a** indicate strong σ donor/acceptor interactions in solution at 20 and −50°C. The observed δ^{11}B values are of the same magnitude as found for inter- and intramolecular borane–amine adducts[17], indicating that the tricyclic isomers **3a–c**, **e**, and **4a** are formed.

Table 3. δ^{11}B values of 3-borabicyclo[3.3.1]nonanes **1a–c**, **e**, **2a**, **e** at 20 and −50°C ($CDCl_3$)

	1a	1b	1c	1e	2a	2e
20°C	0.5	1.1	2.1	7.8	0.6	-53.6
-50°C	0.4	0.3	1.3	6.7	0.4	-50.0

For the alkyl-substituted [(dimethylamino)methyl]borabicyclic compounds **1a–c** a small decrease of the high-field shift is observed for the larger substituents which at 20°C is a little more distinct than at −50°C.

While in the diethylamino compound **2a/4a** the δ^{11}B value is only 0.1 ppm larger than in the dimethylamino derivative **1a/3a**, the value of the methoxy derivative **2e** suggests that no adduct is formed and this compound retains its bicyclic structure. A high-field shift of 3.6 ppm at −50°C relative to 20°C and of only ca. 1.4 ppm relative to the monofunctional methoxy compound **5e**[1] leads to the assumption that in solution there is only a weak interaction of the donor/acceptor pair in **2e**.

Discussion

The intramolecular interaction of the donor/acceptor pair borane/amine has been investigated for the 7-[(dialkylamino)methyl]-3-borabicyclo[3.3.1]nonane derivatives **1a–c**, **e**, and **2a**, **e**.

The absence of an n_N ionization band in the PE spectra of the aminoboraalkanes **1a–c** leaves no doubt that in the gas phase the tricyclic adducts **3a–c** are formed. The presence of this band in the spectra of **1e**, **2a**, and **2e** is only consistent with their bicyclic structures and excludes the adducts **3e**, **4a**, and **4e**, respectively.

In $CDCl_3$ solution, B–N complex formation is noticed for **1a–c**, **e** (→ **3a–c**, **e**) and **2a** (→ **4a**) as well as a weak intramolecular interaction in compound **2e** from the δ^{11}B chemical shift data. The observations for the gas phase and the solution are consistent for compounds **1a–c** and **2e**, while for **1e** and **2a** a different behavior is noticed. Obviously, the adducts **3e** and **4a** of the latter compounds are not stable in the gas phase under the conditions of PE spectral measurements (25°C, ca. 5 Pa).

The observations may be roughly explained by steric and electronic effects: Enlargement of the dialkylamino group and of the substituent on the boron atom weakens the intramolecular tricyclic borane–amine complex. The methoxy group reduces the acceptor strength of the boron atom and by this the complex is destabilized. The difference in the properties of the two methoxy derivatives **1e** and **2e** in solution may be caused by the different size of the dialkylamino groups, but intermolecular effects may also be of importance.

In contrast to the experimental findings, the force-field (MMX) and the quantum-chemical (AM1) calculations always indicate bicyclic structures with conformations unfavorable for interaction of the heteroatoms[13].

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Experimental

For experimental details see ref.[1]. – ^{11}B-NMR: Table 3.

All operations with the highly inflammable and moisture-sensitive organoboron compounds were performed under argon. Solvents were purified by standard procedures, distilled and stored under argon.

endo-7-[(Dimethylamino)methyl]-3-borabicyclo[3.3.1]nonane Derivatives **1**

endo-3-Chloro-7-[(dimethylamino)methyl]-3-borabicyclo-[3.3.1]nonane: 28.45 g (0.14 mol) of the 1-boraadamantane–THF complex is dissolved in 200 ml of anhydrous *n*-hexane in a 500-ml Schlenk-type vessel equipped with an Anschütz adapter, a dropping funnel, and a reflux condenser. To the obtained solution is added 35.80 g of a chlorodimethylamine[18] solution (10.98 g, 0.14 mol) in tetrachloromethane within 3 h. The precipitate is filtered off through a glass frit, washed repeatedly and dried at room temp. in high vacuo. Yield 18.68 g (63%) of crude material. – ^{1}H NMR ($CDCl_3$): δ = 3.16 (d, *J* = 3.7 Hz, 2H, >CH–CH_2N<), 2.86 [s, 6H, $N(CH_3)_2$], 2.06 (broad, 2H, >CH–), 1.94–0.85 (m, 11H). – ^{13}C NMR ($CDCl_3$): δ = 28.7 (C-1, -5), 32.6 (C-7), 37.6 (C-6, -8), 38.1 (C-9), 53.1 [$N(CH_3)_2$], 72.8 (>CH–CH_2N<). – ^{11}B-NMR ($CDCl_3$): δ = 9.0. – IR (CCl_4): $\tilde{\nu}$ = 2980–2820 cm^{-1} (CH_3, CH_2, CH), 2780 (N–CH_2), 1480, 1460 (CH_3, CH_2), 1015 (C–N).

endo-7-[(Dimethylamino)methyl]-3-methoxy-3-borabicyclo-[3.3.1]nonane (**1e**): 150 ml of anhydrous methanol is added slowly with stirring to 12.0 g (56.2 mmol) of 3-chloro-7-[(dimethylamino)-methyl]-3-borabicyclo[3.3.1]nonane. A soluton of sodium methoxide, prepared from 1.29 g (56.3 mmol) of sodium and 52 ml of anhydrous methanol, is added within 30 min. The reaction mixture is refluxed for 1 h. After cooling the methanol is distilled off in vacuo and the residue treated with 30 ml of anhydrous ether. The sodium chloride is filtered off through a glass frit and the solvent removed from the filtrate by suction. The residue is distilled in vacuo through a 10-cm Vigreux column. The product solidifies after cooling in the receiver. Yield 7.27 g (62%), b.p. 145°C/133 Pa (1 Torr), 104°C/1.3 Pa (0.01 Torr), m.p. 23°C. – ^{1}H NMR ($CDCl_3$): δ = 3.29 (d, *J* = 4.5 Hz, 3H, OCH_3), 2.87 (t, *J* = 3.9 Hz, 2H, >CH–CH_2N<), 2.55 [d, *J* = 4.4 Hz, 6H, $N(CH_3)_2$], 1.95–0.66 (m, 11H). – ^{13}C NMR ($CDCl_3$): δ = 28.2 (C-1, -5), 32.6 (C-7), 37.9 (C-9), 38.6 (C-6, -8), 40.7 [$N(CH_3)_2$], 51.2 (OCH_3), 70.0 (>CH–CH_2N<). – ^{11}B-NMR ($CDCl_3$): δ = 7.8. – IR (melt): $\tilde{\nu}$ = 3020 cm^{-1}, 3000, 2890–2860 (CH_3, CH_2, CH), 2800 (N–CH_2), 1480, 1465 (CH_3, CH_2), 1340 (B–O). – MS: *m/z* (%): 209 (2) [M^+], 58 (100) [CH_2=$N(CH_3)_2^+$]. – $C_{12}H_{24}BNO$ (209.1): calcd. C 68.90, H 11.48, N 6.70; found C 69.75, H 12.14, N 6.78.

endo-7-[(Dimethylamino)methyl]-3-methyl-3-borabicyclo-[3.3.1]nonane (**1a**): In a three-necked 250-ml vessel a Grignard reagent solution, obtained from 0.49 g (20.0 mmol) of magnesium and 2.56 g (18.0 mmol) of methyl iodide, is placed. A solution of 3.01 g (14.4 mmol) of **1e** in anhydrous ether is added within 1 h. Subsequently, the mixture is refluxed for 1 h. The ether is removed by suction, and 100 ml of anhydrous *n*-hexane is added to the residue. The solid material is filtered off through a glass frit and washed with 50 ml of hexane. The hexane is removed at reduced pressure, and the remaining white solid is sublimed twice at 120°C/13.3 Pa (0.1 Torr). Yield 2.13 g (79%), m.p. 140–153°C (sintering at 143°C). – ^{1}H NMR ($CDCl_3$): δ = 3.38 (d, *J* = 3.8 Hz, 2H, >CH–CH_2N<), 2.92 [s, 6H, $N(CH_3)_2$], 2.02 (broad, 2H, >CH–), 1.91–0.82 (m, 11H), 0.42 (s, 3H, >BCH_3). – ^{13}C NMR ($CDCl_3$): δ = 29.1 (C-1, -5), 33.0 (C-7), 38.6 (C-9), 39.5 (C-6, -8), 51.9 [$N(CH_3)_2$], 75.5 (>CH–CH_2N<). – ^{11}B NMR ($CDCl_3$): δ = –0.5. – IR (CCl_4): $\tilde{\nu}$ = 3015 cm^{-1}, 3000, 2900–2880 (CH_3, CH_2, CH), 2795 (N–CH_2), 1480–1440 (CH_3, CH_2), 1020 (C–N). – MS, *m/z* (%): 178 (100) [M^+ – CH_3], 58 (35) [CH_2=$N(CH_3)_2^+$]. – $C_{12}H_{24}BN$ (193.1): calcd. C 74.61, H 12.43, N 7.25; found C 74.91, H 13.07, N 7.30.

endo-7-[(Dimethylamino)methyl]-3-ethyl-3-borabicyclo-[3.3.1]nonane (**1b**) is prepared in the same way as **1a**. Yield 11%, m.p. 48–49°C. – ^{1}H NMR ($CDCl_3$): δ = 2.93 (d, *J* = 3.7 Hz, 2H, >CH–CH_2N<), 2.47 [s, 6H, $N(CH_3)_2$], 2.0 (broad, 2H, >CH–), 1.92–0.53 (m, 11H), 0.74 (t, *J* = 7.7 Hz, 3H, >BCH_2CH_3), 0.09 (q, *J* = 7.7 Hz, 2H, >BCH_2CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.7 (>B–CH_2–CH_3), 29.0 (C-1, -5), 33.0 (C-7), 38.8 (C-9), 39.5 (C-6, -8), 51.4 [$N(CH_3)_2$], 73.8 (>CH–CH_2N<). – ^{11}B NMR ($CDCl_3$): δ = 1.1. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 3000, 2980–2800 (CH_3, CH_2, CH), 2780 (N–CH_2), 1475, 1455, 1445 (CH_3, CH_2), 1030 (C–N). – MS, *m/z* (%): 207 (0.4) [M^+], 178 (100) [M^+ – C_2H_5], 58 (34) [H_2C=$N(CH_3)_2^+$]. – $C_{13}H_{26}BN$ (207.2): calcd. C 75.36, H 12.56, N 6.76; found C 75.05, H 13.08, N 6.78.

endo-7-[(Dimethylamino)methyl]-3-isopropyl-3-borabicyclo-[3.3.1]nonane (**1c**) is prepared in the same way as **1a**. Yield 39%, m.p. 68–70°C. – ^{1}H NMR ($CDCl_3$): δ = 2.87 (d, *J* = 3.5 Hz, 2H, >CH–CH_2N<), 2.53 [s, 6H, $N(CH_3)_2$], 2.0 (broad, 2H, >CH–), 1.9–0.3 (m, 12H), 0.80 [d, *J* = 7.0 Hz, 6H, >B$CH(CH_3)_2$]. – ^{13}C NMR ($CDCl_3$): δ = 22.7 [B–$CH(CH_3)_2$], 29.0 (C-1, -5), 32.8 (C-7), 38.8 (C-9), 39.6 (C-6, -8), 52.0 [$N(CH_3)_2$], 74.1 (>CH–CH_2–N<). – ^{11}B NMR ($CDCl_3$): δ = 2.1. – IR (CCl_4): $\tilde{\nu}$ = 3015 cm^{-1}, 3000, 2980–2860 (CH_3, CH_2, CH), 2800 (N–CH_2), 1475–1440 (CH_3, CH_2), 1380, 1370 (CH_3), 1015 (C–N). – MS, *m/z* (%): 221 (2) [M^+], 178 (42) [M^+ – $CH(CH_3)_2$], 58 (100) [H_2C=$N(CH_3)_2^+$]. – $C_{14}H_{28}BN$ (221.2): calcd. C 76.02, H 12.67, N 6.33; found C 76.32, H 12.85, N 6.27.

Attempts to synthesize *endo-3-tert-butyl-7-[(dimethylamino)-methyl]-3-borabicyclo[3.3.1]nonane* (**1d**): In a 50-ml Schlenk-type vessel, equipped with an Anschütz adapter and a reflux condenser, are placed 1.57 g (7.35 mmol) of 3-chloro-7-[(dimethylamino)methyl]-3-borabicyclo[3.3.1]nonane and 20 ml of anhydrous *n*-pentane. To this suspension 4.9 ml (7.4 mmol) of a 1.5 M solution of *tert*-butyllithium in *n*-pentane is added dropwise with stirring. The mixture is stirred for 2 h at room temp. and then refluxed for 3 h. The solid material is filtered off through a glass frit and the solvent removed by suction. Only unreacted starting material could be identified by ^{13}C-NMR spectroscopy.

Attempts to synthesize **1d** by a similar way as **1a–c** from **1e** by using *tert*-butyl chloride or -bromide as reagent and diethyl ether or THF as solvent failed.

endo-7-[(Diethylamino)methyl]-3-borabicyclo[3.3.1]nonane Derivatives **2**

endo-3-Chloro-7-[(diethylamino)methyl]-3-borabicyclo-[3.3.1]nonane and endo-7-[(Diethylamino)methyl]-3-methoxy-3-borabicyclo[3.3.1]nonane (**2e**) are prepared according to the method described in ref.[7].

endo-7-[(Diethylamino)methyl]-3-methyl-3-borabicyclo-[3.3.1]nonane (**2a**) is synthesized from **2e** by the method described

for **1a**. Yield 38%, m.p. 94–99°C. – ^{1}H NMR ($CDCl_3$): δ = 3.45 (m, 4H, NCH_2CH_3), 3.15 (d, J = 4.3 Hz, 2H, >CH–CH_2N<), 2.28 (broad, 2H, >CH–), 2.2–0.7 (m, 11H), 0.32 (s, 3H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 9.9 (N–CH_2CH_3), 29.3 (C-1, -5), 32.5 (C-7), 39.1 (C-9), 40.1 (C-6, -8), 51.5 (N–CH_2CH_3), 67.3 (>CH–CH_2–N<). – ^{11}B NMR ($CDCl_3$): δ = 0.6. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 3000, 2940–2870 (CH_3, CH_2, CH), 2810 (C–NH_2), 1480, 1465, 1455, 1440 (CH_3, CH_2), 1030 (C–N). – MS, *m/z* (%): 221 (1) [M^+], 206 (24) [$M^+ - CH_3$], 86 (100) [$H_2C{=}N(C_2H_5)_2^+$]. – $C_{14}H_{28}BN$ (221.2): calcd. C 76.02, H 12.67, N 6.33; found C 76.31, H 13.26, N 6.35.

endo-3-[(Dimethylamino)methyl]bicyclo[3.3.1]nonane (**6**) is prepared according to ref.[9].

endo-3-[(Diethylamino)methyl]bicyclo[3.3.1]nonane (**7**): In a three-necked 250-ml vessel is placed a solution of 8.00 g (52.2 mmol) of *endo*-3-(aminomethyl)bicyclo[3.3.1]nonane[9] in 150 ml of anhydrous ethanol. 16.00 g (0.15 mol) of bromoethane is added dropwise within 20 min. The mixture is refluxed for 3 h. Then 25.00 g (0.18 mol) of potassium carbonate is added and heating is continued for 4 d. The mixture is filtered and the solvent removed by suction. The residue is subjected to a Hinsberg separation. In the last step, the alkaline solution is extracted with dichloromethane and the extract dried with sodium sulfate. The solvent is removed carefully by suction and the residue distilled through a 5-cm Vigreux column. Because of foaming, rather slow heating is necessary. Yield 1.52 g (14%), b.p. 78–79°C/26.7 Pa (0.2 Torr). – ^{1}H NMR ($CDCl_3$): δ = 2.48 (q, J = 7.2 Hz, 4H, >NCH_2CH_3), 2.16 (d, J = 6.6 Hz, 2H, CHCH_2N<), 2.02–0.70 (m, 15H), 1.0 (t, J = 7.2 Hz, 6H, >NCH_2CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.7 (>NCH_2CH_3), 15.9 (C-3), 25.5 (C-1, -5), 28.4 (C-7), 29.3 (C-9), 32.0 (C-6, -8), 33.5 (C-2, -4), 47.7 (>N–CH_2CH_3), 60.6 (>CH–CH_2N). – IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 2915, 2830 (CH_3, CH_2, CH), 2800 (N–CH_2), 1480–1440 (CH_3, CH_2), 1040 (C–N). – MS, *m/z* (%): 209 (1) [M^+], 86 (100) [$H_2C{=}N(C_2H_5)_2^+$]. – $C_{14}H_{27}N$ (209.4): calcd. C 80.38, H 12.92, N 6.70; found C 80.11, H 13.00, N 6.44.

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