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Study of cyclic borinates obtained from piperidine- and piperazine alcohols by spectroscopic methods and X-ray crystallography

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Abstract

A series of eleven new 2-aminoethyl- and 3-aminopropyl borinate derivatives with a coordinative N → B bond has been synthesized by condensation reactions between piperidine- as well as piperazine alcohols and diphenylborinic acid. The products obtained are analogous to *N*-spiro compounds and bicyclic systems and have been characterized by spectroscopic methods and X-ray crystallography. Thereby the N → B bond and the geometry of this new heterocyclic systems have been studied in more detail. © 1998 Elsevier Science S.A.

Keywords: Borinates; Boron complexes; Piperidine- and piperazine alcohols; Coordinative N → B bond; X-ray crystallography

1. Introduction

Dialkyl- and diarylborinic acids react with 1,2- and 1,3-aminoalcohols to form five- and six-membered heterocycles with a coordinative N → B bond [1–5]. [2] These borinates are called boroxazolidines or tetrahydroboroxazines, respectively.

Theoretical and experimental considerations of borane amines have shown that the coordinative N → B bond strength ranges from 58–152 kJ mol^{-1} depending on the degree of substitution (H or CH_3) on both atoms [13]. In the particular case of the boroxazolidines and tetrahydroboroxazines the N → B bond energy (E_{B-N}) has been determined as 72 kJ mol^{-1} for the 2-aminoethyl diphenylborinate and 131 kJ mol^{-1} for the 3-aminopropyl diphenylborinate [14]. The N → B bond lengths in the corresponding molecular structures are 1.654(3) and 1.638(3) Å, [10–12] respectively, and coincide with these results.

The N → B bond strength is essential for the hydrolytic stability of these boron heterocycles [15]. There exists a certain interest in their bactericidal, fungicidal and herbicidal effects [16–19] and in possible antitumor activities [20]. In general, boron compounds are interesting for boron neutron capture therapy (BNCT) due to the high neutron capture radius of the boron-10 isotope [21].

In organic synthesis, boroxazolidines have been used to increase enantiomeric excess after hydroboration reactions [22] and to separate diastereomeric and racemic methoxyborolane mixtures [23,24].

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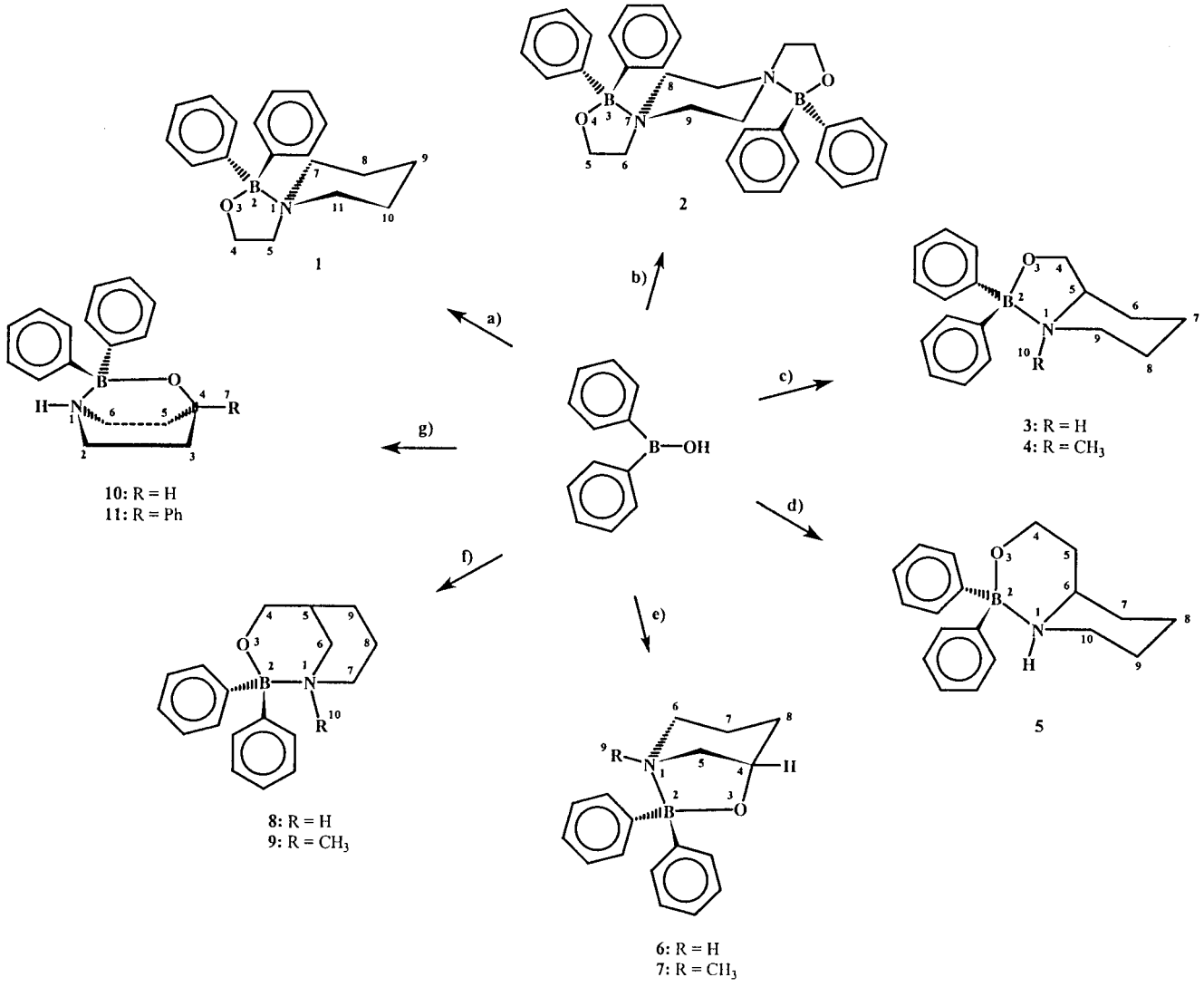
[2] First publications in this area (see Refs. [6–9], X-ray structures, see for example [10–12].

In view of these important features, a study of five- and six-membered cyclic borinates derived from piperidine- and piperazine alcohols was considered interesting, having in mind that piperidine and piperazine derivatives are of pharmacological importance [25,26]. In the present work eleven of these boroxazolidines and tetrahydroboroxazines have been synthesized and analyzed by IR, mass spectrometry, NMR spectroscopy (^{1}H, ^{13}C, ^{11}B), DNMR and X-ray crystallography, if suitable monocrystals could be obtained.

The use of 1-, 2-, 3- and 4-substituted piperidine alcohols permits a comparison of four new heterobicyclic systems with respect to their geometry, spectroscopic properties and N → B bond stability. In order to compare the N → B bond strength of secondary piperidine alcohols with tertiary ones, also the 1-methyl-piperidine alcohols have been reacted with the diphenylborinic acid.

2. Results and discussion

Compounds **1**–**11** have been synthesized by condensation reactions between diphenylborinic acid and the corresponding piperidine- and piperazine alcohols (Scheme 1). Optimal reaction conditions include low solvent polarity and low reaction temperature (≪ 0°C).



Scheme 1. Synthesis of compounds **1**–**11**. Reaction conditions: a) 1-piperidine ethanol, $CHCl_3$, −20°C, b) 1,4-piperazinediethanol, MeOH, −78°C, c) **3**: 2-piperidinemethanol, CH_2Cl_2, −60°C, **4**: 1-methyl-2-piperidinemethanol, THF, −78°C, d) 2-piperidineethanol, MeOH, −78°C, e) **6**: 3-hydroxypiperidine, MeOH, −78°C, **7**: 1-methyl-3-hydroxypiperidine, THF, △, f) **8**: 3-piperidinemethanol, MeOH, −78°C, **9**: 1-methyl-3-piperidinemethanol, $CHCl_3$, −60°C, g) **10**: 4-hydroxypiperidine, THF, △, **11**: 4-phenyl-4-hydroxypiperidine, diethyl ether, △.

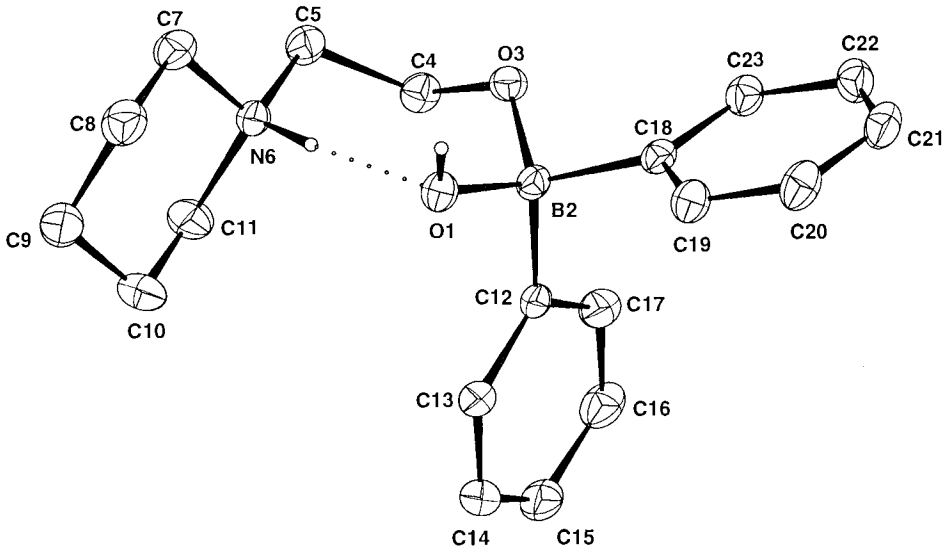
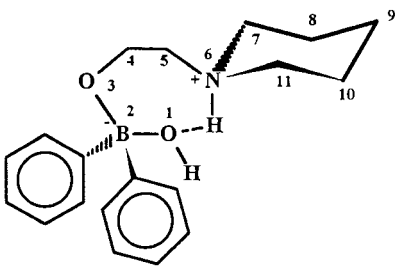


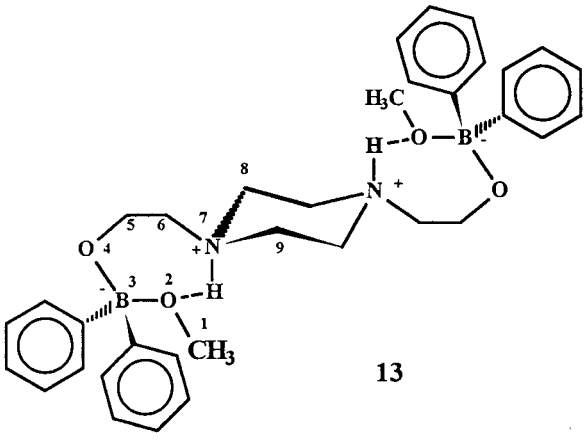
Fig. 1. Molecular structure of compound **12**.

*2.1. Analysis of compounds **1**, **12**, **2** and **13***

Compound **1** is a *N*-spiro[5.4]decane analogue and has been synthesized in $CHCl_3$ at −20°C. [3] When the same reaction was performed in diethyl ether at room temperature, the stable zwitterionic molecule **12** formed, as determined by X-ray crystallography (Fig. 1, Tables 1 and 2). The two products can be differentiated by mass spectrometry, where the molecular ion is detected in each case. Moreover, in the spectrum of **12** the molecular peak of compound **1** is also detected, so that its formation by loss of a water molecule can be inferred.



12



13

The *N,N′*-bis-spiro analogue **2** has been synthesized in methanol at −78°C, but during crystallization from methanol the bis-zwitterionic molecule **13** was formed. The two species could be identified by NMR spectroscopy and the structure determination of **13** by X-ray crystallography confirms the observation that an association of methanol occurred (Fig. 2, Tables 1 and 2).

A comparison of the crystallographic data shows that the two structures **12** and **13** are very similar (Table 1). A striking difference is the B–O (OH and OCH_3) bond length that is significantly shorter in structure **12** (1.499(4) Å ↔ 1.547(3) Å), while the second B–O bond is longer than in structure **13** (1.509(4) Å ↔ 1.470(3) Å). Despite these deviations the B–O bond lengths are in the normal range observed for similar structures, where values ranging from 1.468(4) to 1.574(4) Å have been found [28–33].

[3] The corresponding product from 1-phenyl-2-*N*-piperidineethanol has been analyzed by elemental analysis and reported (see Ref. [27]).

Table 1
Selected bond lengths (Å), bond angles (°), torsion angles (°), H-bond lengths (Å) and H-bond angles (°) for compounds **12** and **13**

Compound **12**		Compound **13**	
Bond lengths (Å)			
O(1)–B(2)	1.499 (4)	O(2)–B(3)	1.547 (3)
B(2)–O(3)	1.509 (4)	B(3)–O(4)	1.470 (3)
B(2)–C(12)	1.633 (5)	B(3)–C(10)	1.628 (4)
B(2)–C(18)	1.617 (5)	B(3)–C(16)	1.617 (4)
O(3)–C(4)	1.414 (4)	O(4)–C(5)	1.401 (3)
C(5)–N(6)	1.490 (4)	C(6)–N(7)	1.506 (3)
N(6)–C(7)	1.497 (4)	N(7)–C(8)	1.496 (3)
N(6)–C(11)	1.500 (4)	N(7)–C(9)	1.494 (3)
Bond angles (°)			
H(11)–O(1)–B(2)	117.8(3)	C(1)–O(2)–B(3)	114.5 (2)
O(1)–B(2)–O(3)	109.4 (3)	O(2)–B(3)–O(4)	109.5 (2)
B(2)–O(3)–C(4)	120.4 (2)	B(3)–O(4)–C(5)	122.1 (2)
O(3)–C(4)–C(5)	112.2 (3)	O(4)–C(5)–C(6)	115.9 (2)
C(4)–C(5)–N(6)	111.9 (3)	C(5)–C(6)–N(7)	113.9 (2)
C(5)–N(6)–H(61)	109.2 (3)	C(6)–N(7)–H(71)	102.6 (3)
C(12)–B(2)–C(18)	110.9 (3)	C(10)–B(3)–C(16)	110.7 (2)
Torsion angles (°)[a]			
O(1)–B(2)–O(3)–C(4)	−74.3	O(2)–B(3)–C(4)–C(5)	−69.6
B(2)–O(3)–C(4)–C(5)	94.8	B(3)–O(4)–C(5)–C(6)	73.1
O(3)–C(4)–C(5)–N(6)	−69.6	O(4)–C(5)–C(6)–N(7)	−70.5
C(4)–C(5)–N(6)–H(61)	38.8	C(5)–C(6)–N(7)–H(71)	49.9
H(11)–O(1)–B(2)–O(3)	−78.2	C(1)–O(2)–B(3)–O(4)	−62.6
H-bond lengths (Å) and H-bond angles (°)			
N(6)–H(61)···O(1)	1.77 (169.5)	N(7)–H(71)···O(2)	1.39 (167.8)
Sum of bond angles in the seven-membered heterocycle (°)			
732.6 = 7 × 104.7(3)		731.8 = 7 × 104.5 (2)	

[a]A positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

A hydrogen bond between the tertiary amino group and the hydroxy/methoxy group at the boron atom (Figs. 1 and 2) leads to the formation of a seven-membered NCCOBOH ring with a twisted chair conformation that is typical for seven membered rings [34].

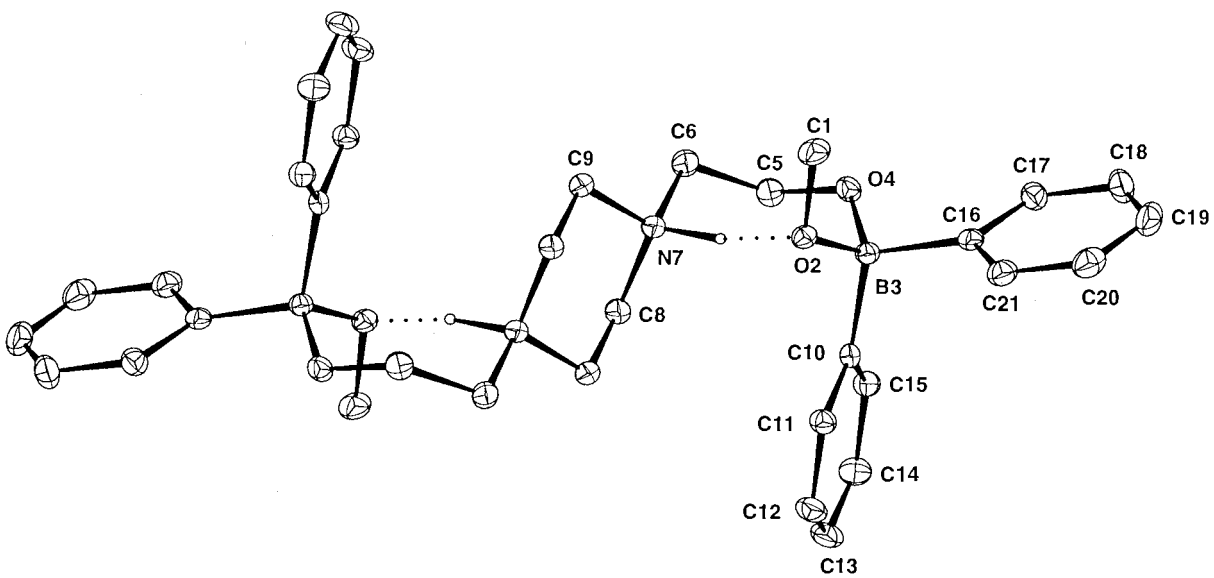


Fig. 2. Molecular structure of compound **13**.

Table 2
Crystallographic data for compounds **3a, 4, 5, 8, 11–14**.

Crystal data	**3a**	**4**	**5**	**8**	**11**	**12**	**13**	**14**
Formula	$C_{18}H_{22}BNO$	$C_{19}H_{24}BNO$	$C_{19}H_{24}BNO$	$C_{18}H_{22}BNO$	$C_{23}H_{24}BNO$	$C_{19}H_{26}BNO_2$, H_2O	$C_{34}H_{44}B_2N_2O_4$	$C_{18}H_{25}BN_2O_2$, 0.5 C_6H_6
Crystal size (mm)	0.20×0.25×0.30	0.15×0.20×0.40	0.30×0.30×0.40	0.15×0.30×0.40	0.20×0.25×0.40	0.10×0.25×0.40	0.20×0.20×0.40	0.20×0.30×x0.40
MW (g mol^{-1})	279.19	293.21	293.21	279.19	341.32	311.23	566.35	312.22
Space group	*C* 2/*c*	*P* 2_1 2_1 2_1	*P* 2_1/*n*	*P* 2_1	*P* 2_1 *c n*	*P* 2_1/*c*	*P* 2_1/*n*	*P* 2_1/*c*
Cell parameters								
a (Å)	20.005 (1)	9.327 (1)	11.358 (1)	7.602 (4)	6.916 (1)	7.166 (1)	9.804 (1)	9.776 (1)
b (Å)	14.419 (1)	13.178 (1)	11.154 (1)	9.840 (2)	16.216 (5)	17.147 (1)	11.873 (2)	13.852 (2)
c (Å)	10.551 (1)	13.216 (1)	13.400 (2)	10.411 (4)	16.323 (4)	15.262 (1)	13.429 (2)	14.280 (2)
b (°)	115.62 (1)	90	100.06 (1)	103.07 (4)	90	100.19 (1)	102.08 (1)	91.00 (3)
V (Å^3)	3124.8 (4)	1624.5 (3)	1671.5 (4)	758.6 (5)	1830 (1)	1845.7 (2)	1528.6 (3)	1933 (1)
Z	8	4	4	2	4	4	2	4
μ (mm^{-1})	0.067	0.067	0.065	0.069	0.070	0.073	0.074	0.072
ρ_{calcd} (kg m^{-3})	1.19	1.20	1.17	1.22	1.24	1.18	1.23	1.21
Data collection								
Scan range (°)	0.39+0.70 tgθ	1.05+0.66 tgθ	0.39+0.49 tgθ	0.98+0.68 tgθ	0.80+0.35 tgθ	0.48+0.52 tgθ	0.58+0.47 tgθ	0.80+0.35 tgθ
θ limits (°)	$2<\theta<28$	$2<\theta<25$	$2<\theta<28$	$2<\theta<27$	$2<\theta<25$	$2<\theta<26$	$2<\theta<28$	$2<\theta<25$
No. collected refl.	4092	1669	4040	1879	1893	3882	4003	3640
No. ind. refl. (R_{int})	3740 (0.02)	1650	4008 (0.03)	1748 (0.03)	1756	3586 (0.02)	3669 (0.02)	3382 (0.03)
No. observed refl.	1966	874	2363	1172	746	1364	1647	1621
Refinement								
R	0.042	0.073	0.039	0.042	0.055	0.038	0.039	0.038
R_w	0.037	0.066	0.033	0.035	0.056	0.035	0.034	0.035
w	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	1.0	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
No. of variables	258	150[a]	273	192	107	219	258	320
GOOF	2.02	4.33	2.12	2.52	–	1.33	1.95	1.54
Max. Δ/σ	0.005	0.002	0.006	0.08	–	0.0002	0.02	0.04
$\Delta\rho_{min}$ (e Å^{-3})	−0.13	−0.25	−0.11	−0.14	–	−0.14	−0.16	−0.20
$\Delta\rho_{max}$ (e Å^{-3})	0.21	0.37	0.20	0.14	–	0.10	0.20	0.14

[a] Phenyl rings were only refined isotropically (with exception of the *ipso*-carbons).

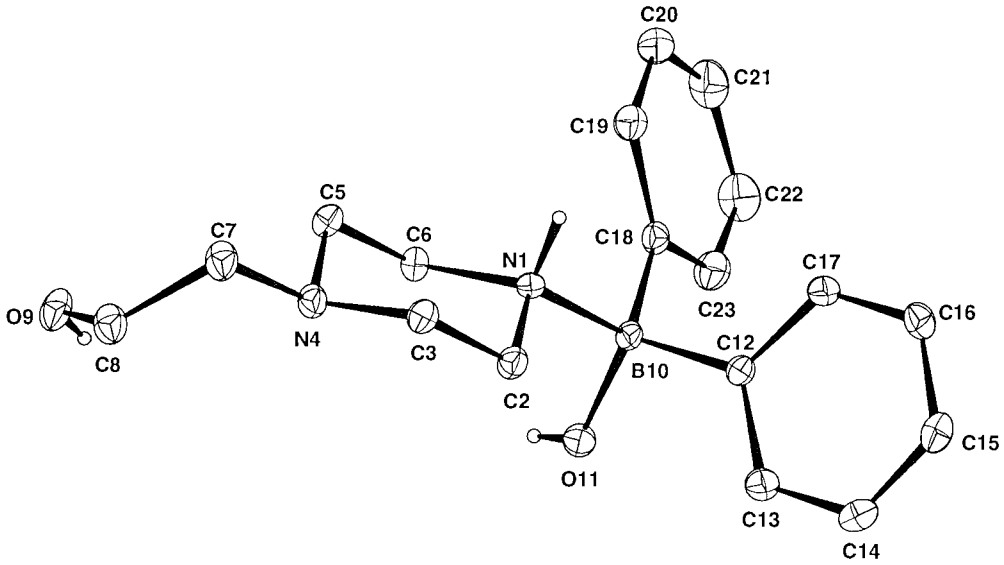
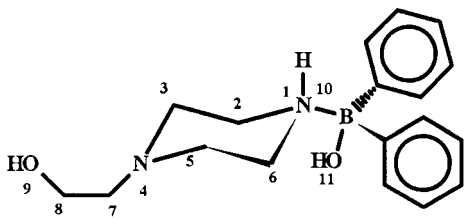


Fig. 3. Molecular structure of compound **14**.

These results indicate that the boroxazolidine ring in the *N*-spiro analogues **1** and **2** can easily be broken up, even by a very weak nucleophile like methanol. Generally, N → B bonds with tertiary amines are weaker than those with primary or secondary ones [35–42].

A further proof of this argument should be given by the reaction between 1-ethanolpiperazine and diphenylborinic acid. The only reaction product formed is compound **14**, whose molecular structure can be seen in Fig. 3 (Tables 3 and 2).



14

In this case the formation of the N → B adduct at the secondary nitrogen atom is preferred to the boroxazolidine or diphenylhydroxy[2-(1-piperazinium)ethoxy]borate (corresponding derivative of **12**). The N → B bond length is 1.665(4) Å and lies in the normal range for cyclic borinates, where values of 1.638(3) Å −1.744(8) Å have been found [11,28,43–45]. The B–O bond (1.464(4) Å) is somewhat shorter than the corresponding bond in compound **12** (1.499(4) Å), probably due to the lack of the bridging hydrogen bond.

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **14**

Compound **14**			
Bond lengths (Å)			
N(1)–B(10)	1.665 (4)	N(1)–C(2)	1.490 (4)
N(1)–C(6)	1.496 (4)	N(4)–C(3)	1.449 (4)
N(4)–C(5)	1.456 (4)	N(4)–C(7)	1.471 (4)
B(10)–O(11)	1.464 (4)	B(10)–C(12)	1.608 (4)
B(10)–C(18)	1.610 (5)	C(2)–C(3)	1.510 (4)
Bond angles (°)			
N(1)–B(10)–O(11)	106.2 (2)	N(1)–B(10)–C(12)	107.2 (3)
N(1)–B(10)–C(18)	108.7 (3)	O(11)–B(10)–C(12)	108.0 (3)
O(11)–B(10)–C(18)	113.4 (3)	C(12)–B(10)–C(18)	112.9 (3)

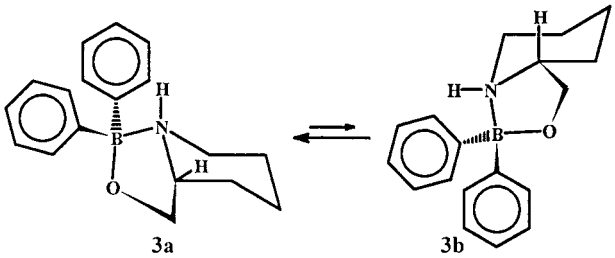


Fig. 4. Conformational equilibrium of compound **3**.

2.2. Analysis of compounds 3–5

Compounds **3** and **4** are bicyclo[4.3.0]nonane analogues with the nitrogen and a carbon atom at the bridgehead positions, while compound **5** is a bicyclo[4.4.0]decane analogue. The three compounds have been synthesized from the corresponding 2-substituted piperidine alcohols and are obtained in high yields (77–85%), when low reaction temperatures are applied.

With the aid of the three compounds two features of the N → B bond strength can be discussed. Compounds **3** and **4** permit evaluation of the influence of the amine substitution (secondary ↔ tertiary), while **3** and **5** allow to compare five- and six-membered borinates. In the ^{1}H NMR spectrum of **3**, two different conformers in a ratio of about 2:1 are observed and a conformational equilibrium can be proposed (Fig. 4).

In the minor product **3b** the diphenylboryl group occupies the less favorable axial site, while the NH hydrogen atom is at the equatorial position.

Besides the conformational equilibrium a second dynamic process that corresponds to an exchange of the two B-phenyl groups by cleavage of the N → B bond takes place [16–19,39–41]. A dynamic NMR experiment (in $CDCl_3$) reveals the kinetics of the two dynamic processes. At −60°C two signals of equal intensity are observed for the two diastereotopic *ortho* carbon atoms of the B-phenyl groups. When the temperature is raised to −20°C, two additional signals appear, indicating the conformational equilibrium, that is therefore the lower energy process. The four signals coalesce at −7.5°C and the free enthalpy of activation for the N → B bond dissociation can be calculated [46]: $\Delta G^{\neq} = 54.7 \pm 1.2$ kJ mol^{-1}. This quantity is similar to a value reported for the N → B dissociation of the diethanolamine ester of diphenylborinic acid, where $\Delta G^{\neq} = 52.7 \pm 1.3$ kJ mol^{-1} (in CD_2Cl_2) [38].

Both **3a** and **3b** display the *cis*-stereochemistry since it presents less intramolecular interactions with the axial hydrogen atoms in the piperidine ring than the corresponding *trans*-isomer. [4] The molecular structure of **3a** has been confirmed by X-ray crystallography (Fig. 5, Tables 4 and 2).

In contrast to compound **3**, the ^{1}H and ^{13}C NMR spectra of compound **4** show only one isomer, even at −60°C. At room temperature all signals are broad, so that a rapid interchange between the coordinated and uncoordinated boron complex can be assumed. Therefore the ^{11}B NMR signal is shifted to relatively low field ($\delta = 10$ ppm). [4] At −60°C the ^{13}C NMR spectrum is well resolved, and at a time two diastereotopic signals for the B-phenyl groups appear.

As for compound **3**, the *cis*-configuration of **4** with the NCH_3 groups in axial orientation should be the most stable one. This has been proved by X-ray crystallography (Fig. 6, Tables 4 and 2).

The free enthalpy of activation for the N → B bond dissociation in compound **4** is: $\Delta G^{\neq} = 53.1 \pm 1.2$ kJ mol^{-1}. This $\Delta G^{\neq}$ value is only slightly smaller than the one determined for compound **3** ($\Delta G^{\neq} = 54.7 \pm 1.2$ kJ mol^{-1}) and it must be concluded that the free enthalpy of activation, a kinetic parameter, does not change significantly between compounds **3** and **4**, although experimental (e.g., synthesis and NMR) and theoretical (e.g., structural study) observations indicate that the tertiary amine in **4** results in a weaker N → B bond. A comparison of the N → B bond lengths in the two molecular structures (Table 4) shows a clear difference of $\Delta d = 0.08$ Å (1.648(3) Å for **3a** and 1.73(1) Å for **4**) confirming the expected lower N → B bond strength of **4**.

The 500 MHz ^{1}H NMR spectrum of compound **5** (in DMSO-d_6) presents a fixed conformation with respect to the NMR time scale and can be completely assigned by a COSY experiment. [5] The NH hydrogen atom at $\delta = 5.98$ ppm couples with only one further axial hydrogen atom ($^{3}J = 11$ Hz), so that the *trans*-isomer, where a coupling with two axial hydrogens is possible, can be excluded. Further evidence are the diastereotopic H-5 hydrogen atoms with a shift difference of $\Delta\delta = 1.15$ ppm, because a diamagnetic protection of such an extent is only possible in the *cis*-isomer (compare $\Delta\delta = 0.61$ ppm for the H-10 hydrogen atoms) [49–52].

[4] The two configurations *cis* and *trans* are distinguishable by the ^{1}H and ^{13}C NMR chemical shifts (see Ref. [47]).
[5] Compound **5** has already been reported, but not studied in detail (see Ref. [48]).

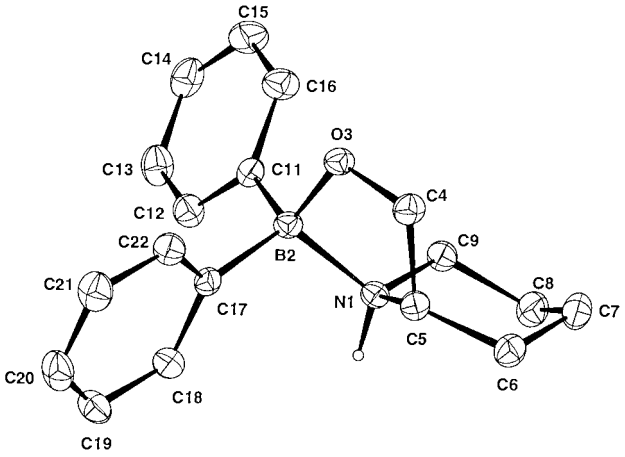


Fig. 5. Molecular structure of compound **3a**.

Interestingly, in the ^{13}C NMR spectrum the diastereotopic *ipso* carbon atoms are separated by $\Delta\delta = 17.6$ ppm, an effect caused probably by the two 1,3-diaxial interactions between the axial B-phenyl group and the axial hydrogen atoms in the borinate heterocycle.

At -60°C in $CDCl_3$ two compounds in different populations can be identified from the ^{13}C NMR spectrum. This may be explained by a conformational equilibrium similar to that of compound **3**. The free activation enthalpy for this process is now lower because of the higher flexibility of the six-membered borinate ring in comparison to the five-membered one in **3**.

The free activation enthalpy for the N → B bond dissociation is $\Delta G^{\neq} = 57.8 \pm 1.2$ kJ mol^{-1}. This value is

Table 4
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compounds **3a** and **4**

Compound **3a**		Compound **4**	
Bond lengths (Å)			
N(1)–B(2)	1.648 (3)	N(1)–B(2)	1.73 (1)
N(1)–C(5)	1.506 (3)	N(1)–C(5)	1.52 (1)
N(1)–C(9)	1.499 (3)	N(1)–C(9)	1.50 (1)
B(2)–O(3)	1.481 (3)	B(2)–O(3)	1.45 (1)
B(2)–C(11)	1.615 (3)	B(2)–C(11)	1.64 (1)
B(2)–C(17)	1.629 (3)	B(2)–C(17)	1.61 (2)
O(3)–C(4)	1.425 (3)	O(3)–C(4)	1.40 (1)
C(4)–C(5)	1.531 (3)	C(4)–C(5)	1.57 (1)
N(1)–C(10)	1.47 (1)		
Bond angles (°)			
N(1)–B(2)–O(3)	98.4 (2)	N(1)–B(2)–O(3)	96.8 (8)
N(1)–C(5)–C(4)	103.1 (2)	N(1)–C(5)–C(4)	102.4 (8)
N(1)–C(5)–C(6)	114.1 (2)	N(1)–C(5)–C(6)	114.2 (9)
B(2)–N(1)–C(5)	99.7 (2)	B(2)–N(1)–C(5)	97.5 (7)
B(2)–O(3)–C(4)	110.1 (2)	B(2)–O(3)–C(4)	112.7 (8)
O(3)–C(4)–C(5)	107.8 (2)	O(3)–C(4)–C(5)	107.1 (8)
C(5)–N(1)–C(9)	112.6 (2)	C(5)–N(1)–C(9)	111.1 (8)
C(11)–B(2)–C(17)	113.1 (2)	C(11)–B(2)–C(17)	114.1 (9)
Torsion angles (°)[a]			
N(1)–B(2)–O(3)–C(4)	−32.2	N(1)–B(2)–O(3)–C(4)	34.6
N(1)–C(5)–C(4)–O(3)	21.9	N(1)–C(5)–C(4)–O(3)	−23.8
B(2)–O(3)–C(4)–C(5)	8.6	B(2)–O(3)–C(4)–C(5)	−10.1
B(2)–N(1)–C(5)–C(4)	−39.6	B(2)–N(1)–C(5)–C(4)	41.1
O(3)–B(2)–N(1)–C(5)	43.8	O(3)–B(2)–N(1)–C(5)	−46.2
Sum of bond angles in the five-membered heterocycle (°)			
519.1 = 5 × 103.8 (2)		516.5 = 5 × 103.3 (8)	

[a]A positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

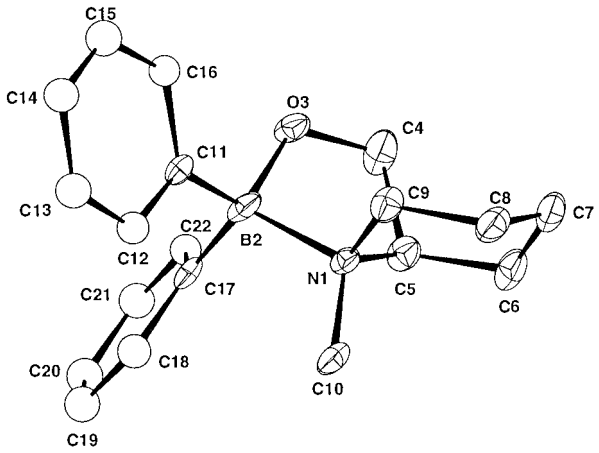


Fig. 6. Molecular structure of compound **4**.

somewhat higher than the one for compound **3** ($\Delta G^{\neq} = 54.7 \pm 1.2$ kJ mol^{-1}), so that it may be assumed that the N → B bond in the six-membered borinate **5** is stronger, as it has been demonstrated for 2-aminoethyl and 3-aminopropyl diphenylborinate by calorimetric measurements (72 kJ mol^{-1} ↔ 131 kJ mol^{-1}) and X-ray structure analyses (1.654(3) Å ↔ 1.638(3) Å) [10,12,14]. [2]

The proposed *cis*-boroxazadecaline type molecular structure of **5** is found also by X-ray crystallography (Fig. 7, Tables 5 and 2). The N → B bond length (Tables 4 and 5) is significantly longer than in compound **3a** (1.673(2) Å ↔ 1.648(3) Å), while the B–O bond is shorter (1.449(2) Å ↔ 1.481(3) Å). The unexpected elongation of the N → B bond could result from the 1,3-diaxial interactions that have been discussed above on the basis of the NMR spectra (splitting of the *ipso* carbon atoms of the B-phenyl groups). The lower ring strain of the six-membered heterocycle **5** in comparison with the boroxazolidine **3a** is best expressed by the sum of the bond angles and its average in the boron heterocycles, where values of $664.0 = 6 \times 110.7(2)°$ and $519.1 = 5 \times 103.8(2)°$ have been calculated (Tables 4 and 5).

*2.3. Analysis of compounds **6**–**9***

Molecular modeling shows that compounds **6** and **7** can only form a bicyclo[3.2.1]octane structure with the diphenylboryl group and the oxygen atom in the axial and the NR group (R = H, CH_3) in the equatorial position. It would be interesting to analyze, if the N → B bond strength is influenced significantly by the sterically unfavored axial orientation of the diphenylboryl group.

The ^{1}H NMR spectrum of compound **6** (in DMSO-d_6) is well resolved and the presence of two diastereotopic signals at a time for the carbon atoms of the B-phenyl groups confirms a fixed conformation in the NMR time scale.

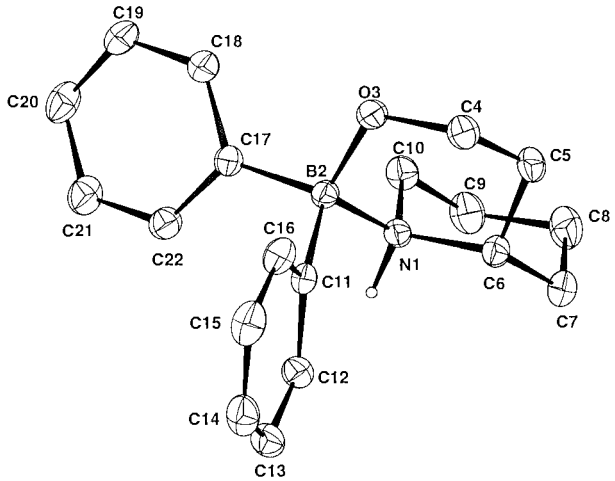


Fig. 7. Molecular structure of compound **5**.

Table 5
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compounds **5** and **8**

Compound **5**		Compound **8**	
Bond lengths (Å)			
N(1)–B(2)	1.673 (2)	N(1)–B(2)	1.674 (5)
N(1)–C(6)	1.519 (2)	N(1)–C(6)	1.504 (5)
N(1)–C(10)	1.504 (2)	N(1)–C(7)	1.500 (5)
B(2)–O(3)	1.449 (2)	B(2)–O(3)	1.437 (5)
B(2)–C(11)	1.623 (3)	B(2)–C(10)	1.626 (6)
B(2)–C(17)	1.617 (2)	B(2)–C(16)	1.615 (6)
O(3)–C(4)	1.423 (2)	O(3)–C(4)	1.431 (5)
C(4)–C(5)	1.508 (3)	C(4)–C(5)	1.540 (6)
C(5)–C(6)	1.521 (3)	C(5)–C(6)	1.505 (6)
Bond angles (°)			
N(1)–B(2)–O(3)	105.8 (2)	N(1)–B(2)–O(3)	106.3 (3)
N(1)–C(6)–C(5)	109.6 (1)	N(1)–C(6)–C(5)	108.1 (4)
N(1)–C(6)–C(7)	111.2 (2)	B(2)–N(1)–C(7)	115.6 (3)
B(2)–N(1)–C(6)	110.5 (1)	B(2)–N(1)–C(6)	108.9 (3)
B(2)–O(3)–C(4)	115.7 (1)	B(2)–O(3)–C(4)	117.8 (3)
O(3)–C(4)–C(5)	110.6 (2)	O(3)–C(4)–C(5)	111.6 (4)
C(4)–C(5)–C(6)	111.8 (2)	C(4)–C(5)–C(6)	109.1 (4)
C(6)–N(1)–C(10)	111.6 (1)	C(4)–C(5)–C(9)	113.1 (4)
C(11)–B(2)–C(17)	110.7 (1)	C(10)–B(2)–C(16)	110.6 (3)
Torsion angles (°)[a]			
N(1)–B(2)–O(3)–C(4)	−58.6	N(1)–B(2)–O(3)–C(4)	53.1
N(1)–C(6)–C(5)–C(4)	55.5	N(1)–C(6)–C(5)–C(4)	−62.5
B(2)–O(3)–C(4)–C(5)	62.6	B(2)–O(3)–C(4)–C(5)	−56.1
B(2)–N(1)–C(6)–C(5)	−53.5	B(2)–N(1)–C(6)–C(5)	62.0
O(3)–B(2)–N(1)–C(6)	53.8	O(3)–B(2)–N(1)–C(6)	−55.4
O(3)–C(4)–C(5)–C(6)	−57.6	O(3)–C(4)–C(5)–C(6)	57.1
Sum of bonding angles in the six-membered heterocycle (°)			
664.0 = 6 × 110.7 (2)		661.8 = 6 × 110.3 (4)	

[a]A positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

The NH hydrogen atom is shifted to lower fields ($\delta = 6.85$ ppm) compared to compounds **3a** and **5a** ($\delta = 6.10$ and 5.98 ppm), proving its equatorial orientation [49–52].

A dynamic NMR experiment could not be performed in this case, because the compound is only slightly soluble in $CDCl_3$.

The spectra of molecule **7** have been recorded in $CDCl_3$, so that at room temperature only broad signals can be seen. When the temperature is lowered to −60°C, all signals in the ^{13}C NMR spectrum become well resolved and diastereotopic signals for the carbons of the B-phenyl groups appear. The dynamic NMR experiment allowed to calculate the free enthalpy of activation for the N → B bond dissociation: $\Delta G^{\neq} = 51.0 \pm 1.2$ kJ mol^{-1}. This quantity is slightly lower (about 2 kJ mol^{-1}) than in the analogous boroxazolidine **4**, where a value of $\Delta G^{\neq} = 53.1 \pm 1.2$ kJ mol^{-1} has been determined. This experimental observation and the fact, that the bulky diphenylboryl group is at the axial site, is interpreted as a decrease of the N → B bond strength in **7**.

The ^{11}B NMR signal at $\delta = 7$ ppm confirms the N → B bond coordination [53,54]. [6]

Compounds **8** and **9** form heterocyclic bicyclo[3.3.1]nonane analogues with the nitrogen atom at one of the bridgeheads.

Compound **8** presents a fixed conformation. The NH group is located at $\delta = 6.37$ ppm and shifted to higher field than in compound **6** ($\delta = 6.85$ ppm). Interestingly, there is a large shift difference of $\Delta\delta = 1.39$ ppm between the axial and equatorial H-8 hydrogen atoms. This difference can only be explained by the deshielding of the axial H-8 hydrogen atom by one of the lone pairs of the oxygen atom at the opposite side. This observation proves, that both

[6] ^{13}C and ^{11}B NMR data (see Ref. [55]).

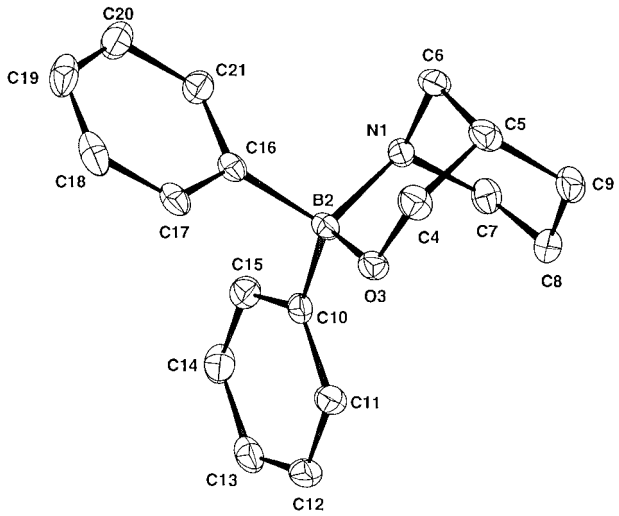


Fig. 8. Molecular structure of compound **8**.

six-membered rings of the bicyclic system have chair conformations, as expected for heterocyclic bicyclo[3.3.1]nonane derivatives [56]. The chair–chair conformation of the bicyclic ring system can be appreciated from its molecular structure (Fig. 8, Tables 5 and 2).

The free enthalpy of activation for the N → B bond dissociation has been determined as: $\Delta G^{\neq} = 59.0 \pm 1.3$ kJ mol^{-1}. This quantity is similar to the one of compound **5** ($\Delta G^{\neq} = 57.8 \pm 1.2$ kJ mol^{-1}), so that the N → B bond strength is comparable. This result could be questionable because of the axial orientation of the diphenylboryl group in compound **8**, however the N → B bond lengths of the six-membered borinates of **5** and **8** are indeed identical (1.673(2) Å ↔ 1.674(5) Å).

Compound **9** is difficult to synthesize and hydrolyzes rapidly. This experimental observation is confirmed by the NMR data, which consist only of broad signals, while at the same time decomposition products can be observed. The broadness of the signals, the absence of the γ-gauche effect on C-8 and the absence of the diastereotopic signals for the B-phenyl carbons indicate that N → B bond dissociation proceeds at lower free enthalpies of activation than in compound **8**. Quantitative measurements of the free enthalpy of activation could not be performed due to the high hydrolysis rate of this compound in $CDCl_3$. The ^{11}B NMR signal appears at $\delta = 2$ ppm.

*2.4. Analysis of compounds **10** and **11***

Compounds **10** and **11** form a heteroatomic bicyclo[2.2.2]octane structure with the nitrogen atoms at the bridgehead, while the boron and oxygen atoms build one of the bridges. In these molecules the two B-phenyl groups are not diastereotopic because of their C_s symmetry. In the ^{1}H NMR spectrum the NH hydrogen atom is at $\delta = 4.13$ ppm for **10** and $\delta = 3.37$ ppm for **11**. The difference indicates that the positive charge on the nitrogen atom is higher in compound **10**.[7] The sharpness of the ^{13}C NMR signals indicates the presence of a fixed conformation, although conclusive evidence on the basis of the observation of diastereotopic B-phenyl carbon atoms is lacking. The ^{11}B NMR signals appear at $\delta = 4$ ppm and $\delta = 5$ ppm for **10** and **11**, respectively.

The boat conformation of compound **11** could be determined also by X-ray crystallography (Fig. 9, Tables 6 and 2). The small number of observed reflections permitted only an isotropic refinement of the non hydrogen atoms.

The structure is slightly twisted in order to avoid eclipsed conformations, where possible. The twist is expressed by the two NCCC and the NBOC torsion angles, which are 13.34, 9.10 and 14.02°, respectively (Table 6). The N → B bond length is of 1.646(8) Å, identical to the one of the boroxazolidine **3a** (1.648(3) Å). It is smaller than the N → B bond length in the corresponding six-membered borinates **5** and **8** (1.673(2) and 1.674(5) Å). The N–B–O bond angle (103.9(4)°) is relatively small in comparison to **5** and **8**, where values of 105.8(2) and 106.3(3)° have been found. This

[7] The high field shift of the NH group in these molecules by more than 2 ppm (in DMSO-d_6) in comparison to compounds **5a**, **6** and **8** cannot be explained.

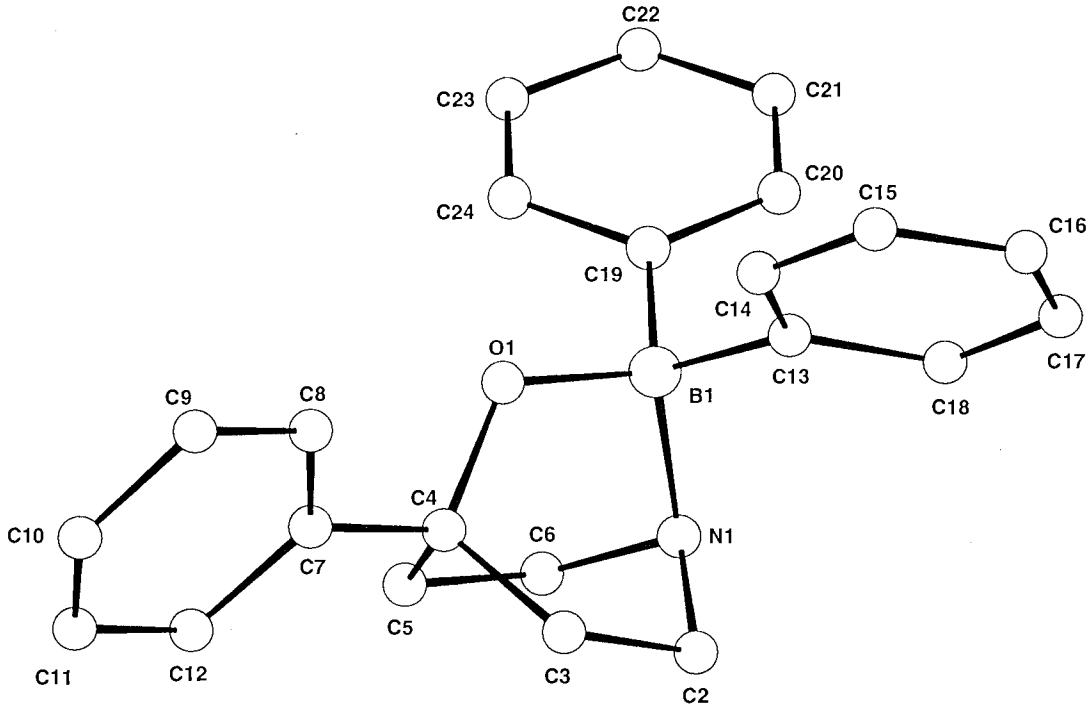


Fig. 9. Molecular structure of compound **11**.

and the fact that the sum of the bond angles in the two six-membered heterocycles with values of $655.9 = 6 \times 109.3(7)°$ and $655.4 = 6 \times 109.2(7)°$ are smaller than the ones in structures **5** and **8** ($664.0 = 6 \times 110.7(2)°$ and $661.8 = 6 \times 110.3(4)°$) seem to indicate a certain ring strain in this structure type.

Table 6
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compound **11**

Compound **11**			
Bond lenghts (Å)			
N(1)–B(1)	1.646 (8)	N(1)–C(2)	1.49 (1)
N(1)–C(6)	1.51 (1)	B(1)–O(1)	1.49 (1)
B(1)–C(13)	1.62 (1)	B(1)–C(19)	1.64 (1)
O(1)–C(4)	1.42 (1)		
Bond angles (°)			
N(1)–B(1)–O(1)	103.9 (4)	N(1)–C(6)–C(5)	108.5 (8)
N(1)–C(2)–C(3)	107.2 (8)	B(1)–N(1)–C(2)	109.1 (7)
B(1)–N(1)–C(6)	109.6 (7)	B(1)–O(1)–C(4)	115.1 (5)
O(1)–C(4)–C(3)	109.1 (7)	O(1)–C(4)–C(5)	108.0 (7)
C(2)–C(3)–C(4)	111.2 (7)	C(4)–C(5)–C(6)	110.3 (8)
C(7)–C(4)–O(1)	108.3 (8)	C(13)–B(1)–C(19)	111.5 (6)
Torsion angles (°)[a]			
B(1)–N(1)–C(2)–C(3)	50.43	B(1)–N(1)–C(6)–C(5)	−62.90
N(1)–C(2)–C(3)–C(4)	13.34	N(1)–C(6)–C(5)–C(4)	9.10
N(1)–B(1)–O(1)–C(4)	14.02	B(1)–O(1)–C(4)–C(5)	−69.40
O(1)–B(1)–N(1)–C(2)	−68.06	O(1)–B(1)–N(1)–C(6)	51.54
O(1)–C(4)–C(3)–C(2)	−67.52	C(2)–N(1)–C(6)–C(5)	56.55
C(2)–C(3)–C(4)–C(5)	49.91	C(3)–C(4)–C(5)–C(6)	−62.64
C(3)–C(4)–O(1)–B(1)	48.52	C(3)–C(2)–N(1)–C(6)	−69.23
C(6)–C(5)–C(4)–O(1)	55.57		
Sum of bond angles in the six-membered heterocycle (°)			
B(1)–O(1)–C(4)–C(3)–C(2)–N(1)		655.9 = 6 × 109.3 (7)	
B(1)–O(1)–C(4)–C(5)–C(6)–N(1)		655.4 = 6 × 109.2 (7)	

[a]A positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

3. Conclusions

Comparison of eleven cyclic borinates derived from piperidine- and piperazine alcohols has revealed a number of new interesting features. In total, two new *N*-spiro analogues and nine new heterobicycles have been synthesized and characterized.

While 1- and 2-substituted piperidine alcohols lead to cyclic borinates with the bulky diphenylboryl group in equatorial orientation, this group has to occupy the axial site in 3- and 4-substituted ones due to the formation of bicyclic systems. Nonetheless, in both cases, the configuration is fixed in solution (DMSO-d_6), if the piperidine alcohol is a secondary amine. In the case of the 1-methyl-piperidine alcohols the N → B bond strength is weaker and dissociation occurs more rapidly.

The free enthalpies of activation indicate that five-membered borinates are less stable than six-membered ones.

By X-ray crystallography it has been shown that 1-methyl substituted borinates have longer N → B bond lengths than the unsubstituted ones (e.g., for compounds **3a** and **4**), so that a weaker N → B bond strength can be assumed. In this case the difference in the N → B bond energy cannot be expressed quantitatively in adequate terms by the free enthalpy of activation. It is also difficult to compare five- and six-membered borinates by DNMR and X-ray crystallography, because the N → B bond length does not only depend on the N → B bond energy, but also on other effects as hybridization changes, steric strains in the molecule and crystal packing effects. But, X-ray crystallography provides good results, when two very similar structures are to be compared, as has been shown for compounds **3** and **4**. Similar results have been obtained with this method for a series of boroxazolidines that differed in the degree of substitution on the nitrogen atom [10–12]. The most detailed information about the coordinative N → B bond in boroxazolidines up to now has been obtained by theoretical studies. Thereby, it could be shown that the N → B bond strength depends on the polarization of the coordinative bond and the degree of substitution on the nitrogen and boron atoms [2].

4. Experimental part

4.1. Instrumentation

NMR studies were performed with the following spectrometers: Jeol FX 90 Q (^{1}H, ^{13}C, ^{11}B), Jeol GSX 270 (^{1}H, ^{13}C, ^{11}B) and Bruker DMX-500 (^{1}H, ^{13}C). Special techniques (APT, INEPT, COSY, HETCOR) were applied when necessary to assign the spectra adequately. Standards were TMS (^{1}H, ^{13}C) and $BF_3 \cdot OEt_2$ (^{11}B). Chemical shifts are stated in ppm; they are positive, when the signal is shifted to higher frequencies than the standard.

The dynamic ^{13}C NMR experiments have been performed in $CDCl_3$ based on the diastereotopic *ortho* carbon atoms of the B-phenyl groups.

IR spectra have been recorded with a Perkin Elmer 16F-PC FT-IR spectrophotometer.

Mass spectra were obtained with an HP 5989 A spectrometer.

Melting points were determined with a Gallenkamp MFB-595 apparatus and have not been corrected.

X-ray diffraction studies of monocrystals were realized on an Enraf-Nonius CAD4 diffractometer ($\lambda_{MoK\alpha} = 0.71069$ Å, monochromator: graphite, $T = 293$ K, ω-2θ scan). Crystals were generally mounted in LINDEMAN tubes. Cell parameters were determined by least squares refinement on diffractometer angles for 24 automatically centered reflections. Absorption correction was not necessary, corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution and the CRYSTALS (version 9, 1994) software package for refinement and data output. $I > 3\sigma(I)$. $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. In all cases only independent reflections on the basis of Friedel's law have been collected and a reflection–parameter ratio > 5 has been considered sufficient for the type of structural studies performed in here.

4.2. Reagents

Solvents were used without further purification, but monocrystals were grown from spectrophotometric grade solvents. All starting materials were commercial.

Diphenylborinic acid was prepared from 2-aminoethyldiphenylborinate (5% of molar excess) as described in the literature [57].

*4.2.1. Preparation of (N → B)-diphenyl[2-(1-piperidylethoxy)]borane (**1**)*

0.50 g (3.87 mmol) of 1-piperidineethanol were dissolved in $CHCl_3$ and the solution was cooled to −20°C. The diphenylborinic acid prepared from 0.90 g (4.00 mmol) of 2-aminoethyldiphenylborinate was filtered over Na_2SO_4,

liberated from diethylether and dissolved in $CHCl_3$ before it was added to the solution. The solvent was slowly evaporated and after addition of hexane a colourless precipitate formed. The product was filtered under N_2 and dried to obtain 0.48 g (1.64 mmol) of **1**. The compound hydrolyses after a few days.

$C_{19}H_{24}BNO$ (MW = 293.21 g mol^{-1}), m.p. 134–137°C, yield 42%.

^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.54$ (2H, m, H-9), 1.61 (4H, m, H-8, H-10), 2.80 (4H, m, H-7, H-11), 2.89 (2H, t, H-5), 4.07 (2H, t, H-4), 7.25–7.33 (6H, m, *m*-H, *p*-H), 7.78 (4H, d, *o*-H), ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 22.93$ (br, C-8, C-10), 23.34 (C-9), 53.57 (br, C-5, C-7, C-11), 59.57 (br, C-4), 127.13 (*p*), 127.47 (*m*), 133.23 (*o*), ^{11}B NMR (28.9 MHz, $CDCl_3$): $\delta = 6$ (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3446 (br, m), 3343 (br, m), 3198 (br, w), 3056 (m), 3014 (m), 2994 (m), 2950 (m), 2874 (m), 1652 (s), 1646 (m), 1636 (m), 1558 (m), 1540 (m), 1506 (m), 1460 (m), 1430 (m), 1190 (m), 1150 (s), 1090 (s).

MS (EI, 70 eV, DIP) *m/z*: 293 (M^+, 1), 216 (M^+-C_6H_5, 2), 165 (5), 129 (4), 98 ($C_6H_{12}N^+$, 100), 77 ($C_6H_5^+$, 6), 55 (38), 43 (40), 42 ($C_2H_4N^+$, 24).

*4.2.2. Preparation of (N → B), (N → B)′-bisdiphenyl-[2,2′-(1,4-piperazinediethoxy)]bisborane (**2**)*

1.00 g (5.75 mmol) of 1,4-piperazinediethanol was dissolved in methanol and the solution was cooled to −78°C. Diphenylborinic acid prepared from 2.70 g (12.00 mmol) of 2-aminoethyldiphenylborinate was added and a white precipitate formed. The colourless product was filtered under N_2, washed with hexane and dried to obtain 2.25 g (4.48 mmol) of **2**. The compound could not be obtained from benzene under reflux.

$C_{32}H_{36}B_2N_2O_2$ (MW = 502.27 g mol^{-1}), m.p. 174–178°C, yield 78%.

^1H NMR (270 MHz, DMSO-d_6): $\delta = 2.68$ (8H, br, H-8, H-9), 3.4–3.7 (8H, br, H-5, H-6), 7.29 (12H, br, *m*-H, *p*-H), 7.70 (8H, dd, *o*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): $\delta = 50.9$ (br, C-8, C-9), 58.3 (br, C-5, C-6), 127.14 (*p*), 127.80 (br, *m*), 132.95 (br, *o*), ^{11}B NMR (86.6 MHz, DMSO-d_6): $\delta = 3$ ($h_{1/2} = 577$ Hz) ppm.

IR (KBr) $\tilde{\nu}$(cm^{-1}): 3422 (br, m), 3068 (m), 3036 (m), 2982 (m), 2966 (m), 2922 (m), 2866 (m), 1661 (m), 1460 (s), 1430 (s), 1280 (s), 1190 (m), 1150 (s), 1100 (m), 1070 (s), 1015 (m).

MS (EI, 70 eV, DIP) *m/z*: 321 (M^+-$C_{12}H_{10}BO$, 14), 307 ($C_{19}H_{24}BN_2O^+$, 15), 243 ($C_{14}H_{20}BN_2O^+$, 5), 203 (9), 165 (33), 125 ($C_7H_{13}N_2^+$, 28), 98 ($C_5H_{10}N_2^+$, 32), 91 (39), 56 (69), 43 (100), 42 ($C_2H_4N^+$, 76).

*4.2.3. Preparation of (N → B)-diphenyl(2-piperidylmethoxy)borane (**3**)*

1.00 g (8.68 mmol) of 2-piperidinemethanol was dissolved in CH_2Cl_2 and the solution was cooled to −60°C. Diphenylborinic acid prepared from 2.00 g (8.88 mmol) of 2-aminoethyldiphenylborinate was added and the solvent was slowly evaporated at 0°C. The colourless product was washed with diethylether, filtered and dried to obtain 2.04 g (7.31 mmol) of **3**. When the reaction was performed in diethylether at room temperature, only 1.11 g (3.98 mmol) of **3** were obtained.

Crystals suitable for X-ray crystallography were obtained after recrystallization in THF/hexane.

$C_{18}H_{22}BNO$ (MW = 279.19 g mol^{-1}), m.p. 169–170°C, yield 84% (46%).

3a: ^1H NMR (270 MHz, DMSO-d_6): $\delta = 1.15$–1.75 (6H, m, H-6, H-7, H-8), 2.10 (1H, dd, H-9), 2.74 (1H, m, H-9′), 3.45 (1H, m, H-5), 3.83 (1H, d, H-4), 4.14 (1H, dd, H-4′), 6.10 (1H, dd, H-1), 7.10 (6H, m, *m*-H, *p*-H), 7.52 (4H, d, *o*-H), ^{13}C 67.8 MHz, DMSO-d_6) $\delta = 22.25$, 23.08, 24.47 (C-6, C-7, C-8), 46.79 (C-9), 60.65 (C-5), 67.25 (C-4); 124.94 (*p* and *p*′), 126.34 (*m*), 126.47 (*m*′), 131.48 (*o*), 132.94 (*o*′), 148.5 (br, *i* and *i*′), ^{11}B NMR (28.9 MHz, $CDCl_3$): $\delta = 7$ (br) ppm.

3b: ^1H NMR (270 MHz, DMSO-d_6): $\delta = 1.15$–1.75 (7H, m, H-6, H-7, H-8, H-9), 2.36 (1H, br, H-9′), 3.46 (3H, m, H-4, H-5), 6.48 (1H, br, H-1), 7.10 (6H, m, *m*-H, *p*-H), 7.52 (4H, d, *o*-H),), ^{13}C NMR (67.8 MHz, DMSO-d_6): $\delta = 17.68$ (C-7), 22.51, 22.94 (C-6, C-8), 43.20 (C-9), 53.08 (C-5), 62.91 (C-4), 124.80 (*p*, *p*′), 125.23 (*m*), 126.72 (*m*′), 130.54 (*o*), 131.67 (*o*′), ^{11}B NMR (28.9 MHz, $CDCl_3$): $\delta = 1$ ($h_{1/2} = 2160$ Hz) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3416 (br, m), 3168 (m), 3068 (m), 2998 (w), 2940 (s), 2862 (s), 1654 (s), 1646 (s), 1636 (s), 1558 (s), 1540 (s), 1456 (m), 1432 (m), 1210 (m), 1148 (m), 1062 (s), 1024 (m).

MS (EI, 70 eV, DIP) *m/z*: 279 (M^+, 4), 278 (M^+-H, 7), 202 (M-C_6H_5, 100), 98 ($C_6H_{12}N^+$, 14), 84 ($C_5H_{10}N^+$, 23), 77 ($C_6H_5^+$, 10), 42 ($C_2H_4N^+$, 7).

*4.2.4. Preparation of (N → B)-diphenyl(1-methyl-2-piperidylmethoxy)borane (**4**)*

0.90 g (6.97 mmol) of 1-methyl-2-piperidinemethanol were dissolved in THF and the solution was cooled to −78°C. Diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyldiphenylborinate was added and the solvent was slowly evaporated at 0°C. The colourless product was washed with hexane, filtered and dried to obtain 1.74 g (5.93 mmol) of **4**. The reaction did not proceed in THF or benzene, neither at room temperature nor at reflux.

Crystals suitable for X-ray crystallography were obtained after recrystallization in THF/hexane.

$C_{19}H_{24}BNO$ (MW = 293.21 g mol^{-1}), m.p. 169–171°C, yield 85%.

^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.52–1.62$ (6H, br, H-6, H-7, H-8), 2.56 (1H, br, H-9), 2.66 (3H, s, H-10), 2.93 (1H, br, H-9′), 3.16 (1H, br, H-5), 4.06–4.32 (2H, br, d, H-4), 7.15 (2H, t, H-*p*), 7.26 (4H, t, *m*-H), 7.75 (4H, d, *o*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): $T = 273$ K: $\delta = 17.97$, 19.15 (br, C-6, C-7, C-8), 40.06 (br, C-10), 51.64 (br, C-9), 61.11 (br, C-5), 64.29 (br, C-4), 126.16 (*p*), 127.18 (*m*), 132.72 (*o*), $T = 213$ K: $\delta = 16.93$ (C-7), 18.42 and 18.54 (C-6, C-8), 40.27 (C-10), 50.78 (C-9), 60.25 (C-5), 63.82 (C-4), 125.83 (*p*), 126.08 (*p*′), 127.24 (*m*), 127.83 (*m*′), 131.30 (*o*), 133.34 (*o*′), 147.1 (br, *i*), 147.6 (br, *i*′), ^{11}B NMR (28.9 MHz, DMSO-d_6): $\delta = 10$ (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3457 (br, m), 3068 (m), 3044 (m), 2992 (m), 2978 (m), 2952 (m), 2872 (m), 1654 (m), 1638 (m), 1560 (m), 1542 (w), 1534 (w), 1468 (s), 1430 (s), 1200 (m), 1178 (m), 1160 (m), 1136 (m), 1096 (s), 1086 (s), 1026 (m).

MS (EI, 70 eV, DIP) *m*/*z*: 293 (M^+, 1), 292 (M-H, 1), 216 (M^+-C_6H_5, 15), 165 (4), 98 ($C_6H_{12}N^+$, 100), 77 ($C_6H_5^+$, 4), 42 ($C_2H_4N^+$, 13).

*4.2.5. Preparation of (N → B)-diphenyl[2-(2-piperidyl)ethoxy]borane (**5**)*

0.90 g (6.97 mmol) of 2-piperidineethanol were dissolved in methanol and the solution was cooled to −78°C. Diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyldiphenylborinate was added and the solvent was slowly evaporated at 0°C. The colourless product was washed with diethylether, filtered and dried to obtain 1.57 g (5.35 mmol) of **5**. The reaction was also performed at room temperature in THF. After evaporation of the solvent the product was precipitated with hexane (1.56 g, 4.64 mmol).

Crystals suitable for X-ray crystallography were obtained after recrystallization in benzene/hexane.

$C_{19}H_{24}BNO$ (MW = 293.21 g mol^{-1}), m.p. 169–171°C, yield 77% (67%).

^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 1.04$ (1H, d, H-5), 1.38–1.60 (4H, m, H-7, H-8, H-9), 1.71 (1H, m, H-9′), 1.88 (1H, m, H-7′), 2.29 (2H, m, H-5′, H-10), 2.90 (1H, dd, H-10′), 3.50 (1H, d, H-6), 3.68–3.80 (2H, m, H-4), 5.98 (1H, d, H-1), 6.93 (1H, t, *p*-H), 7.01 (1H, t, *p*′-H), 7.04 (2H, t, *m*-H), 7.16 (2H, t, *m*′-H), 7.36 (2H, d, *o*-H), 7.52 (2H, d, *o*′-H), $^2J_{H\text{-}10} = 15$ Hz, $^2J_{H\text{-}5} = 15$ Hz, ^{13}C NMR (125.8 MHz, DMSO-d_6): $\delta = 17.02$ (C-8), 23.15 (C-9), 25.16 (C-5), 28.93 (C-7), 39.82 (C-10), 51.34 (C-6), 59.71 (C-4), 124.28 (*p*), 124.51 (*p*′), 126.40 (*m*), 126.98 (*m*′), 131.37 (*o*, *o*′), 133.6 (br, *i*),151.2 (br, *i*′), ^{11}B NMR (28.9 MHz, $CDCl_3$):$\delta = 1$ (br), ^{11}B NMR (28.9 MHz, DMSO-d_6): $\delta = 5$ (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3438 (br, m), 3230 (m), 3066 (m), 2998 (s), 2944 (m), 1636 (s), 1560 (w), 1540 (w), 1508 (w), 1458 (w), 1430 (m), 1368 (w), 1262 (m), 1230 (s), 1196 (s), 1065 (w), 1030 (w), 1025 (w).

MS (EI, 70 eV, DIP) *m*/*z*: 293 (M^+, 6), 292 (M^+-H, 11), 216 (M^+-C_6H_5, 100), 84 ($C_5H_{10}N^+$, 81), 77 ($C_6H_5^+$, 24), 55 (28), 42 ($C_2H_4N^+$, 13).

*4.2.6. Preparation of (N → B)-diphenyl(3-piperidyloxy)borane (**6**)*

1.00 g (7.27 mmol) of 3-hydroxypiperidine hydrochloride was dissolved in 5 ml H_2O and 0.29 g (7.25 mmol) of solid NaOH were added. After addition of 25 ml benzene the solution was refluxed for 30 min, whereby the water in the reaction solution was separated by a Dean-Stark trap. After addition of diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyldiphenylborinate a white precipitate of **6** formed that was separated, washed with diethylether and dried (0.75 g, 2.83 mmol). A higher yield could be obtained by the following method: The 3-hydroxypiperidine hydrochloride was dissolved in 5 ml of methanol and solid NaOH was added. After filtration the solution was cooled to −78°C and the diphenylborinic acid was added. Evaporation of the solvent under cooling and workup provided 1.10 g (4.15 mmol) of **6**.

$C_{17}H_{20}BNO$ (MW = 265.16 g mol^{-1}), m.p. 216–218°C, yield 39% (57%).

^{1}H NMR (270 MHz, DMSO-d_6): $\delta = 1.12$ (1H, dd, H-7), 1.42 (1H, m, H-8), 1.67 (1H, dd, H-8′), 1.80 (1H, m, H-7′), 2.70–2.98 (4H, m, H-5, H-6), 4.39 (1H, t, H-4), 6.85 (1H, s, H-1), 6.98 (2H, m, *p*-H), 7.12 (4H, m, *m*-H), 7.51 (2H, d, *o*-H), 7.58 (2H, d, *o*′-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): $\delta = 17.17$ (C-7), 30.66 (C-8), 46.81 (C-6), 53.51 (C-5), 68.85 (C-4), 124.59 (*p*), 126.61 (*m*), 130.74 (*o*), 130.90 (*o*′), 151.1 (br, *i*), 153.6 (br, *i*′), ^{11}B NMR (86.6 MHz, DMSO-d_6): $\delta = 6$ ($h_{1/2} = 619$ Hz) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3276 (br, m), 3064 (m), 3022 (m), 2998 (m), 2968 (m), 2944 (s), 2904 (s), 1638 (s), 1470 (s), 1454 (m), 1430 (s), 1316 (w), 1294 (m), 1238 (s), 1210 (s), 1176 (m), 1136 (s), 1108 (s), 1056 (m), 1040 (s).

MS (EI, 70 eV, DIP) *m*/*z*: 265 (M^+, 10), 264 (M^+-H, 12), 188 (M^+-C_6H_5, 100), 113 (13), 104 (40), 91 (42), 84 ($C_5H_{10}N^+$, 67), 77 ($C_6H_5^+$, 32), 44 ($C_2H_6N^+$, 100).

*4.2.7. Preparation of (N → B)-diphenyl(1-methyl-3-piperidyloxy)borane (**7**)*

0.25 g (2.22 mmol) of 1-methyl-3-hydroxypiperidine were dissolved in THF and diphenylborinic acid prepared from 0.54 g (2.40 mmol) of 2-aminoethyldiphenylborinate was added. After 4 h of reflux the solvent was slowly evaporated. The colourless product was washed with diethylether and hexane, filtered and dried to obtain 0.40 g (1.43 mmol) of **7**.

$C_{18}H_{22}BNO$ (MW = 279.19 g mol^{-1}), m.p. 169–171°C, yield 64%.

^1H NMR (270 MHz, $CDCl_3$): δ = 1.27 (1H, m, H-7), 1.40 (1H, m, H-8), 1.86 (1H, m, H-8′), 1.97 (1H, m, H-7′), 2.34 (1H, d, H-5), 2.45 (3H, s, H-9), 2.52 (1H, br, H-6), 3.10 (1H, br, H-6′), 3.20 (1H, br, H-5′), 4.56 (1H, br, H-4), 7.26 (6H, m, *p*-H, *m*-H), 7.68 (4H, d, *o*-H), ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 19.17 (C-7), 30.08 (C-8), 47.06 (C-9), 58.37 (C-6), 63.28 (C-5), 68.78 (C-4), 127.24 (*m*), 127.24 (*p*), 132.94 (*o*), 147.9 (br, i), ^{11}B NMR (28.9 MHz, DMSO-d_6): δ = 7 (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2934 (s), 1437 (m), 1145 (m), 1012 (m).

MS (EI, 70 eV, DIP) *m/z*: 279 (M^+, 13), 278 (M^+-H, 11), 202 (M^+-C_6H_5, 14), 165 (50), 105 (58), 97 (49), 77 ($C_6H_5^+$, 85), 51 (97), 42 ($C_2H_4N^+$, 100).

*4.2.8. Preparation of (N → B)-diphenyl(3-piperidylmethoxy)borane (**8**)*

0.80 g (6.95 mmol) of 3-piperidinemethanol were dissolved in methanol and the solution was cooled to −78°C. Diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyldiphenylborinate was added and the solvent was slowly evaporated at 0°C. The colourless product was washed with diethylether, filtered and dried to obtain 1.21 g (4.33 mmol) of **8**. The reaction was also performed in THF at room temperature. After evaporation of the solvent the product was washed with benzene, filtered and dried to obtain 0.73 g (2.61 mmol) of **8**.

Crystals suitable for X-ray crystallography were obtained after recrystallization in THF/hexane.

$C_{18}H_{22}BNO$ (MW = 279.19 g mol^{-1}), m.p. 207–209°C, yield 62% (38%).

^1H NMR (500 MHz, DMSO-d_6): δ = 1.26 (1H, m, H-8), 1.54 (1H, m, H-5), 1.70 (1H, m, H-9), 1.82 (1H, m, H-9′), 2.65 (1H, m, H-8′), 2.67 (2H, m, H-7), 2.83 (1H, d, H-6), 3.20 (1H, d, H-6′), 3.84 (1H, d, H-4), 3.95 (1H, d, H-4′), 6.37 (1H, m, H-1), 6.95 (1H, t, *p*-H), 6.99 (1H, t, *p*′-H), 7.07 (2H, t, *m*-H), 7.16 (2H, t, *m*′-H), 7.45 (2H, d, *o*-H), 7.50 (2H, d, *o*′-H), $^2J_{H\text{-}4}$ = 11 Hz, $^2J_{H\text{-}6}$ = 11 Hz, ^{13}C NMR (67.8 MHz, DMSO-d_6): δ = 19.69 (C-8), 28.28 (C-9), 29.39 (C-5), 47.10 (C-7), 49.50 (C-6), 66.15 (C-4), 124.49 (*p*), 124.57 (*p*′), 126.48 (*m*), 127.02 (*m*′), 130.68 (*o*), 130.75 (*o*′), 151.36 (br, *i*), 151.56 (br, *i*′), ^{11}B NMR (28.9 MHz, DMSO-d_6): δ = 3 (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3446 (br, m), 3260 (m), 3060 (w), 3038 (w), 3016 (w), 2996 (s), 2970 (m), 2914 (m), 2890 (m), 2846 (m), 1700 (w), 1684 (m), 1670 (w), 1652 (w), 1646 (m), 1636 (m), 1304 (m), 1262 (m), 1220 (s), 1180 (s), 1080 (m).

MS (EI, 70 eV, DIP) *m/z*: 279 (M^+, 9), 278 (M^+-H, 26), 202 (M^+-C_6H_5, 100), 98 ($C_6H_{12}N^+$, 22), 84 ($C_5H_{10}N^+$, 10), 77 ($C_6H_5^+$, 25), 42 ($C_2H_4N^+$, 21).

*4.2.9. Preparation of (N → B)-diphenyl(1-methyl-3-piperidylmethoxy)borane (**9**)*

0.90 g (6.97 mmol) of 1-methyl-3-piperidinemethanol were dissolved in $CHCl_3$ and the solution was cooled to −60°C. Diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyldiphenylborinate was filtered over Na_2SO_4, liberated from diethylether and dissolved in $CHCl_3$ before added to the solution. The solvent was slowly evaporated at 0°C. The very unstable colourless product was contaminated with a green substance that could be separated by washing with hexane. 0.52 g (1.77 mmol) of **9** were obtained. The reaction did not proceed in methanol and THF under the same conditions nor at higher temperatures.

$C_{19}H_{24}BNO$ (MW = 293.21 g mol^{-1}), m.p. 88–91°C, yield 25%.

^1H NMR (270 MHz, DMSO-d_6): δ = 1.25–1.70 (5H, m, H-5, H-8, H-9), 2.03-2.84 (4H, br, H-6, H-7), 2.37 (3H, s, H-10), 3.45 (2H, br, d, H-4), 7.28 (6H, br, *m*-H, *p*-H), 7.60 (4H, br, *o*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): δ = 23.26 (br, C-9), 26.42 (br, C-8), 36.07 (br, C-5), 46.78 (br, C-10), 56.68 (br, C-7), 59.01 (br, C-6), 64.89 (C-4), 126.94 (*m*), 127.1 (*p*), 133.78 (*o*), ^{11}B NMR (28.9 MHz, DMSO-d_6): δ = 2 (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3424 (br, m), 3040 (m), 2994 (m), 2928 (s), 2896 (s), 2856 (s), 1731 (w), 1660 (w), 1630 (w), 1476 (s), 1450 (s), 1432 (s), 1250 (m), 1170 (s), 1120 (s), 1080 (m), 1050 (m).

*4.2.10. Preparation of (N → B)-diphenyl(4-piperidyloxy)borane (**10**)*

0.22 g (2.20 mmol) of 4-hydroxypiperidine were dissolved in THF and diphenylborinic acid prepared from 0.54 g (2.40 mmol) of 2-aminoethyldiphenylborinate was added. After 4 h of reflux the solvent was slowly evaporated. The colourless product was washed with diethylether and hexane, filtered and dried to obtain 0.42 g (1.58 mmol) of **10**.

$C_{17}H_{20}BNO$ (MW = 265.16 g mol^{-1}), m.p. 219–221°C, yield 72%.

^1H NMR (270 MHz, DMSO-d_6): δ = 1.70 (4H, m, H-3, H-5), 2.75 (4H, m, H-2, H-6), 3.62 (1H, m, H-4), 4.13 (1H, m, H-1), 7.20–8.00 (10 H, *o*-H, *m*-H, *p*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): δ = 26.53 (C-3, C-5), 41.94 (C-2, C-6), 60.75 (C-4), 124.54 (*p*), 126.41 (*m*), 130.78 (*o*), 153.09 (br, *i*), ^{11}B NMR (28.9 MHz, DMSO-d_6): δ = 4 (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 1437 (m), 1310 (m), 1185 (m), 1030 (m).

MS (EI, 70 eV, DIP) *m/z*: 265 (M^+, 31), 264 (M^+-H, 40), 188 (M^+-C_6H_5, 55), 165 (41), 105 (41), 84 ($C_5H_{10}N^+$, 78), 77 ($C_6H_5^+$, 71), 68 (54), 56 (88), 55 (88), 42 ($C_2H_4N^+$, 93).

*4.2.11. Preparation of (N → B)-diphenyl(4-phenyl-4-piperidyloxy)borane (**11**)*

1.77 g (10.00 mmol) of 4-phenyl-4-hydroxypiperidine were dissolved in diethylether and diphenylborinic acid prepared from 2.70 g (12.00 mmol) of 2-aminoethyldiphenylborinate was added. The solution was refluxed for 1 h, whereupon the solvent was evaporated slowly. The colourless product was washed with diethylether and hexane, filtered and dried to obtain 1.21 g (3.55 mmol) of **11**.

Crystals suitable for X-ray crystallography were obtained after recrystallization in THF/hexane.

$C_{23}H_{24}BNO$ (MW = 341.25 g mol^{-1}), m.p. 250–252°C, yield 36%.

^{1}H NMR (270 MHz, DMSO-d_6): δ = 1.76 (2H, m, H-3, H-5), 2.07 (2H, m, H-3′, H-5′), 2.97 (4H, t, H-2, H-6), 3.37 (1H, m, H-1), 7.0 (2H, t, *p*-H), 7.14 (4H, t, *m*-H), 7.25 (1H, t, H-10), 7.40 (2H, t, H-9, H-11), 7.69 (4H, d, *o*-H), 7.76 (2H, d, H-8, H-12), ^{13}C NMR (67.8 MHz, DMSO-d_6): δ = 32.7 (C3, C-5), 42.3 (C-2, C-6), 68.4 (C-4), 124.6 (*p*), 124.8 (C-8, C-12), 126.0 (C-10), 126.5 (*m*), 127.7 (C-9, C-11), 130.7 (*o*), 148.9 (C-7), 153.2 (br, *i*), ^{11}B NMR (28.9 MHz, DMSO-d_6): δ = 5 (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 1174 (s), 1024 (s).

MS (EI, 70 eV, DIP) m/z: 341 (M^+, 6), 340 (M^+-H, 10), 264 (M^+-C_6H_5, 68), 103 (17), 91 ($C_7H_7^+$, 16), 77 ($C_6H_5^+$, 32), 42 ($C_2H_4N^+$, 100).

*4.2.12. Preparation of diphenylhydroxo[2-(1-piperidinium)ethoxy]borate (**12**)*

1.00 g (7.74 mmol) of 1-piperidineethanol was dissolved in a small amount of diethylether and diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyl-diphenylborinate was added. Immediately, colourless crystals of **12** formed, which were filtered under vacuum and dried (2.30 g, 7.39 mmol). The compound is stable for months in contrast to compound **1**.

Crystals suitable for X-ray crystallography were obtained by slow diffusion of diphenylborinic acid into a solution of 1-piperidineethanol in diethylether.

$C_{19}H_{26}BNO_2$ (MW = 311.23 g mol^{-1}), m.p. 104–106°C, yield 95%.

^{1}H NMR (270 MHz, DMSO-d_6): δ = 1.41–1.51 (6H, br, H-8, H-9, H-10), 2.70–2.82 (6H, br, H-5, H-7, H-11), 3.89 (2H, br, H-4), 3.95 (2H, br, H-1, H-6), 7.12–7.24 (6H, m, *m*-H, *p*-H), 7.68 (4H, d, *o*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): δ = 21.7, 22.7 (C-8, C-9, C-10), 53.1 (C-7, C-11), 54.0 (br, C-5), 59.3 (C-4), 126.2 (*p*), 126.8 (*m*), 132.9 (*o*), ^{11}B NMR (86.6 MHz, DMSO-d_6): δ = 12 ($h_{1/2}$ = 1170 Hz) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3568 (m, OH), 3448 (br, m), 3198 (br, m), 3056 (m), 3014 (m), 2994 (m), 2950 (m), 2874 (m), 1654 (m), 1470 (m), 1550 (w), 1494 (w), 1460 (m), 1440 (m), 1170 (m), 1160 (m), 1110 (s), 1090 (m), 1030 (w).

MS (EI, 70 eV, DIP) *m/z*: 311 (M^+, 1), 293 (M^+-H_2O, 3), 216 (M^+-H_2O-C_6H_5, 4), 165 (7), 98 ($C_6H_{12}N^+$, 100), 77 ($C_6H_5^+$, 7), 55 (16), 41 (19).

*4.2.13. Preparation of bisdiphenylmethoxy-[2,2′-(1,4-piperaziniumdiethoxy)]bisborate (**13**)*

Compound **13** was obtained from compound **2** by recrystallization in methanol. The crystals obtained were suitable for X-ray crystallography.

$C_{34}H_{44}B_2N_2O_4$ (MW = 566.35 g mol^{-1}), m.p. 187–192°C.

^{1}H NMR (270 MHz, DMSO-d_6): δ = 2.62 (8H, br, H-8, H-9), 3.39 (10H, br, H-1, H-6), 3.67 (4H, br, H-5), 4.12 (2H, br, H-7), 7.33 (12H, br, *m*-H, *p*-H), 7.69 (8H, m, *o*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): δ = 51.06 (br, C-1, C-8, C-9), 58.82 (br, C-5, C-6), 127.25 (*p*), 128.70 (br, *m*), 133.81 (br, *o*), ^{11}B NMR (86.6 MHz, DMSO-d_6): δ = −1 ($h_{1/2}$ = 2164 Hz) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3436 (br, m), 3036 (m), 3016 (m), 2982 (m), 2918 (m), 2888 (m), 2864 (s), 1462 (s), 1432 (s), 1396 (w), 1362 (w), 1284 (m), 1188 (m), 1148 (s), 1104 (s), 1072 (s), 1026 (s).

MS (EI, 70 eV, DIP) *m/z*: 503 (M^+-MeOH-CH_3O, 5), 502 (M^+-2 × MeOH, 4), 425 (M^+-2 × MeOH-C_6H_5, 17), 320 ($C_{20}H_{25}BN_2O^+$, 100), 307 ($C_{19}H_{24}BN_2O^+$, 74), 243 ($C_{14}H_{20}BN_2O^+$, 25), 203 (48), 165 (82), 125 ($C_7H_{13}N_2^+$, 83), 98 ($C_5H_{10}N_2^+$, 67), 91 (100), 56 (90), 42 ($C_2H_4N^+$, 66).

*4.2.14. Preparation of (N → B)-diphenylhydroxo-4-[1-(2-hydroxyethyl)]piperazylborane (**14**)*

1.00 g (7.68 mmol) of 1-piperazineethanol was dissolved in 100 ml benzene and diphenylborinic acid prepared from 1.80 g (8.00 mmol) of 2-aminoethyldiphenylborinate was added. The solution was shaken and permitted to react without stirring at room temperature. After 4–5 h colourless crystals of **14** (1.66 g, 5.32 mmol) formed, which were filtered under vacuum and dried.

Crystals suitable for X-ray crystallography were obtained after recrystallization in THF/benzene.

$C_{18}H_{25}BN_2O_2$ (MW = 312.22 g mol^{-1}), m.p. 110–112°C, yield 69%.

^{1}H NMR (270 MHz, DMSO-d_6): δ = 2.50–2.66 (10H, br, m, H-2, H-3, H-5, H-6, H-7), 3.45 (2H, br, t, H-8), 7.02

(2H, t, *p*-H), 7.14 (4H, t, *m*-H), 7.36 (benzene at special position in the crystal lattice), 7.55 (4H, d, *o*-H), ^{13}C NMR (67.8 MHz, DMSO-d_6): $\delta = 43.7$ (br, C-2, C-6), 51.49 (C-3, C-5), 58.7 (br, C-7, C-8), 125.04 (*p*), 126.48 (*m*), 128.20 (benzene in the crystal lattice), 132.17 (br, *o*), 150.0 (br, i), ^{11}B NMR (28.9 MHz, DMSO-d_6): $\delta = 4$ (br) ppm.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3578 (w, OH), 3242 (br, m), 3130 (s), 3068 (m), 3044 (m), 2998 (m), 2916 (m), 1734 (w), 1718 (w), 1700 (w), 1684 (w), 1676 (w), 1570 (w), 1470 (s), 1440 (s), 1350 (m), 1255 (m), 1211 (m), 1180 (m), 1030 (s).

MS (EI, 70 eV, DIP) *m/z*: 312 (M^+, 2), 263 (19), 165 (14), 112 (27), 99 ($C_6H_{13}N^+$, 100), 78 ($C_6H_6^+$, 100), 77 ($C_6H_5^+$, 28), 56 (86), 42 ($C_2H_4N^+$, 63).

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