

A tricyclic *N*-pyrrolylborane with an exceptionally stable B–N bond

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Received 16 July 1997

Abstract

Hydroboration of 2,5-diallylpyrrole by using a mixture diethylborane/triethylborane ($\text{Et}_2\text{BH}/\text{Et}_3\text{B}$) leads to the first tricyclic *N*-pyrrolylborane **3** which possesses an exceptionally stable B–N bond. In accordance with the pronounced Lewis-acidic character of **3**, it is readily converted into adducts (**6**) or borates (**9**). The crystal structure of **3** was determined by X-ray analysis (triclinic, space group $\text{P}\bar{1}$, $Z = 8$) showing a fairly long B–N bond (mean value 144 pm), the first example of a diorgano *N*-pyrrolyl borane in which the pyrrole ring is not twisted against the C_2BN -plane. Nuclear magnetic shielding (^{11}B , ^{13}C , ^{14}N) was calculated using the GIAO procedure. BN(pp) π bonding is discussed on the basis of MO calculations. © 1998 Elsevier Science S.A.

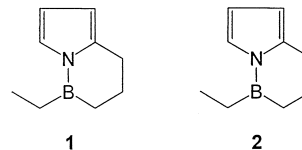
Keywords: Boron; Borates; Hydroboration; Pyrrole; MO calculations; X-ray analysis

1. Introduction

Bearing in mind the isoelectronic substitution of a CC by the BN unit, there is a striking analogy between fulvenes and *N*-pyrrolylboranes, in particular with respect to the formation of substituted cyclopentadienyl anions and *N*-pyrrolylborates (Scheme 1).

In contrast with cyclopentadienyl anions, the synthetic potential of triorgano(*N*-pyrrolyl)borates appears to be low and has never been studied in great detail [1–4]. This can be traced to easy cleavage of the B–N bond together with relatively fast redistribution reactions. Therefore, we have set out to prepare *N*-pyrrolylboranes with an exceptionally stable B–N bond. Although bicyclic *N*-pyrrolylboranes such as **1** [5] and **2**

[6] could be prepared, the stability of their B–N bonds proved to be insufficient for certain transformations [7]. Therefore, the incorporation of the *N*-pyrrolylborane into a tricyclic framework should help to solve this problem.



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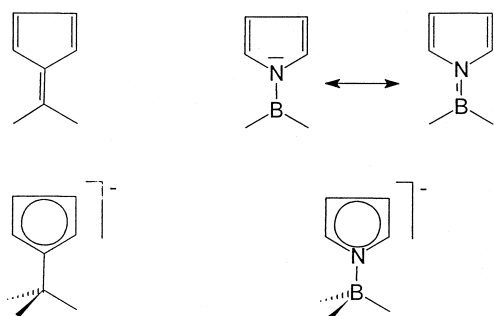
2. Results and discussion

2.1. Synthesis and properties of **3**

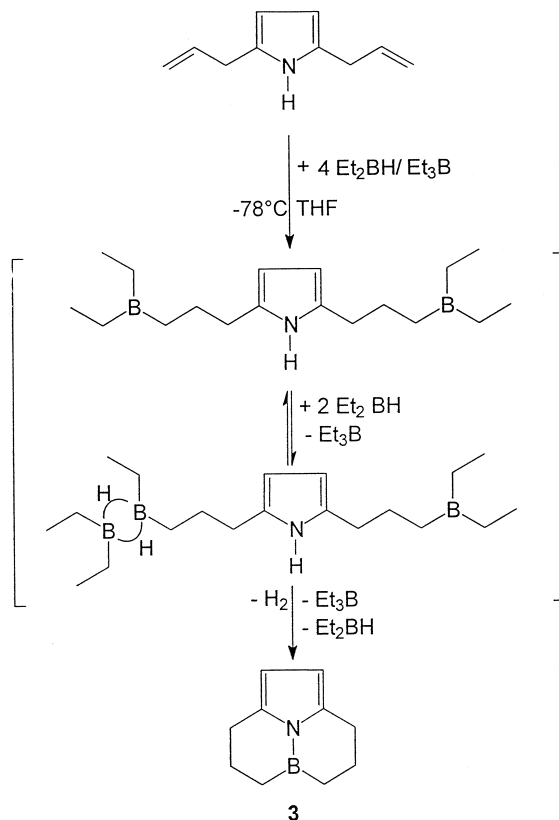
As shown in Scheme 2, the tricyclic *N*-pyrrolylborane **3** (see Table 1 for NMR data) is obtained by hydroboration of 2,5-diallylpyrrole accompanied by H_2 elimination. If one uses borane in tetrahydrofuran (BH_3 –THF/THF) as the apparently logical hydroboration reagent, unidentified polymeric material is formed and **3** can be isolated only in low yield (< 5%). It proved necessary to use diethylborane in THF, generated from BH_3 –THF and a large excess of triethylborane [8,9] in order to obtain **3** in good yield of > 70%.

The existence of the first intermediate shown in Scheme 2 is proposed on the basis of the results of the reaction of 2,5-diallylpyrrole with 9-borabicyclo[3.3.1]nonane (9-BBN). This hydroboration proceeds stepwise to give the compounds **4** and **5** (Scheme 3; for NMR data see Table 2). In the case of **5**, attempts at *N*-borylation using an excess of 9-BBN failed. Therefore, it can be assumed that an excess of Et_2BH at first ensures fast exchange of B–C bonds [10] as shown by the example in Scheme 2, followed by fast intramolecular H_2 elimination and further exchange to give finally the desired product **3**.

The borane **3** is stable towards water, it does not react with methanol or ethanol, even at elevated temperature, and it is recovered completely after treatment with acetic acid or trifluoromethylsulfonic acid (Scheme 4, compounds **7** and **8**; see Table 3 for NMR data of **7**, **8**). This behaviour is strongly in contrast with that of aminoboranes and other diorgano-*N*-pyrrolylboranes, including the highly reactive bicyclic *N*-pyrrolylboranes of type **1** and **2**. NMR spectroscopic data for **3** (see Table 1), in comparison with data for other *N*-pyrrolylboranes [5–7,11], structural parameters (vide infra), and MO calculations (vide infra) do not support strong $BN(pp)\pi$ bonding. This is also in accordance with the pronounced Lewis-acidic character of **3** (Scheme 4: **3** reacts with γ -picoline to give the adduct **6**, and with $nBuLi$ to give the borate **9**; see Table 1 for NMR data of compounds **6** and **9**). Protonation of the borate **9** does



Scheme 1.



Scheme 2.

not cleave the B–N bond but leads to the 2-*H*-pyrrole adducts **10** (Scheme 4; see Table 3 for NMR data of **10**). Hence, the tricyclic system is responsible for the stability of the B–N bond in **3**. 1H and ^{13}C NMR spectra at $-80^\circ C$ do not show any changes as compared to room temperature; thus the barrier to ring-inversion is low as predicted by MO calculations (vide infra), and the tricycle adopts on average a planar structure in solution.

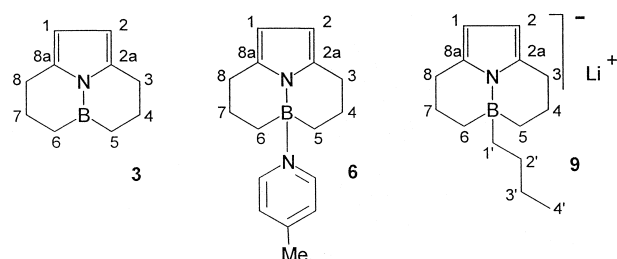
2.2. Crystal structure of **3**¹

The molecular structure of **3** is shown in Fig. 1, and the packing in the pseudo-hexagonal cell is depicted in Fig. 2. The triclinic unit cell however, contains four independent molecules which is rather unusual.² The molecules of **3** arrange themselves to form columns on a pseudo threefold screw axis (shortest contacts between separate molecules: 371 pm) thus forming an almost

¹ Further details of the crystal structure analysis can be obtained on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD 407281.

² The Inorganic Crystal Structure Database (ICSD), FIZ, Karlsruhe, 1994, lists only 370 examples of triclinic unit cells with $Z = 4$, in contrast to 15,000 to 18,000 examples with $Z = 2$ or $Z = 1$.

Table 1
 ^{11}B , ^{13}C and ^{14}N NMR data [a] of **3**, **6** and **9**:



No	3	6	9 [b]
$\delta^{11}\text{B}$	54.0	7.0	-10.7
$\delta^{14}\text{N}$	-207.5	n.m.	-178.8 [c]
$\delta^{13}\text{C}$	C-1/2	107.7	104.4
	C-2a/8a	133.7	131.1
	C-3/8	25.6	27.6
	C-4/7	21.5	23.9
	C-5/6	16.8 [br]	21.6 [br]
	C-1'	-	28.0 [br]
	C-2'	-	30.8
	C-3'	-	28.2
	C-4'	-	14.6

[a] C_6C_6 , 25°C ; [br]: broad signal owing to partially relaxed scalar ^{13}C - ^{11}B coupling; n.m. = not measured.

[b] $\text{C}_6\text{D}_6/\text{THF}$ (1:1), 25°C .

[c] Na-salt, 60°C , ^{14}N resonance not observed with Li^+ as counter ion.

hexagonal close-packed system (shortest contacts between separate columns: 272 pm). Bond lengths and angles in the different molecules **3** are almost identical, and all molecules **3** adopt the same conformation with a local, non-crystallographic C_2 symmetry. The surroundings of the boron and nitrogen atoms are exactly trigonal planar within the experimental errors. In contrast with the averaged structure of **3** in solution, the aliphatic carbon atoms C(14,17) are in mutual *trans*-positions,

Table 2
 ^{11}B , ^{13}C and ^{14}N NMR data [a] of **4** and **5**:

No	$\delta^{11}\text{B}$	$\delta^{14}\text{N}$	$\delta^{13}\text{C}$								
			C-2	C-3/4	C-5	C-1'	C-2'	C-3'	C-1''	C-2''	C-3''
4	88.0	[c]	127.7	105.8/ 106.3	131.6	31.2	25.4	28.5[br]	31.4[br]	33.5	23.6
5	88.2	224.3	131.5	105.2	131.5	31.5	25.4	27.0[br]	28.4[br]	33.6	23.7

[a] C_6D_6 , 25°C ; [br]: broad signal owing to partially relaxed scalar ^{13}C - ^{11}B coupling.

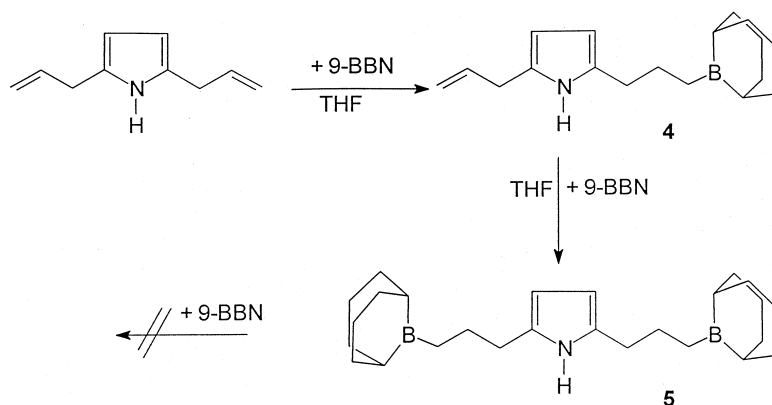
[b] $\delta^{13}\text{C}$ (allyl group) = 32.8 (CH_2); 136.8 (CH); 115.7 ($=\text{CH}_2$).

[c] In mixture with 2,5-diallpyrrole.

slightly shifted out of the best plane (mean deviation < 4 pm) formed by the other eight carbon atoms and the boron and the nitrogen atom. The B–N bond length (mean value 143.8 pm) is more indicative of a B–N_{azole} single bond than of strong BN(pp) π bonding. The latter would lead to a B–N bond length of about 140 ppm or even less as found frequently in aminoboranes [12,13].

2.3. Calculation of ^{11}B , ^{13}C and ^{14}N nuclear magnetic shielding of **3**; BN(pp) π interactions

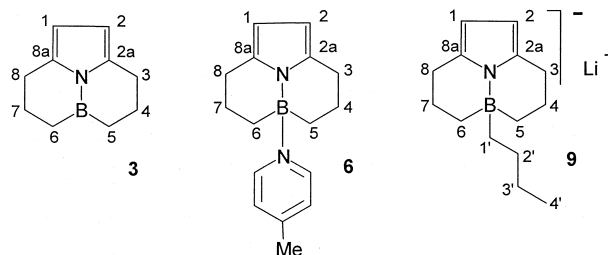
Nuclear shielding calculations were performed within the GIAO ab initio framework [14,15] using a 6-31G(2d, 2p) basis set for the ^{11}B , ^{13}C and ^{14}N nuclei of **3** (Table 4). The agreement with experimental data is remarkably good. The structure employed for the shielding calculations was fully optimised using the 6-311** basis set. This structure was characterised as minima on the potential energy surface by the calculation of second order energy derivatives. All MO calculations were performed using Gaussian 94 [16]. The calculated B–N distance for **3** is 143 ppm which is in good agreement with the experimental data (mean value 143.8 pm) from the



Scheme 3.

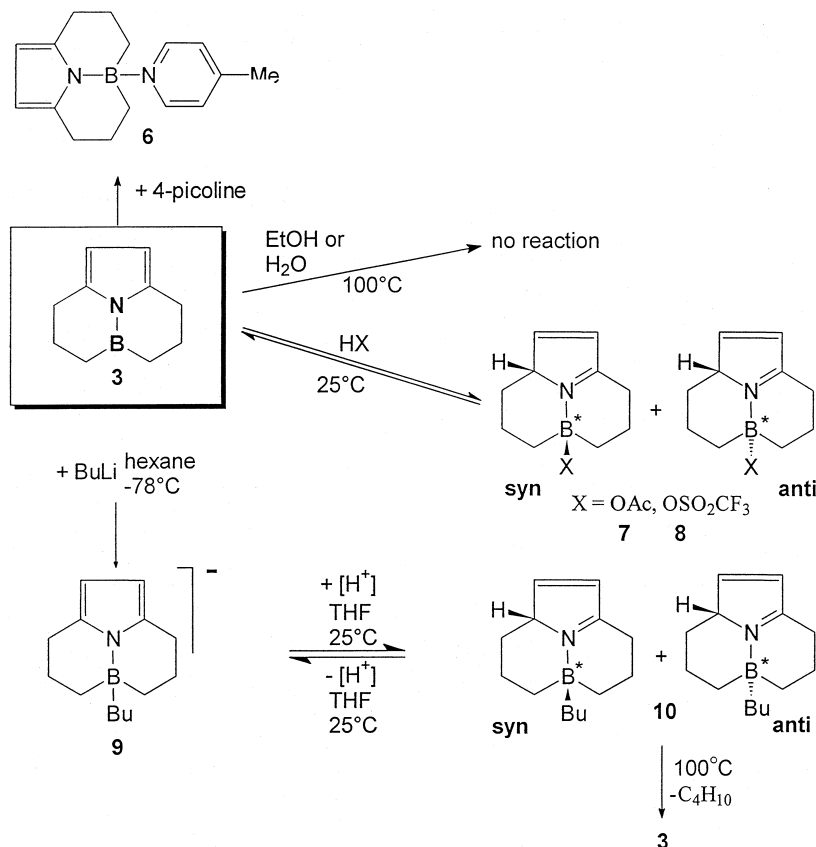
X-ray analysis. From the results of the MO calculations, C(14) and C(17) are found to be out of the plane formed by the other ring atoms. The NBC(14)C(15) and NBC(16)C(17) dihedral angles are 24.5° for the *cis* form and 20° for the *trans* form (mean experimental value: 20.5°). The *cis*–*trans* interconversion energy is calculated to be 1.5 kJ/mol with the *cis* form having the lower energy. A 6-311G(2d,2p) basis set was used for this energy calculation. The experimentally observed *trans* form may be favoured by the packing in the crystal.

An NBO analysis [16,17] of the B–N bonds in **3** and in the related tricyclic compound **11** has been performed using an 6-31G** basis set. The results reveal that the extent of σ bonding in the two compounds is essentially the same. In contrast the π bond occupancy is 1.899 for **11** and only 1.748 for **3** which is consistent with the shorter B–N bond calculated for **11** (140 pm). This is also supported by calculated and experimental ^{11}B , ^{13}C and ^{14}N nuclear shielding data (Table 4) for **3** and **11**.



3. Conclusions

For the first time a tricyclic *N*-pyrrolylborane **3** was prepared and fully characterised. MO calculations show that BN(pp) π bonding in **3** is significantly reduced with respect to a comparable tricyclic enaminoborane **11**. As a result of the exceptionally stable B–N bond in **3** numerous useful transformations can be carried out [18] which are not typical for trigonal boranes with a B–N



Scheme 4.

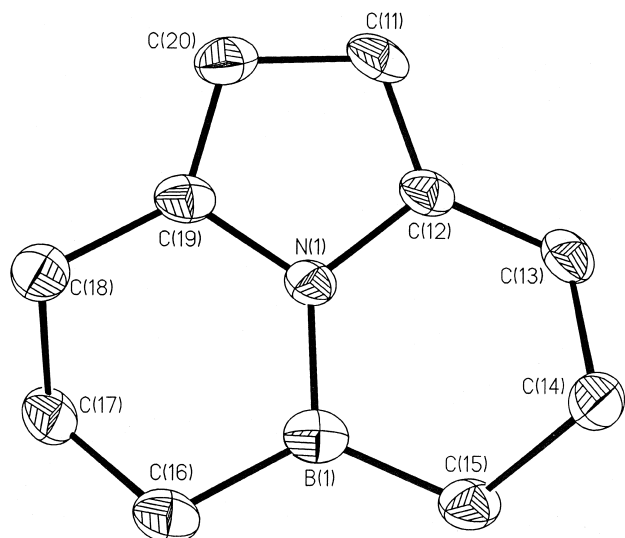


Fig. 1. Ellipsoid plot (50%) of the molecular structure of one of the four independent molecules of **3**. Mean bond lengths (pm) and selected bond angles ($^{\circ}$), based on C_2 symmetry: N–B 143.8(3), B–C 157.1(3), N–C 140.9(2), C(11)–C(20) 143.9(4), C(11)–C(12) 136.0(2), C(12)–C(13) 150.0(2), C(13)–C(14) 153.2(2), C(14)–C(15) 151.4(2); C–B–C 128.6(2), C–N–C 108.6(2), C–B–N 115.8(1), C–N–B 125.7(2), C(11)–C(12)–C(13) 134.1(2).

bond. *N*-pyrrolylborates of type **7**, being isolobal with substituted cyclopentadienyl anions, are expected to become of particular interest as η^5 -bonded ligands in transition metal complexes [19–21].

4. Experimental

All reactions were performed in an atmosphere of dry nitrogen, using carefully dried solvents and oven-dried glassware. Starting materials such as pyrrole, allyl bromide, Et_2O-BF_3 , $NaBH_4$, 1,5-cyclooctadiene, γ -picoline, *n*-BuLi in hexane (1.6 M) were used as commercial products; 2,5-diallylpyrrole [22,23], BH_3-THF/THF [24], Et_3B [25], and 9-BBN [26] were prepared following the literature procedures. EI-MS (70 eV): VARIAN MAT CH7 with direct inlet. 1H , ^{11}B , ^{13}C , ^{14}N NMR spectra were measured by using Bruker ARX 250, AC 300 or DRX 500 instruments, all equipped with multinuclear units and variable temperature control; chemical shifts are given with respect to Me_4Si [$\delta^1H(C_6D_5H) = 7.15$, ($CHCl_3/CDCl_3$) = 7.24, ($C_6D_5CD_2H$) = 2.03; $\delta^{13}C(C_6D_6) = 128.0$, ($CDCl_3$) = 77.0, ($C_6D_5CD_3$) = 20.4], Et_2O-BF_3 [$\delta^{11}B = 0$ for

Table 3

^{11}B , ^{13}C and ^{14}N NMR data^[a] of the 2-*H*-pyrrole-borane adducts **7**, **8**, **10**

R	$^nBu^{[c]}$ (1) 10	$^nBu^{[c]}$ (2) 10	$OCOCH_3^{[d]}$ 7	$OSO_2CF_3^{[e]}$ (1) 8	$OSO_2CF_3^{[e]}$ (2) 8
$\delta^{11}B$	-6.6	-6.0	2.0 ^[j]	13.9 ^[m]	13.9 ^[m]
$\delta^{14}N$	-120.0	-120.0	n.m.	n.m.	n.m.
$\delta^{13}C$					
C-1	153.8	147.8	156.1	159.0	161.0
C-2	128.1	129.7	127.8	131.2	n.m.
C-2a	174.3	178.7	176.2	183.4	194.5
C-3	30.1	n.m.	21.5	29.9	29.9
C-4	23.3	20.3	29.4	20.7	20.4
C-5	24.9 [br]	n.m.	n.m.	n.m.	n.m.
C-6	20.5 [br]	n.m.	n.m.	n.m.	n.m.
C-7	20.0	n.m.	20.0	17.1	16.7
C-8	35.7	30.4	34.0	32.1	n.m.
C-8a	73.3	62.3	73.9	74.1	63.2

[a] C_6D_6 , 25°C; [br]: broad resonance signal owing to partially relaxed scalar ^{13}C - ^{11}B coupling; n.m. means not measured or not observed. [b] The atomic numbering corresponds to 8b-Azonia-5a-borata-3,4,5,6,7,8,8a-octahydroacenaphthylene. No assignment was made to signals of the *syn*- or *anti*-isomer.

[c] $\delta^{13}C$: 25.7 [br]: (C-1'); 30.1 (C-2'); 27.8 (C-3'); 15.0 (CH_3); same chemical shifts of *syn*- and *anti*-isomer.

[d] $\delta^{13}C$: 178.4 (-O-CO); 20.1 (CH_3).

[e] $\delta^{13}C$: 119.4 (q); $^1J[^{19}F, ^{13}C] = 317.5$ Hz.

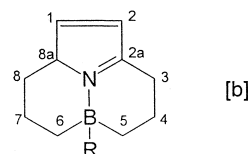


Table 4

Comparison of calculated^[a] with experimental chemical shifts $\delta^{11}\text{B}$, $\delta^{13}\text{C}$ and $\delta^{14}\text{N}$ in the tricyclic compounds **3** and **11**

	3 (calcd.)	3 (exp.)	11 (calcd.)	11 (exp.) ^[c]
$\delta^{11}\text{B}^{[b]}$	50.3	54.0	43.4	42.6
$\delta^{14}\text{N}$	-214.0	-207.5	-251.2	-229.4
$\delta^{13}\text{C}(1)$	102.5	107.7	92.6	103.9
$\delta^{13}\text{C}(8a)$	131.0	133.7	144.0	145.2

[a] Absolute σ values were calculated (see 2.3) and, for convenience, converted to the $\delta^{13}\text{C}$ and $\delta^{14}\text{N}$ scales by using $\sigma^{13}\text{C}(\text{Me}_4\text{Si}) = -185.4$ [14] and $\sigma^{14}\text{N}(\text{MeNO}_2) = -135.0$ [14].

[b] The absolute σ value was calculated for H_3BO_3 (+96.7) and converted to the $\delta^{11}\text{B}$ scale by using $\sigma\text{B}(\text{Et}_2\text{O-BF}_3) = +115$.

[c] Experimental data were obtained for the derivative with a *sec*-butyl group in 2-position [15].

$\Xi(^{11}\text{B}) = 32.083971 \text{ MHz}$], and neat MeNO_2 ($\delta^{14}\text{N} = 0$ for $\Xi(^{14}\text{N}) = 7.226455 \text{ MHz}$).

4.1. 8b-aza-5a-bora-3,4,5,5a,6,7,8,8b-octahydro-acenaphthylene **3**

A mixture of BH_3 -THF in 50 ml of THF (21.4 mmol BH_3) and 8 g of BET_3 (81 mmol) was stirred at room temperature for 5 h, cooled to -78°C and a solution of 3.15 g (21.4 mmol) of 2,5-diallylpyrrole in 20 ml of THF was added dropwise. After slowly warming to room temperature the reaction mixture was stirred for 2 days. Then the solvent and excess of BET_3 were removed in vacuo. Distillation of the yellowish residue gave 2.55 g (75%) of **3** as a colourless liquid (b.p.: $70^\circ\text{C}/0.5 \text{ Torr}$; m.p.: 25°C) which crystallized as colourless needles (m.p. 24°C) ^1H NMR (C_6D_6 , 250 MHz) $\delta^1\text{H}$ [$J(^1\text{H}, ^1\text{H})$] = 5.99 (s) (H-1/H2); 2.83 (t) [6.2 Hz] (H-3/H-8); 1.88 (quint) (H-4/H-7); 1.34 (t) (H-5/H-6). EI-MS: m/z (%) = 159 (75) [M^+]; 158 (100) [$\text{M}^+ - \text{H}$].

4.2. Allyl-5-[3'-(9''-borabicyclo[3.3.1]nonyl)propyl]pyrrole **4** and 2,5-bis-[3'-(9''-borabicyclo[3.3.1]nonyl)propyl]pyrrole **5**

A solution of 2 g (16 mmol) of 9-BBN in 100 ml of THF was added dropwise at room temperature to a

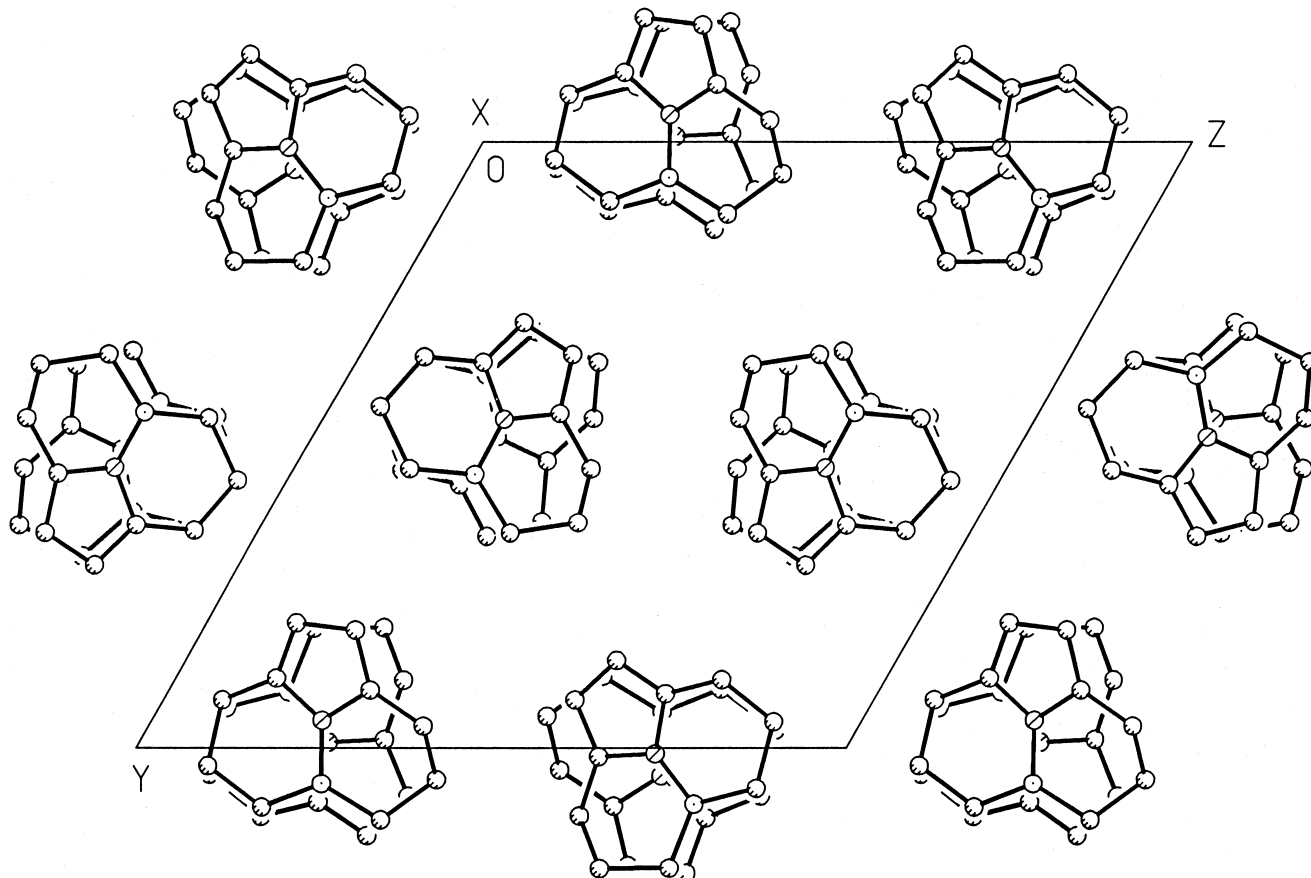


Fig. 2. The packing of the molecules of **3** in the pseudo hexagonal cell.

mixture of 1.18 g (8 mmol) of 2,5-diallylpyrrole in 100 ml of THF. The mixture was stirred at room temperature for 15 h. After that all volatile material was removed in vacuo. The oily yellowish residue (3.2 g; 100%) was identified as the pure (^1H NMR: > 95%) compound **5**. For the preparation of **4** 0.8 g (6.4 mmol) of 9-BBN in 30 ml of THF were used. The excess of 2,5-diallylpyrrole was removed in vacuo (10^{-4} Torr, room temperature). ^5H NMR (C_6D_6 , 250 MHz) $\delta^1\text{H}$ [$J(^1\text{H}, ^1\text{H})$] = 7.11 [br] (NH); 5.99 (d) [2.6 Hz] (H-1/H-2); 2.48 (t) [7.7 Hz] (H-3/H-8); overlapping multiplets at 2.00–1.18 (H-4/H-5/H-6/H-7/9-BBN groups).

4.3. γ -Picoline adduct of **3** (**6**)

After dissolving of 100 mg (0.63 mmol) of **3** in 0.5 ml of C_6D_6 in an NMR tube (5 mm o.d.), γ -picoline was added at room temperature, and the formation of the adduct became evident from the ^{11}B and ^{13}C NMR data (Table 1). After removing the C_6D_6 in vacuo, a colourless solid was left which was recrystallized from hexane (m.p. 82°C). ^1H NMR (C_6D_6 , 250 MHz) $\delta^1\text{H}$ [$J(^1\text{H}, ^1\text{H})$] = 7.46 (m) H-2'/H-6'; 7.16 (m) H-3'/H-5'; 5.77 (s) H-1/H-2; 2.58 (t) [6.3] H-3/H-8; 2.37 (s) CH_3 ; 1.31 (quint.) H-4/H-7; 0.76 (t) H-5/H-6.

4.4. Reaction of **3** with acetic acid to **7** and with trifluoromethylsulfonic acid to **8**

The reactions were carried out under the same conditions as described for **6**, and the results were deduced from consistent ^{11}B and ^{13}C NMR data (Table 3). ^1H NMR data confirm that **7** is in fast equilibrium with **3**, and therefore, the *syn*- and *anti* isomers cannot be distinguished. In the case of **8**, the ^1H NMR spectra confirm the results of ^{13}C NMR spectra that both isomers are present in a ratio of 2:1 (without assignment). The starting material **3** was recovered almost quantitatively by fractional distillation.

4.5. Lithium-8b-aza-5a-borata-5-butyl-3,4,5,5a,6,7,8,8b-octahydro-acenaphthylene **9**

A solution of 1 g (6.3 mmol) of **3** in 10 ml of hexane was cooled to -78°C and 10.8 ml of $^n\text{BuLi}$ (1.6 M in hexane) was added after 1 min. The mixture became white. Filtration gave 1.3 g (92%) of **9** as a white powder. ^1H NMR ($\text{C}_6\text{D}_6/\text{THF}$ (1:1), 25°C) [$^nJ(^1\text{H}, ^1\text{H})$]: 5.21 (s) (H-1/H-2); 2.41 (m)/2.31 (m) (H-3/H-8); 1.68 (m)/1.42 (m)/1.14 (m) (H-4/H-7/H-2'/H-3'); 0.15 (m)/0.00 (m) (H-5/H-6); 0.76 (t) [6.9 Hz] (CH_3); 0.48 (m) (H-1').

4.6. Protonation of **9**: 2-pyrrole-borane adducts **10**

Acetic acid (0.12 ml, 2 mmol) was added to a solution of 0.43 of **9** (2 mmol) in 5 ml of THF and the

mixture was stirred at room temperature for 24 h. Then the solvent was removed in vacuo and the residue was taken up in hexane. After filtration, fractional distillation gave 0.37 g (90%) of **10** (b.p. $120^\circ\text{C}/10^{-1}$ Torr; colourless liquid) as a mixture of isomers. ^1H NMR (C_6D_6 , 250 MHz) $\delta^1\text{H}$ [$J(^1\text{H}, ^1\text{H})$] = 6.69 (m) H-1; 5.82 (m) H-2; 3.93 (m) H-8a; 2.20 (m) H-2'; 2.00 (m) H-3; 1.70 (m) H-4/H-7; 1.40 (m) H-3'; 1.32/1.12 (m) H-8; 0.99 (t) [7.0] CH_3 ; 0.84 (m) H-5; 0.58 (m) H-3; 0.50/0.32 (m) H-6/H-1'.

4.7. Crystal structure determination of **3**

The neat sample of **3**, $\text{C}_{10}\text{H}_{14}\text{BN}$, (MG 150.03) was sealed in a 0.3 mm Lindemann capillary and cooled on a Siemens–Nicolet R3 four circle diffractometer until a polycrystalline material emerged below the melting point at 245 K. A cylindric single crystal was grown by means of a miniature zone melting procedure applying an IR laser beam [27]. The cell dimensions $a = 8.419(2)$, $b = 15.618(2)$, $c = 15.812(3)$ Å, $\alpha = 119.41(3)$, $\beta = 91.38(3)$, $\gamma = 94.60(3)^\circ$, $V = 1800.5(6)$ Å³, were determined at 133(2) K with graphite monochromated MoK_α radiation. Triclinic space group $\text{P}\bar{1}$ with $Z = 8$, density (calc.) = 1.173 Mg m^{-3} , $\mu = 0.067 \text{ mm}^{-1}$, 3514 intensities collected ($2\theta_{\text{max}} = 40^\circ$), 3348 independent ($R_{\text{int}}(F^2) = 0.1544$), 3005 observed ($F_o^2 \geq 2\sigma(F^2)$), structure solution (Direct Methods) and refinement (434 parameters, H atoms as rigid groups) with Siemens-SHELX (Version 5.1), $R1 = 0.0454$, $wR2 = 0.1169$, $\text{GOF} = 1.053$, residual electron density 0.189 and -0.322 e Å^{-3} .

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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