Structural Requirements for the Formation of the $B_2El^{VI}N_2$ Heterocycles

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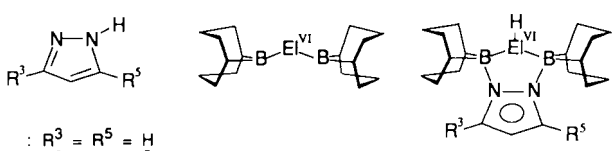
The reactions of the bis(diorganoboryl) chalcogenides $(R_2B)_2El^{VI}$ [R = Et, El^{VI} = O (**9**); R_2 = 1,5-C_8H_{14} (**1**, El^{VI} = O), (**2**, El^{VI} = S)] with 3-methyl-, 3,5-dimethyl-, 3-methyl-5-phenyl-, 3,5-diphenyl-, and 3,5-di-*tert*-butylpyrazole [**mPz, m$_2$Pz, mpPz, p$_2$Pz,** and **(tb)$_2$Pz**, respectively] have been investigated. **mPz** reacts with **2** to form the heterocycle **m5**, which due to the interaction of the methyl substituent with the carbon skeleton of **2** is unstable and readily rearranges to the novel heterocycle **7** (X-ray analysis) when dissolved in toluene at room temperature. In contrast the analogues **m4** (El = O), formed from **mPz** and **1**, is stable even when heated at 100°C. The reaction of **1** with **m$_2$Pz** and **mpPz** does not produce stable heterocycles of the type **4**, instead the 1:1 adducts **m$_2$Pz-1** and **mpPz-1** are formed in which the pyrazole fluctuates between the two boron atoms of **1**. The diboryl oxide **1** showed only weak interactions with **mpPz** and none with **p$_2$Pz** and **(tb)$_2$Pz**. With **9** the pyrazoles **m$_2$Pz, mpPz,** and **p$_2$Pz** form readily the corresponding heterocycles **10**, however no reaction was observed with **(tb)$_2$Pz** (^{1}H-, ^{11}B-, ^{13}C-NMR).

Strukturelle Voraussetzungen für die Bildung der $B_2El^{VI}N_2$-Fünfringe

Die Reaktionen der Bis(diorganoboryl)chalkogenide $(R_2B)_2El^{VI}$ [R = Et, El^{VI} = O (**9**); R_2 = 1,5-C_8H_{14} (**1**, El^{VI} = O), (**2**, El^{VI} = S)] mit 3-Methyl-, 3,5-Dimethyl-, 3-Methyl-5-phenyl-, 3,5-Diphenyl- und 3,5-Di-*tert*-butylpyrazol [**mPz, m$_2$Pz, mpPz, p$_2$Pz** und **(tb)$_2$Pz**] werden untersucht. **mPz** reagiert mit **2** zu **m5**, das durch sterische Wechselwirkungen der Methyl-Gruppen von **mPz** mit dem C-Gerüst von **2** destabilisiert ist und sich in Toluol leicht in den neuen Heterocyclus **7** (Röntgenstrukturanalyse) umwandelt. **m4** (El = O) (aus **mPz** und **1**) ist demgegenüber bis 100°C stabil. **1** bildet mit **m$_2$Pz** und **mpPz** keine Heterocyclen des Typs **4**, sondern die 1:1-Additionsverbindungen **m$_2$Pz-1** und **mpPz-1** mit zwischen den zwei Bor-Atomen von **1** fluktuierenden **Pz**-Basen. Zwischen **1** und **mpPz** lassen sich nur schwache, zwischen **1** und **p$_2$Pz** bzw. **(tb)$_2$Pz** keine Wechselwirkungen nachweisen. **9** reagiert mit **m$_2$Pz, mpPz** und **p$_2$Pz** zu den Heterocyclen des Typs **10**. Zwischen **(tb)$_2$Pz** und **9** werden keine Wechselwirkungen beobachtet (^{1}H-, ^{11}B-, ^{13}C-NMR).

Recently, we reported[1] that the bis(diorganoboryl) oxides **1**, El = O form only 1:1 adducts with monobasic donors such as pyridines or quinuclidine (**Q**). In these, only one of the boron atoms of **1** becomes coordinated by the base. Further[2] we showed that the dibasic pyrazoles (**Pz**) readily undergo simultaneous double coordination with both boron atoms of the oxide **1**, the sulfide **2**, and the selenide **3** yielding stable adducts in the form of the new class of $B_2El^{VI}N_2$ (El = O, S, Se) heterocycles **4**, **5**, and **6**. In experiments carried out to further explore the scope of the reaction of these chalcogenides with different pyrazoles we have now found that heterocycles of the type **4** and **5** are rendered unstable or that their formation is hindered when sterically bulky α-substituents are on the pyrazoles employed. Some of these reactions, deemed to be interesting extensions of those previously described[2], are the subject of this publication.



Pz : $R^3 = R^5 = H$
mPz : R^3 = Me; R^5 = H
m$_2$Pz : $R^3 = R^5$ = Me
mpPz : R^3 = Me; R^5 = Ph
p$_2$Pz : $R^3 = R^5$ = Ph
(tb)$_2$Pz : $R^3 = R^5$ = t-Bu

	El^{VI}
1	O
2	S
3	Se

	El^{VI}
4	O
5	S
6	Se

Results and Discussions

In a procedure analogous to those employed previously[1] that led to the formation of the stable heterocycle **m4**, a toluene solution of equimolar quantities of **2** and 3-methylpyrazole (**mPz**) was briefly stirred at room temperature. From the resulting colourless solution crystals of **7** were obtained at −60°C in 85% yield. These showed a molecular ion at m/z = 356 in its mass spectrum corresponding to the molecular formula $C_{20}H_{34}B_2N_2S$ with predominant fragment ions at m/z = 246 (45%, loss of C_8H_{14}) and 245 (40%, loss of C_8H_{15}). In the IR or Raman spectra of **7** >NH or −SH bonds were not indicated. The ^{11}B-NMR spectrum showed two signals at δ = 55.9 ($h_{1/2}$ = 780 Hz) and 5.9 ($h_{1/2}$ = 270 Hz) of approximately equal intensity. These correspond to tricoordinated and tetracoordinated boron atoms, respectively, with one of the substituents on the tricoordinated boron being probably a nitrogen atom[3]. The ^{1}H-NMR spectrum, with mainly a complex multiplet for aliphatic protons at δ ≈ 1.8, was uninformative. The ^{13}C-NMR spectrum showed far too few lines than expected for the heterocycle

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Table 1. NMR data (δ in ppm) for products derived from the sulfide **2**

Compounds	Solvent	δ ^{13}C (50.4 MHz)						δ ^{11}B[a–c] (64.2 MHz)	δ ^{1}H (200 MHz)				
		Pyrazole moiety			Organoboron moiety				Pyrazole moiety			Organoboron moiety	
		C^3 R^3	C^4	C^5 R^5	αC(br)	βC	γC	(no of B atoms)	H^3 R^3	H^4	H^5 R^5	αH	(β, γ, δ, ε)H (no of H atoms)
5	C_7D_8	134.4	107.6	134.4	24.6; 24.0	35.6; 33.5 31.1; 30.3	24.6 23.6	5.4[a]	7.45	5.84	7.45	0.93(2) 0.78(2)	1.5–2.1(24) 1.0(1)
5 + Q	C_7D_8	133.8	107.3	133.8	25.0	34.5; 30.7	24.8 23.6	5.2[b]	7.45	5.85	7.45	0.76(4)	1.6–2.2(24) 1.0(1)
m5	$CDCl_3$ (–50°C)	143.7 16.3	109.3	134.4	26.2; 25.0 23.5; 22.5	38.6; 35.2 33.0; 32.8 30.1; 30.0 29.4; 29.1	24.0 23.4 23.0 22.9	7.3[b,d](1) 3.2[b,d](1)	– 2.51	6.11 –	7.79 –	0.88(2) 0.82(1) 0.76(1)	1.3–2.3(25)
m5 + Q	C_7D_8	144.1 15.6	109.4	134.8	25.5; 24.4	36.2(br); 34.7 30.5 30.3	24.6 24.2(br) 23.5 23.4	7.4[b](1) 3.5[b](1)	– 2.17	6.67 –	7.48 –	1.0(2) 0.82(2)	1.3–2.5(24) 7.30(1)
7	$CDCl_3$	143.4 13.7	111.3	139.4	26.0 cyclooctyl (βC to εC) 26.0	34.2; 30.3 29.2; 27.0 26.7; 26.8	24.7 23.0	56.4[c](1) 5.9[b](1)	– 2.50	6.32 –	8.03 –	0.47(2)	1.3–2.5(27)
8[e]	$CDCl_3$	144.4 12.2	106.7	144.4 12.2	23.6	30.9	23.5	4.2[b]	– 2.20	5.73	– 2.20	1.48(4)	1.70(20) 1.32(4)

[a] $h_{1/2}$ <150 Hz. – [b] $h_{1/2}$ = 150–300 Hz. – [c] $h_{1/2}$ >300 Hz. – [d] Measured at room temperature. – [e] Cf. ref.[5].

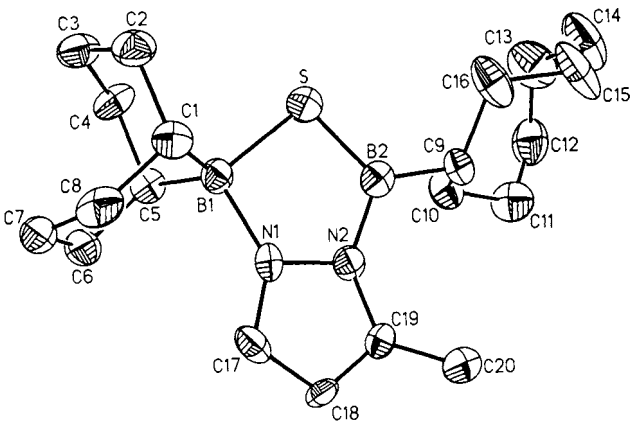


Figure 1. Molecular structure of **7**

of type **m5** (cf. Table 1). The molecular structure of **7**, determined by X-ray diffraction[4], is shown in Figure 1.

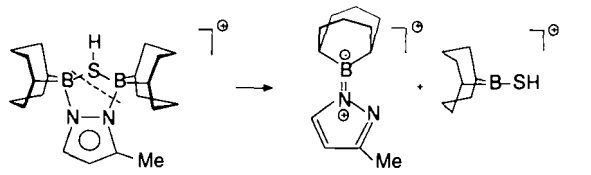
It can be seen that in the course of the reaction of **2** with **mPz** the 1,5-cyclooctanediylboryl ring adjacent to the methyl group of the **mPz** moiety has undergone a ring opening resulting in a cyclooctyl substituent on the central B_2SN_2 heterocycle. This ring is planar and no longer symmetrical (compare with structure of unsubstituted **5**[2]), the B1–S and B1–N1 bonds being significantly longer than the B2–S and B2–N2 bonds (cf. Table 2).

The intermediate **m5** is, however, stable at low temperatures. When equimolar quantities of **2** and **mPz** were dissolved in chloroform at –50°C, the ^{11}B- and ^{13}C-NMR spectra obtained at –50°C showed all the features to be expected for **m5**. Thus the ^{11}B-NMR spectrum exhibited two peaks of equal intensity at δ = 7.3 ($h_{1/2}$ = 240 Hz) and 3.2 ($h_{1/2}$ = 300 Hz) and the ^{13}C-NMR spectrum 16 lines for the carbon atoms of the two borabicyclic rings: Four broad doublets for the four α carbon atoms, eight triplet peaks for the β carbon atoms and four triplet peaks for the γ carbon atoms (cf. Table 1).

When a dichloromethane solution of **m5**, prepared at –50°C, was further cooled to –80°C, crystals of **m5** with melting range 120–127°C were obtained. These had a characteristic –SH band at 2525 cm^{-1} in its Raman spectrum [for **5** ν(SH) = 2530 cm^{-1}], and showed only a trace of the molecular ion at m/z = 356 in its mass spectrum. The principal fragment ion at m/z = 202 corresponds to loss of 9-mercapto-9-borabicyclo[3.3.1]nonane (M^+ = 154, B_1, cf. MS data in experimental section). This lability of **m5** under electron bombardement in the mass spectrum when compared to the MS data for **m4** [M^+ = 242 (B_2, base peak)[2]] shows another feature of the destabilizing effect of the methyl group in **m5**.

Table 2. Selected bond lengths and bond angles of **7**

Bond lenghts [Å]		Bond Angles [°]	
B1 – S	1.955(10)	B1 S B2	96.0(5)
B2 – S	1.736(10)	S B1 N1	99.6(5)
B1 – N1	1.617(12)	S B2 N2	113.0(6)
B2 – N2	1.510(13)	B1 N1 N2	118.6(6)
N1 – N2	1.394(9)	B2 N2 N1	112.3(7)

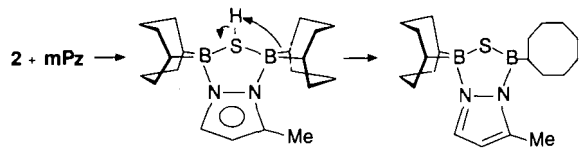


M⁺: m/z = 356 M⁺: m/z = 202 M⁺: m/z = 154

Surprisingly, the chloroform solution of **m5** proved to be rather stable, the compound converting at room temperature only slowly to **7**. After being heated for 24 h at 50°C complete transformation to **7** was achieved. We associate this relative stability of **m5** to the presence of traces of HCl in the solvent chloroform. **m5** proved to be also rather stable when traces of the strong base quinuclidine (**Q**) was admixed in a toluene solution of **2** and **mPz**. The room-temperature ^{11}B-NMR spectrum obtained from this solution showed the two peaks associated to **m5**, slightly shifted, at δ = 7.4 and 3.5, respectively. The ^{13}C-NMR spectrum revealed a new feature: The dissymmetry imparted by the position of the proton on the sulfur atom of **m5** being removed by fast exchange with the base **Q**. The ^{13}C-NMR spectrum reduces to ten peaks for the nonequivalent α, β, and γ carbon atoms: Two very broad doublets for the four α, four triplets (one broad) for the eight β, and four triplets (one broad) for the four γ carbon atoms. In an analogous experiment a trace of **Q** was admixed with **5**. The eight-line spectrum associated to the β and γ carbon atoms reduced to four peaks, two for the carbon atoms facing and two for those on the far side of the **Pz** moiety (cf. Table 1).

While toluene solutions of **5** with or without added **Q** proved to be stable when heated to 100°C for several hours, in toluene solutions of **m5** and **Q** when heated to 100°C **m5** readily (1 – 2 h) converted to **7** (^{1}H, ^{11}B, ^{13}C NMR).

Obviously the formation of **7** must have been preceeded by the intermediate **m5** which is destabilized by the close proximity of the relatively large methyl substituent on the pyrazole moiety. As shown below, the borabicyclic ring probably opens by way of a 1,3-migration of the proton from the sulfur atom to one of the α-C atoms of the C_8H_{14} residues.



m5 **7**

For the relative ease of rearrangement of **m5** to **7**, contrasting the stability of all its oxygen analogues investigated (see below), a degree of ring-strain release in the sulfur heterocycle **m5** is probably also involved [compare changes in the angles in the B_2SN_2 heterocycle in **7** (Table 2) and those for the corresponding unsubstituted **5**[2]].

We also attempted to prepare analogues of **7** by the reaction of more bulky pyrazoles such as $\mathbf{m_2Pz}$ with **2** and also by that of the selenide **3** with **Pz**. We were, however, unable to isolate and characterize a heterocycle of the type **7** or their precursors of type **m5**, although the ^{11}B-NMR spectra of the reaction products indicated their formation as part of a complex mixture. Also in the mass spectrum of the reaction product of the selenide **3** with **mPz** a molecular ion peak with the typical isotopic abundance pattern for a B_2Se ion at m/z = 404 (30%) with a fragment ion at m/z = 294 ($M^+ - C_8H_{15}$, 20%) strongly suggested the presence of the selenium analogue of **7**. However, the extreme moisture and air sensitivity of this compound has so far prevented its isolation and characterization. The reaction of two equivalents of $\mathbf{m_2Pz}$ with one of **2** gave a solid compound analyzing for the 2:1 adduct **8**[5]. The mass spectrum of **8** showed only molecular ions corresponding to those of the reactants, and in the ^{11}B-NMR spectrum one peak at δ = 4.2 was observed. This value suggests that both boron atoms have an equivalent tetravalent environment. The adduct **8** is possibly also one of the components in the 1:1 reaction product mixture described above. Its ready formation suggests that the presence of substituents on both of the α-positions of the N-base hinders, or prevents, the simultaneous approach and thus the bidental coordination of one pyrazole to the two boron atoms of **2**. This would lead to the preferred formation of an adduct in which each of the boron atoms of **2** becomes separately coordinated by one N-base molecule.

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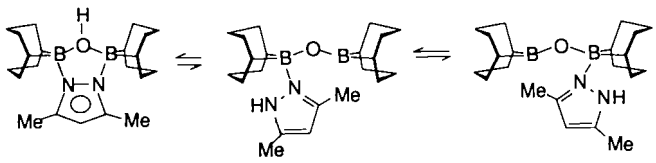
With the assumption that it is the steric interaction of the methyl group of **mPz** with the neighbouring 1,5-cyclooctanediylboryl ring which forces the rearrangement of **m5** to **7** we also heated a toluene solution of **m4**[2], the oxygen analogue of **m5**, for 8 h at 100°C without affecting any transformation. Similarly, when toluene solution of **1** was treated under reflux with 3,5-dimethylpyrazole ($\mathbf{m_2Pz}$) the NMR spectra showed no indication of rearrangement to a **7** analogue. Instead the spectra suggested the presence of a mixture of two components. Thus the ^{11}B-NMR spectrum showed two peaks in a 1:5 ratio at δ = 8.8 and 40.1. The ^{13}C-NMR spectrum contained a set of peaks consistent with that expected for the B_2ON_2 heterocycle $\mathbf{m_24}$ (minor component) (cf. Table 3) and another group of peaks conforming to the adduct structure $\mathbf{m_2Pz\text{-}1}$ in which one nitrogen atom of the $\mathbf{m_2Pz}$ fluctuates between the two boron atoms of **1**. Compounds $\mathbf{m_24}$ and $\mathbf{m_2Pz\text{-}1}$ are, as described below, in equilibrium. At –30°C their NMR spectra show a 1:1 ratio of the two components indicating a greater stability of the heterocycle $\mathbf{m_24}$ at lower temperatures. At room temperature the peaks in the ^{13}C-NMR spectrum for $\mathbf{m_2Pz\text{-}1}$ are sharp, however, the corresponding peaks at –30°C are all broad. This would suggest the beginning of coalescence at this temperature. Since at both temperatures only one signal was observed for both of the methyl substituents as well as for the C-3 and C-5 carbon atoms of the pyrazole group, it

has to be assumed that simultaneously with the fluctuation of the latter between the two boron atoms of **1** the two nitrogen atoms of $\mathbf{m_2Pz}$ moiety also exchange rapidly[6].

1 + m_2Pz ⟶



m_24 m_2Pz-1

The sterically more demanding 3-methyl-5-phenylpyrazole (**mpPz**) reacts with **1**, and at room temperature an ^{11}B-NMR signal at $\delta = 49.6$ indicating only very weak interactions of the two components appears. The 3,5-diphenyl- and di-*tert*-butylpyrazoles [$\mathbf{p_2Pz}$ and $\mathbf{(tb)_2Pz}$] have NMR spectra which show the presence of the individual components only (cf. Table 3).

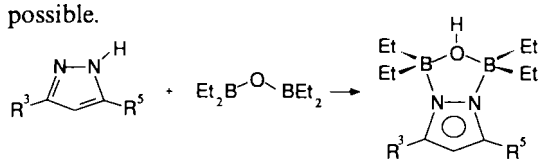
Finally, intrigued by this large steric sensitivity of various pyrazoles in their interactions with **1** and **2**, we also extended the reaction of these pyrazoles with the sterically less demanding and less rigid bis(diethylboryl) oxide (**9**). According to our previous report[2], **Pz** and **mPz** yielded smoothly the B_2ON_2 heterocycles **10** and **m10**. Reactions of the pyrazoles

Table 3. NMR data (δ in ppm) for the products derived from the bis(diorganoboryl) oxides **1**–**9**

Reactants	Product(s)	δ ^{13}C (50.4 MHz), $CDCl_3$						$\delta^{11}B$[a–d] (64.2 MHz)	δ ^1H (200 MHz), $CDCl_3$ (no of H atoms)					
		Pyrazole moiety			Organoboron moiety				Pyrazole moiety			Organoboron moiety		
		C^3 R^3	C^4	C^5 R^5	αC(br)	βC	γC	$CDCl_3$	H^3 R	H^4	H^5 R	αH(br)	(β,γ)H	H^x
m_2Pz, 1	**m_2Pz-1**	143.6 11.8	105.6	143.6	25.9	32.5	23.1	41.7[c]	– 2.29	5.79	– 2.29	1.03 (4)	1.7(20) 1.26(4)	10.8
	m_24	141.2 14.6	112.0	142.1 14.6	24.5	34.1 30.3	23.3 22.9	9.0[b]	– 2.39	5.85	– 2.39	0.68 (4)	≈1.70(20) 1.48(4)	3.60
m_2Pz, 1 (–30°C)	**m_2Pz-1**	143.4(br)	106.5(br)	143.6(br)	25.6	32.4(br)	23.4(br)	–	– 2.38	5.88	– 2.38	1.00 (4)	1.80(20) 1.27(4)	
	m_24	142.0 15.0	112.2	142.0 15.0	24.2	34.0 30.2	23.5 23.0	–	– 2.39	5.91	– 2.39	0.67 (4)	≈1.6;1.50 (20) (4)	3.48
mpPz, 1	**mpPz-1**	145.1 12.3	103.5 –	147.2 103.2 i 128.4 o 128.2 p 125.8 m	26.6	32.7(br)	23.0	49.6[c]	– 2.43	6.30 –	– 7.60(2) 7.27(3)	1.24 (4)	1.82(20) 1.39(4)	10.59
m_2Pz, 1	**m_2Pz + 1**	148.0 106.4 i 128.5 o 128.2 p 125.5 m	104.0	148.0 106.4 i 128.5 o 128.2 p 125.5 m	27.6	33.1	22.8	58.9[b]	– 7.65 7.27	6.76	– 7.65 7.27	1.06 (4)	1.79 (2)	1.33 (2)
$(tb)_2Pz$, 1	**$(tb)_2Pz$+1**	157.1 31.1(1C) 30.2(3C)	96.9	157.1 31.1(1C) 30.2(3C)	28.0	33.1	22.9	58.9[b]	– 1.36	5.89 –	– 1.36	1.15 (4)	1.82;1.39 (20) (4)	11.43
m_2Pz, 9	**m_210**	139.4 10.6	107.9	139.4 10.6	13.3	8.5	–	9.4[b]	– 2.23	5.92 –	– 2.23	0.61 (8)	0.83 (12)	3.14
mpPz, 9	**mp_{10}**	139.9 11.1	108.8	144.9 130.9 i 13.3 128.9 o 128.4 p 127.7 m	14.3	8.7	–	9.7[c]	– 2.28	6.14 –	– 7.42	≈0.8(4) 0.5(4)	0.92(6) 0.78(6)	3.6 (br)
p_2Pz, 9	**p_210**	145.5 130.6 i 128.9 o 128.5 p 127.7 m	109.3	145.4 130.6 i 128.9 o 128.5 p 127.7 m	14.2	8.6	–	9.9[c]	– 7.4	6.39 –	– 7.4	0.52 (8)	0.70 (12)	3.54
$(tb)_2Pz$, 9	**$(tb)_2Pz$+9**	157.1 31.1(1C) 30.2(3C)	96.9	157.1 31.1(1C) 30.2(3C)	14.0	7.1	–	53.2[a]	– 1.35	5.90 –	– 1.35	0.9 (8)	0.9 (12)	10.6

[a] $h_{1/2}$ <150 Hz. – [b] $h_{1/2}$ = 150–300 Hz. – [c] $h_{1/2}$ >300 Hz.

m_2Pz, mpPz, and **p_2Pz** with **9** readily gave the adducts **$m_2$10, mp10,** and **$p_2$10.** At room temperature the NMR spectra of the very bulky **$(tb)_2$Pz** and **9** showed only the presence of the two compounds (cf. Table 3). It could have been expected that through the interaction between **$(tb)_2$Pz** and **9** the formation of at least a simple adduct of the type **mPz-1** would be possible.



9

$m_2$10: $R^3 = R^5 = Me$
mp10: $R^3 = Me$; $R^5 = Ph$
$p_2$10: $R^3 = R^5 = Ph$

It is thus evident that the presence of very large substituents at the 3,5-positions of pyrazoles will also prevent any interaction with the sterically less demanding diboryl oxide **9** the ethyl groups of which, in contrast to the large and rigid carbon skeleton of **1** and **2**, are smaller and conformationally more flexible.

Experimental

Instruments: Büchi melting point apparatus, sealed capillary tubes, uncorrected m.p. – Infrared spectra: 7199 FT-IR system. – Raman spectra: CODERG LRT 800. – Mass spectra: MAT CH 5. – ^1H, ^{11}B, ^{13}C NMR: Bruker AC 200 with $(CH_3)_4Si$ as internal and diethyl ether–BF_3 as external standards. – Sources for the boron reagents used are as cited in refs.[1,2]. The pyrazoles **mpPz, p_2Pz,** and **$(tb)_2$Pz,** unavailable commerically, were prepared by the reaction of the corresponding 1,3-diketone with hydrazine hydrate solution[7].

2,2 : 4,4-Bis(1,5-cyclooctanediyl)-6-methyl-3-thionia-1-aza-5-azonia-2,4-diboratabicyclo[3.3.0]octa-6,8-diene (**m5**): In a 5-mm NMR tube at −50°C to a solution of 0.10 g (0.36 mmol) of **2** in 0.5 ml of $CDCl_3$ was added 0.03 g (0.36 mmol) of 3-methylpyrazole (**mPz**). After sealing and mixing, NMR spectra were obtained at −50°C and at room temperature (results in Table 1). The above reaction carried out in a larger scale (1.0 g of **2**) in CH_2Cl_2 on further slow cooling to −80°C gave colourless crystals of **m5**, 0.8 g (61%), melting range 120–127°C (**m5** could not be further purified since in solution it slowly transforms into **7**). – Raman: ν(SH) = 2525 cm^{-1}. – MS: *m/z* (%) = 356 (M^+, trace), 202 (60); 201 (95); 174 (75); 173 (76); 159 (85); 154 (B_1, 58); 145 (85); 95 (100). – NMR data see Table 1.

NMR Experiment with **m5** *in the Presence of a Trace of* **Q**: An equimolar solution of **2** and **mPz** in 0.5 ml of [D_8]toluene was prepared in a 5-ml NMR tube at −50°C, small crystals of **Q** added and the tube sealed. The solution, after brief mixing, was warmed to room temperature. For data of NMR spectra obtained see Table 1.

4,4-(1,5-Cyclooctanediyl)-2-cyclooctyl-8-methyl-3-thia-1-aza-5-azonia-2-bora-4-boratabicyclo[3.3.0]-octa-5,7-diene (**7**): To a stirred solution of 2.33 g (8.50 mmol) of **2** in 10 ml of toluene was added dropwise a solution of 0.70 g (8.53 mmol) of **mPz** in 15 ml of toluene. The colourless solution was slowly cooled to −60°C. The resulting colourless crystals were collected by filtration, 2.58 g (85%) of **7**, m.p. 126°C. – MS: *m/z* (%) = 356 (M^+, B_2, 95); 246 (45); 245 (40); 189 (55); 163 (60); 162 (60); 137 (100). – NMR data see Table 1.

$C_{20}H_{34}B_2N_2S$ (356.2) Calcd. C 67.74 H 9.62 B 7.86
Found C 67.51 H 9.53 B 7.59

X-Ray Single-Crystal Structure Determination of **7**: Data collection was carried out on a Syntex R 3 m V four-circle diffractometer, and calculations were performed with Microvax II using SHEXTL-PLUS software[8]. The structure solution was carried out by direct methods, and in the refinement all hydrogen atoms were included as rigid groups (C–H bond lengths at 0.96 Å, C–C–H and H–C–H angles at 109.5 and 120°, respectively). The isotropic displacement parameters (IDPs) of all the H atoms were refined without constraints.

Structural data: crystal size 0.13 × 0.12 × 0.10 mm, monoclinic, $P2_1/c$, $Z = 4$, $a = 12.493(3)$, $b = 12.049(4)$, $c = 13.926(4)$ Å, $V = 2046.1(9)$ Å^3, $\beta = 102.55(2)°$, $T = 293$ K, $d_{calcd.} = 1.148$ g/cm^3, $\mu = 0.15$ mm^{-1}, radiation Mo-K_α, $2\Theta_{max} = 40°$, total number of reflections = 1908, observed reflections = 1255 [$F_o \geq 4\sigma(F)$], $R = 0.077$, $R_w = 0.080$ [$w^{-1} = \sigma(F_o) + gF_o^2$] with $g = 1.18 \times 10^{-3}$, number of parameters refined = 227, residual electron density = 0.41 e/Å^3. The atom coordinates are listed in Table 4[9].

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors (Å × 10^3) for **7**

	x	y	z	U_{eq}
S	9307(2)	2309(2)	4770(2)	70(1)*
B(1)	10682(7)	3032(8)	4668(8)	46(4)*
B(2)	8538(8)	2829(7)	3688(8)	45(4)*
N(1)	10258(5)	3746(6)	3689(5)	43(3)*
N(2)	9190(5)	3580(5)	3163(6)	45(3)*
C(1)	11178(6)	3764(7)	5612(6)	49(4)*
C(2)	11409(7)	2976(7)	6516(6)	62(4)*
C(3)	12117(7)	1970(7)	6415(7)	61(4)*
C(4)	11813(7)	1375(7)	5430(6)	58(4)*
C(5)	11597(6)	2152(6)	4529(6)	45(3)*
C(6)	12622(6)	2744(8)	4374(7)	59(4)*
C(7)	13080(6)	3634(8)	5144(7)	59(4)*
C(8)	12222(7)	4374(7)	5474(6)	60(4)*
C(9)	7309(6)	2503(7)	3230(6)	48(4)*
C(10)	7334(7)	1533(8)	2503(7)	64(4)*
C(11)	6270(8)	1244(9)	1777(7)	76(5)*
C(12)	5648(8)	264(10)	2016(9)	92(5)*
C(13)	5492(10)	192(10)	3074(10)	109(7)*
C(14)	4917(9)	1039(11)	3469(11)	120(7)*
C(15)	5399(8)	2184(9)	3656(11)	113(7)*
C(16)	6659(7)	2282(8)	4031(8)	80(5)*
C(17)	10697(7)	4458(7)	3145(8)	53(4)*
C(18)	9948(8)	4753(7)	2325(7)	47(4)*
C(19)	9008(7)	4213(7)	2350(7)	42(4)*
C(20)	7946(7)	4251(7)	1586(7)	65(4)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Bis(3,5-dimethylpyrazole) Adduct of Bis(1,5-cyclooctanediylboryl) Sulfide (**8**): To a 10-ml toluene solution of 1.43 g (5.22 mmol) of **2** was added dropwise a solution of 1.01 g (10.51 mmol) of **m_2Pz** in 20 ml of toluene. The resulting colourless solution after concentration to about 15 ml gave colourless crystalline **8**, 0.9 g, m.p. 143–144°C. The filtrate on further concentration to about 5 ml gave a further crop of 0.7 g of crystalline **8** (total yield: 66%). – IR (nujol): ν(NH) = 3200 cm^{-1}. – NMR data see Table 1.

$C_{26}H_{44}B_2N_4S$ (466.3) Calcd. C 66.97 H 9.51 B 4.64
Found C 66.92 H 9.59 B 4.39

Pyrazole Adducts of **1** *and* **9**: The pyrazole adducts of **1** and **9** as listed in Table 3 were generally prepared by mixing equimolar quantities of the reactants in the appropriate solvents directly in the NMR tube without isolating the products. In two cases larger scale preparations were carried out. These are described below:

a) *2,2,4,4-Tetraethyl-6,8-dimethyl-3-oxonia-1-aza-5-azonia-2,4-diboratabicyclo[3.3.0]octa-5,7-diene* (**$m_2$10**): To a solution of 2.5 g (26.0 mmol) of **m_2Pz** in 5 ml of hexane was added a solution of 4.0 g (26.0 mmol) of **9** in 5 ml of hexane. The solution was stirred and briefly heated to reflux and slowly cooled to −60°C. Then the colourless crystals of **$m_2$10**, 5.6 g (86%), were collected; m.p. 36−37°C. − IR (nujol): ν(OH) = 3650 cm^{-1}. − MS: *m/z* (%) = 221 (M − 29, B_2, 75); 191 (100); 135 (80); 109 (70); 57 (100).

$C_{13}H_{28}B_2N_2O$ (250.0) Calcd. C 62.25 H 11.29 B 8.65
Found C 62.13 H 11.38 B 8.81

b) *2,2,4,4-Tetraethyl-6-methyl-8-phenyl-3-oxonia-1-aza-5-azonia-2,4-diboratabicyclo[3.3.0]octa-5,7-diene* (**mp10**): To a solution of 2.0 g (12.7 mmol) of **mpPz** in 5 ml of toluene was added a solution of 1.96 g (12.7 mmol) of **9** in 5 ml of toluene. The mixture was stirred and heated to about 80°C for 10 min and cooled slowly to −78°C. Colourless crystals of **mp10**, 2.1 g, were collected by filtration. From the filtrate upon concentration and cooling a further crop of 1.6 g of crystalline **mp10** was obtained (total yield 92%). m.p. 48 to 49°C. − IR (nujol): ν(OH) = 3600 cm^{-1}. − MS: *m/z* (%) = 283 (M^+ − 29, B_2, 5); 253 (10); 197 (20); 158 (35); 125 (55); 69 (75); 41 (100). − NMR data see Table 3.

$C_{18}H_{30}B_2N_2O$ (312.1) Calcd. C 69.28 H 9.69 B 6.93
Found C 69.58 H 9.66 B 6.82

CAS Registry Numbers

1: 74744-62-0 / **mpPz1**: 120610-78-8 / **m_2Pz1**: 120610-76-6 / **2**: 116928-43-9 / **$m_2$4**: 120610-77-7 / **5**: 116928-38-2 / **m5**: 120610-73-3 / **7**: 120610-74-4 / **8**: 120610-75-5 / **9**: 7318-84-5 / **$m_2$10**: 120610-79-9 / **mp10**: 120610-80-2 / **$p_2$10**: 120610-81-3 / **Q**: 100-76-5 / **mPz**: 1453-58-3 / **m_2Pz**: 67-51-6 / **mpPz**: 3347-62-4 / **p_2Pz**: 1145-01-3 / **$(tb)_2$Pz**: 1132-14-5

[1] M. Yalpani, J. Serwatowski, R. Köster, *Chem. Ber.* **122** (1989) 3.
[2] M. Yalpani, R. Köster, R. Boese, *Chem. Ber.* **122** (1989) 19.
[3] B. Wrackmeyer, R. Köster in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), 4th ed., vol. XIII/3c (R. Köster, Ed.), p. 496, Thieme, Stuttgart 1984.
[4] Due to disorder of the segment, comprising the atoms C12−C15 of the cyclooctyl substituent, the refinement of the structure calculation reached a limiting *R* value of only 0.077.
[5] A Similar dicoordination of pyridine bases with **2** has been described earlier, cf. R. Köster, G. Seidel, *Z. Naturforsch., Teil B*, **43** (1988) 687.
[6] In *N*-(trimethylsilyl)pyrazole a similar exchange of the trimethylsilyl substituent between the two nitrogen atoms of **Pz** has been described, cf. D. H. Obrien, C. P. Hrung, *J. Organomet. Chem.* **27** (1971) 185.
[7] R. v. Rothenburg, *Ber. Dtsch. Chem. Ges.* **27** (1894) 1097.
[8] G. M. Sheldrick, SHELXTL-PLUS (Version 2, 1987), an *Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, University of Göttingen.
[9] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53902, the names of the authors, and the journal citation.

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