Novel Substituted $B_2El^{VI}N_2$ Heterocycles

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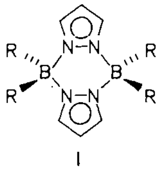
The bis(diorganoboryl) chalcogenides $(R_2B)_2O$ [R = C_2H_5 (**3**); R_2 = 1,5-C_8H_{14} (**1**)], $(R_2B)_2S$ [R_2 = 1,5-C_8H_{14} (**5**)], and $(R_2B)_2Se$ [R_2 = 1,5-C_8H_{14} (**7**)] react with pyrazole (**Pz**) and its derivatives 3-methylpyrazole (**3-MePz**) and indazole (**benzo-Pz**) to form in high yields (65−92%) stable 1:1 adducts [e.g. **2** (El = O), **4** (El = O), **6** (El = S) and **8** (El = Se)]. ^1H-, ^{13}C-, ^{11}B-NMR spectra and X-ray analyses (of **2** and **6**) show a basic structure with a central B_2ElN_2 (El = O, S, Se) heterocycle. The reaction of **2** with R_2BH and the thermolysis of **4** give the dimeric 1-pyrazolylboranes **9a** and **9b**, respectively.

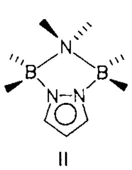
Neuartige substituierte $B_2El^{VI}N_2$-Heterocyclen

Die Bis(diorganoboryl)chalkogenide $(R_2B)_2O$ [R = C_2H_5 (**3**); R_2 = 1,5-C_8H_{14} (**1**)], $(R_2B)_2S$ [R_2 = 1,5-C_8H_{14} (**5**)], und $(R_2B)_2Se$ [R_2 = 1,5-C_8H_{14} (**7**)] reagieren mit Pyrazol (**Pz**) und dessen Derivaten 3-Methylpyrazol (**3-MePz**) und Indazol (**benzo-Pz**) in hohen Ausbeuten (65−92%) zu stabilen 1:1-Additionsverbindungen [z.B. **2** (El = O), **4** (El = O), **6** (El = S), **8** (El = Se)]. ^1H-, ^{13}C-, ^{11}B-NMR-Spektren und Röntgenstrukturanalysen (von **2** und **6**) zeigen eine Grundstruktur mit einem zentralen B_2ElN_2-Heterocyclus (El = O, S, Se). Die Reaktion von **2** mit R_2BH und die Thermolyse von **4** führen zu den dimeren 1-Pyrazolylboranen **9a** bzw. **9b**.

By analogy to the ready bidentate coordination of pyrazole (**Pz**) with various boron compounds leading to the formation of the unusually stable dimers of 1-pyrazolylboranes of the type **I**, it was tempting to expect and propose a similar type of coordination in the products of the reactions of **Pz** with triorganoboroxins[1]. However, we showed that at least in solutions the two components of these adducts fluctuate, and when cooled to as low as −80°C clearly only one of the nitrogen atoms of the pyrazole ring is involved in the continued fluctuation process[2]. This was in agreement with our previous findings that in triorganoboroxins[3] and in tetraorganodiboroxanes [bis(diorganoboryl) oxides][4] only one of the boron atoms serves as an acceptor for the nitrogen base, irrespective of the type and amount of the latter. Surprisingly, we have now found that the isolable 1:1 adducts of bis(diorganoboryl) oxides and **Pz** are an exception to this rule. Herein we describe the formation and structures of these novel compounds and of the related sulfur and selenium analogues.



I



II

Results and Discussions

The reaction of bis(diorganoboryl) oxides (tetraorganodiboroxanes) with **Pz** has previously been reported to yield derivatives of **I**[1]. In this reaction an excess of the nitrogen heterocycle, elevated temperatures, and prolonged reaction times were employed. We envisaged that in the multistep reaction leading to **I** initially a 1:1 adduct of the diboroxane and **Pz** is involved. We therefore stirred a dichloromethane solution of an equimolar mixture of bis(1,5-cyclooctanediylboryl) oxide (**1**) and **Pz** for a few minutes at room temperature followed by a gradual cooling to −60°C. A nearly quantitative yield of the colourless crystals of **2** was obtained. **2**, m.p. 184−185°C, showed a molecular ion at m/z = 326 (70%) in its mass spectrum, corresponding to the molecular formula $C_{19}H_{32}B_2N_2O$. The infrared spectrum of this 1:1 adduct revealed a sharp OH band at 3580 cm^{-1}. A single narrow ^{11}B-NMR signal at δ = 8.1 was indicative for the equal tetracoordination of the two boron atoms. The ^1H-NMR spectrum showed two signals for the three protons of the pyrazole moiety at δ = 7.75 (d) and 6.34 (t) in a 1:1 molar ratio to the group of signals centred at $\delta \approx 1.7$ (m) for the protons at the β and γ positions and δ = 0.54 (br) for the protons on the α carbon atoms of the two 1,5-cyclooctanediyl groups. The broad singlet at δ = 3.5 is assignable to an acidic proton. The ^{13}C-NMR spectrum had two signals at δ = 132.4 and 107.8 (doublets) for the carbon atoms of the pyrazole moiety, one single broad peak at $\delta \approx 25.0$ (doublet) for the α carbon atoms, but two sets of signals at δ = 32.8 and 31.9 (triplets) for the β carbon atoms and two further signals at δ = 25.6 and 24.4 (triplets) for the γ carbon atoms of the **2** moiety (cf. Table 1).

These spectral results are suggestive of a simultaneous bonding of the two nitrogen atoms of the pyrazole ring to the two boron atoms of **1** making them tetracoordinated. This renders the two lower and upper wings of the bicyclic

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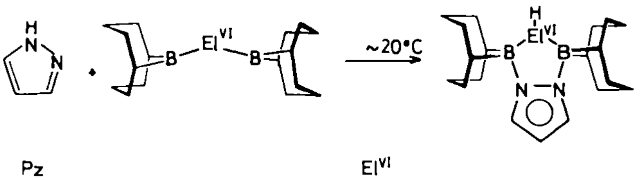
Table 1. ^{13}C-NMR data for the 1,5-C_8H_{14} moieties of **2**, **6**, **8**, **Me-2**, and **benzo-2**

	Solvent	Temp. [°C]	δ^{13}C (ppm) [H, C Multiplicity] (No. of C Atoms) α C [br, d]	β C [t]	γ C [t]
2	$CDCl_3$	30	25.0 (4)	32.8 (4) 31.9 (4)	25.6 (2) 24.4 (2)
2	CD_2Cl_2	−80	24.6 (4)	32.9 (4) 31.8 (4)	25.8 (2) 25.4 (2)
6	C_7D_8	30	24.6 (2) 24.0 (2)	35.6 (2) 33.5 (2) 31.1 (2) 30.3 (2)	24.8 (2) 23.6 (2)
6	C_7D_8	100	25.0 (4)	35.6 (2) br 34.0 (4) br 30.8 (2) br	24.6 (2) 23.5 (2)
8	C_7D_8	30	27.5 (2) 24.8 (2)	37.1 (2) 34.3 (2) 31.4 (2) 30.4 (2)	24.7 (2) 23.5 (2)
Me−2	$CDCl_3$	30	23.8 (4)	33.8 (2) 32.1 (2) 30.3 (2) 30.2 (2)	23.8 (2) 23.3 (4) 23.1 (2)
benzo−2	C_7D_8	30	24.8 (2) 23.6 (2)	33.6 (2) 32.0 (2) 30.6 (2) 30.2 (2)	23.7 (1) 23.6 (1) 23.3 (1) 23.2 (1)

ring chemically unequal, resulting in a structure as in **2** which has similar structural elements as the previously reported **II**[5] with nitrogen as the third hetero atom.

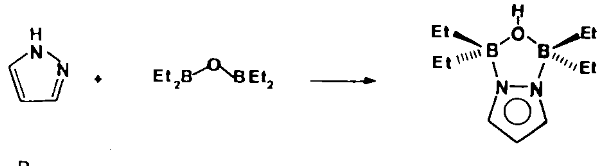


Pz

	El^{VI}	
1	O	2
5	S	6
7	Se	8

Other derivatives of **2** are also formed easily. Thus, bis(diethylboryl) oxide (**3**) reacts with pyrazole at room temperature. In this case, however, the 1:1 adduct **4** formed is a slightly viscous liquid which does not solidify even on cooling to −196°C. The spectroscopic properties of **4** are very similar to those of **2**, e.g., it has a sharp OH band at 3600 cm^{-1} in its infrared spectrum, a single ^{11}B-NMR signal at $\delta = 9.85$, and in its ^{1}H- and ^{13}C-NMR spectra it shows the equivalence of the α-protons and -carbons of the pyrazole moiety as well as a single set of signals for the protons and carbon atoms (cf. Table 1) of the ethyl groups on the diboroxane side of the adduct. The mass spectrum showed an intense fragment ion (M^+ − Et) at m/z = 193 (100%) corresponding to a molecular formula of $C_{11}H_{24}B_2N_2O$.

A 1:1 adduct with a structure analogous to **2** or **4** was also obtained when pyrazole was treated with bis(1,5-cyclooctanediylboryl) sulfide **5**[6]. The crystalline **6** formed decomposed on melting at 174−175°C, showed a sharp SH band at 2530 cm^{-1} in its Raman spectrum, and had a molecular ion at m/z = 342 in its mass spectrum corresponding to a molecular formula of $C_{19}H_{32}B_2N_2S$. Its ^{11}B-NMR spectrum showed a single peak at $\delta = 5.4$ which indicates tetracoordinated boron atoms as found in **2** and **4**. Also the ^{1}H-NMR spectrum was very similar to that of **2** with the exception that two signals at $\delta = 0.93$ and 0.78 were observed for the protons on the α carbon atoms of the bicyclic rings.



Pz 3 4

The ^{13}C-NMR spectrum of **6** had some features which are dissimilar to that of **2** (cf. Table 1). Thus, the room temperature spectrum displayed six signals for the methylene carbons and two very broad peaks for the boron-bound carbon atoms of the bicyclic rings of the **5** moiety. Therefore, unlike in the spectrum of **2**, where besides the single broad signal for the α carbon atoms two chemically distinct sets of β and γ carbon atoms were discernible (the carbon atoms facing the pyrazole ring and those on the far side of it), in **6** each of the eight carbon atoms of the $C_8H_{14}B$ bicyclic rings are chemically distinct. Assuming basic similarities in the structures of **2** and **6**, the observed differences in their ^{13}C-NMR spectra can be assumed to arise either from the conformational changes in the $N_2El^{VI}B_2$ five-membered ring heterocycle from El = O to El = S, or as observed in the case of the 9-(alkylthio)-9-borabicyclo[3.3.1]nonane dimer[7] to result from the changed configuration of the El−H bond in **6**.

To confirm these structural assignments and to determine the position of the acidic protons in **2** and **6**, the low temperature solid-state structure was determined by X-ray diffraction. Figure 1 shows the molecular geometry of **2**, obtained at −163°C. The two boron atoms of the **1** moiety are tetracoordinated by bonding to the two nitrogen atoms of the pyrazole ring which forms a nearly perpendicular interplanar angle of 86.6° with the planes defined by the two sets of atoms C1B1C5 and C9B2C13. The oxygen atom of the central B1N1N2B2O rings is bent out of the plane of the ring by 173°. As a result, the two bicyclic C_8 rings on either side of the molecule are slightly bent upwards, as seen by the shorter nonbonding intramolecular distance of the two α carbon atoms C1 and C13 (4.01 Å) above the central plane as compared to the corresponding distance of the two carbon atoms C5 and C9 (4.76 Å) below the plane. The two bicyclic C_8 rings are also twisted away from the pyrazole ring. The position of the oxygen-bound hydrogen atom could not be determined exactly due to the high isotropic thermal parameter observed for this atom despite the low temperatures employed in the measurement. Selected bond lengths and angles of the atoms around the central heterocycle are shown in Table 2a.

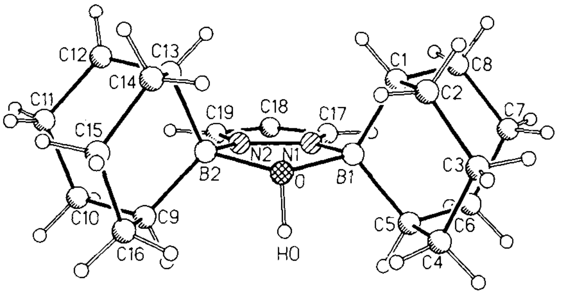


Figure 1. Molecular structure of **2**

Table 2. Selected bond lengths and angles: (a) for **2** and (b) for **6**

(a) **2**		(b) **6**	
O – B1	1.566(2) Å	S – B1	1.986(2) Å
O – B2	1.563(2) Å	S – B2	1.988(2) Å
B1 – N1	1.579(2) Å	B1 – N1	1.575(3) Å
B2 – N2	1.583(3) Å	B2 – N2	1.585(3) Å
N1 – N2	1.353(2) Å	N1 – N2	1.364(3) Å
B1 – O – B2	116.3(1)°	B1 – S – B2	95.3(1)°
O – B1 – N1	96.5(1)°	S – B1 – N1	98.4(1)°
O – B2 – N2	96.0(1)°	S – B2 – N2	98.3(1)°
B1 – N1 – N2	114.2(1)°	B1 – N1 – N2	119.7(2)°
B2 – N2 – N1	114.5(1)°	B2 – N2 – N1	120.0(2)°

Figure 2 displays the molecular geometry of **6** at −163°C. The most important difference in the two structures appears to be the larger interplanar angle of 28.4° between the planes defined by the atoms B1SB2 and B1N1N2B2. This increased bending, caused by the smaller B1SB2 bond angle of 95.3° as compared to the B1OB2 bond angle of 116.3° for **2**, also forces the borabicyclic rings to further bend upwards, resulting in a shortening of the nonbonding intramolecular distance of the α carbon atoms C1 and C13 to 3.89 Å and the concomitant widening of the distance between the corresponding atoms C5 and C9 below the central molecular plane to 5.47 Å. The sulfur-bound hydrogen atom which in this case could be accurately located is, together with the sulfur atom, bent below the central molecular plane and forms an angle of 98.4° (av.) to the boron atoms B1 and B2.

The side-on projections as depicted in Figures 3a and 3b also exhibit the electron difference maps (H0 omitted) through the noncrystallographic mirror planes of the molecules **2** and **6**. It can be seen that while in **6** there is a concentration of electron density on one side of this plane, in **2** the electron density is about equally distributed on both sides of the plane. This may indicate a disorder or fluctuation of the proton in the crystal and would also explain the differences observed in their respective NMR spectra. In **6** the longer B–S bonds and the larger bending of the B1SB2 plane compared to the BO bond lengths and the tilting of the B1OB2 plane of **2**, places the larger sulfur atom in close proximity of the two carbon atoms C4 and C16. In addition to this the position of the hydrogen atom with the resulting uneven electron density distribution about the sulfur atom also contributes to an increase of the induced chemical dissymmetry in the atoms of the borabicyclic rings.

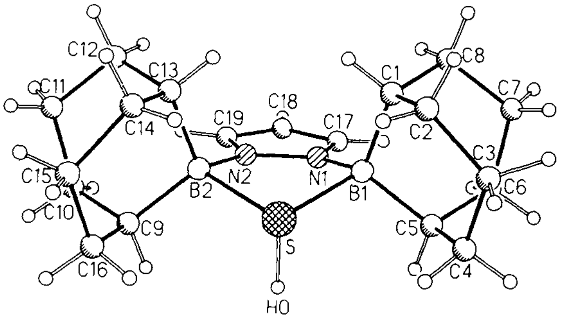


Figure 2. Molecular structure of **6**

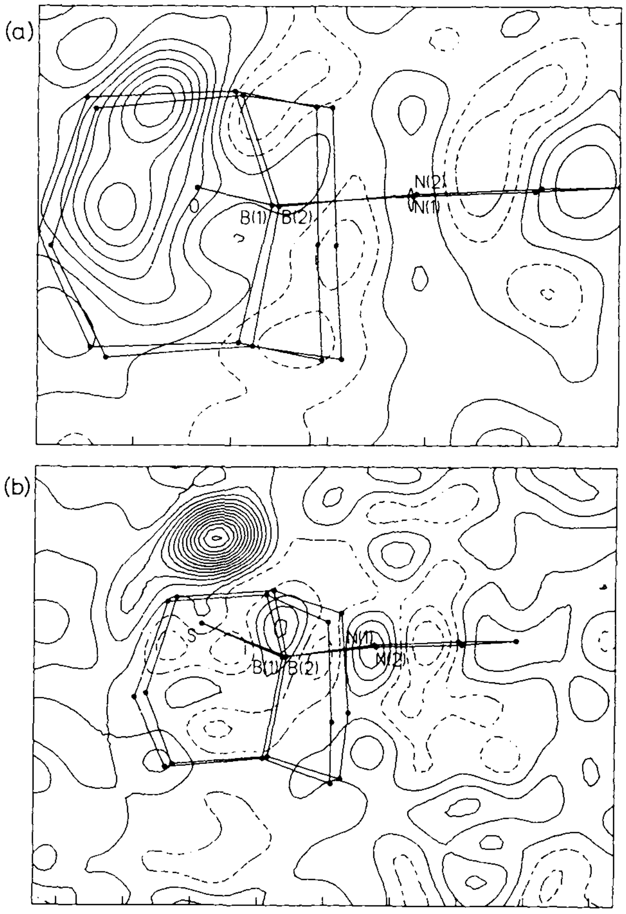


Figure 3. Electron difference maps through O (S) and perpendicular to the plane of the atoms N1N2C17C18C19: (a) for **2** and (b) for **6** (H0 omitted)

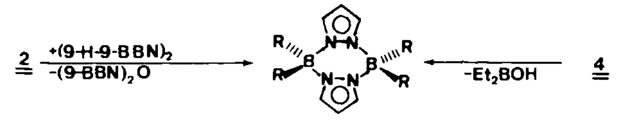
It can be imagined that in solutions the position of the sulfur atom together with its attached hydrogen atom is not fixed as in the solid state and a rapid ring interconversion removes the observed sideways dissymmetry. In effect, this motion is restricted to room temperature. However, in the ^{13}C-NMR spectrum of **6** at +100°C, while the signals for the γ carbon atoms at δ = 24.78 and 23.16 continued to remain sharp, a coalesence of the sets of signals at δ = 35.59 and 33.44 and at δ = 31.09 and 30.26, assignable to the β carbon atoms and at δ = 23.13 and 24.77 for the α carbon atoms of the borabicyclic rings, was observed. Conversely, in the ^{13}C-NMR spectrum of **2**, obtained at −80°C, the signals remained unchanged compared to the room temperature spectrum. This shows that while for **2** the energy barrier for ring inversion is very low, for **6** an extremely high activation energy for the interconversion of the B1N1N2B2S ring is implied.

Spectral properties similar to that of **6** were also observed for the selenium derivative **8** obtained from bis(1,5-cyclooctandediylboryl) selenide (**7**)[8] and pyrazole in which the B−Se bond lengths and B1SeB2 bond angle can be expected to have comparable overall values.

The formation of adducts of the type **2**, **4**, **6**, and **8** is not restricted to pyrazole itself.

They can also be prepared from pyrazole derivatives such as 3-methylpyrazole (**MePz**) and indazole (**benzo-Pz**). The preparation of some of these (e.g. **Me-2** and **benzo-2**) together with their spectral properties are described in the experimental part and in Table 1.

The new substituted $B_2El^{IV}N_2$ heterocycles (s. Table 1) are stable when exposed to air for several days. **2**, **6**, and **8** react with excess of hydroborane reagents at elevated temperatures (60−90°C) to liberate one equivalent of hydrogen, and the solid product formed was found to be the so-called[9] pyrazabole **9a**. Some of the adducts are thermally unstable. Thus, **4** decomposes during vacuum distillation at a bath temperature of about 80°C to the pyrazabole **9b** and diethylhydroxyborane.



9a: R,R = 1,5-C_8H_{14}
9b: R = C_2H_5

Triazole and tetrazole, however, react with bis(diorganoboryl) oxides and their sulfur or selenium analogues to form insoluble polymeric materials.

Experimental

Instruments: Büchi melting point apparatus, sealed capillary tubes, uncorrected. − DSC analyses: DuPont 1090. − Infrared spectra: Nicolet 7199 FT-IR system. − Raman spectra: CODERG LRT 800. − Mass spectra: MAT CH 5. − ^{1}H-, ^{11}B-, and ^{13}C-NMR spectra: Bruker AC 200, with $(CH_3)_4Si$ as internal standard and $(C_2H_5)_2O-BF_3$ as external standards.

2,2:4,4-Bis(1,5-cyclooctandiyl)-3-oxonia-1-azonia-5-aza-2,4-diboratabicyclo[3.3.0]octa-6,8-diene (**2**): A solution of 0.25 g (3.68 mmol) of pyrazole (**Pz**) and 0.95 g (3.68 mmol) of **1** in 10 ml of CH_2Cl_2 was stirred for 10 min and cooled to −80°C. The colourless prisms were separated, 1.1 g (92%), m.p. 184−185°C. − IR (KBr): 3580 cm^{-1}. − ^{1}H-NMR ($CDCl_3$): δ = 7.75 (d, *J* = 2.3 Hz, 2H); 7.15 (br, s, 1H); 6.34 (d, *J* = 2.3 Hz, 1H); 1.7 (m, 24H); 0.54 (br, 4H). − ^{13}C-NMR ($CDCl_3$, room temp.): signals for the pyrazole moiety: δ = 132.4 (d, 2C); 107.8 (d, 1C); signals for **1** moiety: cf. Table 1. − ^{11}B-NMR ($CDCl_3$): δ = 8.11 ($h_{1/2}$ = 314 Hz). − MS (70 eV): *m/z* (%) = 326 (M$^+$, B_2, 70), 215 (B_2, 100), 107 (30).

$C_{19}H_{32}B_2N_2O$ (326.1) Calcd. C 69.98 H 9.89 B 6.63
Found C 70.03 H 9.78 B 6.81

2,2,4,4-Tetraethyl-3-oxonia-1-azonia-5-aza-2,4-diboratabicyclo[3.3.0]octa-6,8-diene (**4**): A solution of 1.3 g (19.1 mmol) of **Pz** and 2.9 g (19.1 mmol) of **3**[10b] in 5 ml of CH_2Cl_2 was stirred for 10 min and the solvent evaporated in vacuo. The residue of 4.2 g was a slightly viscous colourless liquid. − IR (film): 3600 cm^{-1}. − ^{1}H-NMR (CD_2Cl_2): δ = 7.70 (d, *J* = 2.2 Hz, 2H); 6.7 (d, *J* = 2.2 Hz, 1H); 3.5 (br, 1H), 0.95 (m, 20H). − ^{13}C-NMR (CD_2Cl_2): signals for the **Pz** moiety: δ = 129.4 (d, 2C); 108.6 (d, 1C); Signals for the **3** moiety: 14.7 (br, t, 4C); 9.1 (q, 4C). − ^{11}B-NMR (CD_2Cl_2): δ = 9.85 ($h_{1/2}$ = 180 Hz). − MS (70 eV): *m/z* (%) = 193 [(M$^+$ − 29), B_2, 100], 163 (B_2, 35), 107 (B_1, 80), 81 (75), 57 (80).

$C_{11}H_{24}B_2N_2O$ (221.9) Calcd. C 59.53 H 10.90 B 9.74
Found C 59.98 H 10.81 B 9.89

Vacuum Distillation of **4**: 3.2 g of **4** at 80°C/10^{-2} Torr gave a liquid fraction of 1.2 g (97%) identical to diethylhydroxyborane[11] and a colourless solid residue, recrystallized from C_2H_5OH, 1.8 g (92%), m.p. 105−106°C, IR identical to dimeric diethyl-1-pyrazolylborane **9b**[9].

2,2:4,4-Bis(1,5-cyclooctandiyl)-3-thionia-1-azonia-5-aza-2,4-diboratabicyclo[3.3.0]octa-6,8-diene (**6**): A solution of 0.53 g (7.78 mmol) of **Pz** and 2.14 g (7.81 mmol) of **5**[6] in 10 ml of CH_2Cl_2 was stirred for 15 min. A small amount of colourless crystalline solid was slowly formed. The mixture was cooled to −80°C, the colourless prisms were separated, 1.87 g (70%), m.p. 174−175°C. − Raman: 2530 cm^{-1}. − ^{1}H-NMR ([D_8]toluene): δ = 7.45 (d, *J* = 2.3 Hz, 2H); 5.84 (t, *J* = 2.3 Hz, 1H), 1.9 (m, 24H); 1.0 (s, 1H); 0.93 (br, 2H), 0.78 (br, 2H). − ^{13}C-NMR (CD_2Cl_2, room temp.): signals for the pyrazole moiety: δ = 134.4 (d, 2C); 107.6 (d, 1C); signals for the **5** moiety: cf. Table 1. − ^{11}B-NMR (CD_2Cl_2) δ = 5.41 ($h_{1/2}$ = 164 Hz). − MS (70 eV): *m/z* (%) = 342 (M$^+$, B_2, 100), 232 (70), 231 (68), 187 (70), 123 (70), 81 (70).

$C_{19}H_{32}B_2N_2S$ (342.2) Calcd. C 66.69 H 9.43 B 6.32
Found C 66.54 H 9.27 B 6.43

2,2:4,4-Bis(1,5-cyclooctandiyl)-3-selenonia-1-azonia-5-aza-2,4-diboratabicyclo[3.3.0]octa-6,8-diene (**8**): A solution of 0.39 g (5.73 mmol) of **Pz** and 1.83 g (5.70 mmol) of **7**[8] in 20 ml of CH_2Cl_2 was stirred for 15 min. A small amount of a colourless crystalline solid began to separate. The mixture was slowly cooled to −60°C. A crystalline solid separated, 1.44 g (65%), m.p. 164−165°C. − Raman: 2280 cm^{-1}. − ^{1}H-NMR ([D_8]toluene): δ = 7.52 (d, *J* = 2.4 Hz, 2H); 6.87 (t, *J* = 2.4, Hz, 1H); ca. 2.0 (m, 24H); 1.54 (s, 1H); 0.94 (br, 2H); 0.79 (br, 2H). − ^{13}C-NMR ([D_8]toluene): signals for the **Pz** moiety: δ = 134.3 (d, 2C); 107.2 (d, 1C); signals for the **7** moiety: cf. Table 1. − ^{11}B-NMR ([D_8]toluene): δ = 7.81 ($h_{1/2}$ = 185 Hz). − MS (70 eV): *m/z* (%) = 390 (M$^+$; B_2Se, 5), 188 (45), 187 (80), 132 (90), 81 (100).

$C_{19}H_{32}B_2N_2Se$ (387.9) Calcd. C 58.82 H 8.31 B 5.57
Found C 59.01 H 8.26 B 5.41

2,2:4,4-Bis(1,5-cyclooctandiyl)-6-methyl-3-oxonia-1-azonia-5-aza-2,4-diboratabicyclo[3.3.0]octa-6,8-diene (**Me2**): A solution of 0.50 g (6.1 mmol) of **3-MePz** and 1.57 g (6.1 mmol) of **1**[10a] in 10 ml of CH_2Cl_2 was stirred for about 15 min at room temperature. A small amount of crystalline solid began to separate. The mixture was slowly cooled to −60°C. The crystalline colourless solid was separated, 1.7 g (82%), m.p. 119−120°C. − IR (KBr): 3580 cm^{-1}. − ^{1}H-NMR ($CDCl_3$): δ = 7.54 (d, *J* = 2.4 Hz, 1H); 6.10 (d,

J = 2.4 Hz, 1H); 3.48 (s, 1H); 2.44 (s, 3H); 1.7 (m, 24H); 0.71 (br, 2H); 0.53 (br, 2H). – ^{13}C-NMR ($CDCl_3$): signals for the 3-methylpyrazole moiety: δ = 141.75 (s, 1C); 131.5 (d, 1C); 109.2 (d, 1C); signals for the **1** moiety cf. Table 1. – ^{11}B-NMR ($CDCl_3$): δ = 10.0 (1B, $h_{1/2}$ = 420 Hz); 7.8 (1B, $h_{1/2}$ = 270 Hz). – MS (70 eV): m/z (%) = 340 (M^+, B_2, 2), 258 (B_2, 100), 217 (25), 120 (50), 82 (100).

$C_{20}H_{34}B_2N_2O$ (340.1) Calcd. C 70.63 H 10.08 B 6.36
Found C 70.81 H 9.96 B 6.10

2,2,4,4-Bis(1,5-cyclooctandiyl)-3-oxonia-1-azonia-5-aza-2,4-diborata-6,7-benzobicyclo[3.3.0]octa-6,8-diene (**benzo-2**): To a solution of 0.81 g (3.1 mmol) of **1**[10a] in 10 ml of CH_2Cl_2 was added a solution of 0.37 g (3.1 mmol) of indazole in 10 ml of warm CH_2Cl_2. The mixture was briefly stirred and heated to reflux and cooled slowly to −78°C. The colourless crystalline solid was separated, 1.1 g (93%), m.p. 191–192°C. – IR (nujol): 3560 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 8.2 (s, 1H); 7.82 (d, J = 9.0 Hz, 1H); 7.67 (d, J = 9.0 Hz, 1H); 7.33 (t, J = 7.5 Hz, 1H); 7.09 (t, J = 7.5 Hz, 1H); 3.69 (s, 1H); 1.8 (m, 24H); 0.72 (br, 2H); 0.61 (br, 2H). – ^{13}C-NMR ($CDCl_3$): signals for the indazole moiety: δ = 140.2 (s, 1C); 127.5 (d, 1C); 125.9 (d, 1C); 124.4 (s, 1C); 121.3 (d, 1C); 120.9 (d, 1C); 114.4 (d, 1C); signals for the **1** moiety: cf. Table 1. – ^{11}B-NMR ($CDCl_3$): δ = 9.5 ($h_{1/2}$ = 450 Hz). – MS (70 eV): m/z (%) = 376 (M^+, B_2, 20), 258 (B_2, 100), 238 (75), 118 (100).

$C_{23}H_{34}B_2N_2O$ (376.2) Calcd. C 73.44 H 9.11 B 5.75
Found C 73.31 H 9.32 B 5.89

Bis(1,5-cyclooctanediyl-1-pyrazolylborane) (**9a**): A solution of 0.74 g (2.3 mmol) of **2** and 0.28 g (1.15 mmol) of 9-borabicyclo[3.3.1]nonane[12] in 4 ml of heptane was heated to 85–90°C. Hydrogen gas [52 ml (2.2 mmol)] evolved during 2.5 h. After about 1.5 h a colourless solid began to separate. After cooling, the pre-

Table 3. Crystallographic data and data collection procedure

	2	6
Formula	$C_{19}H_{32}B_2N_2O$	$C_{19}H_{32}B_2N_2S$
Crystal size (mm)	0.21 x 0.27 x 0.33	0.31 x 0.32 x 0.41
Space group	$P2_1/n$	P bca
Z	4	8
a (Å)	10.033(4)	13.350(2)
b (Å)	13.432(8)	19.839(4)
c (Å)	13.828(7)	14.146(2)
β (deg)	108.69(3)	90
T (K)	110	110
V (Å^3)	1765(1)	3746.6(8)
d_{calcd} (g/cm^3)	1.22	1.21
μ (cm^{-1})	0.07	0.17
Radiation	Mo-K_α	Mo-K_α
2 Θ_{max} (deg)	45	45
Total no. of unique reflections	2305	2429
Observed reflections [$F_o \geq 4\sigma(F)$]	2116	2136
R	0.040	0.038
R_w [$w^{-1}=\sigma^2(F_o)+g(F_o{}^2)$]	0.051	0.042
g	9.05 x 10^{-4}	1.63 x 10^{-4}
residual electron density (e/Å^3)	0.28	0.21

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **2**

Atom	x	y	z	U(eq)
O	-31(1)	3964(1)	2435(1)	20(1)*
B(1)	-945(2)	4922(2)	2369(2)	18(1)*
B(2)	1474(2)	3982(2)	3239(2)	18(1)*
N(1)	-19(1)	5389(1)	3417(1)	18(1)*
N(2)	1200(1)	4898(1)	3870(1)	18(1)*
C(1)	-1003(2)	5571(1)	1396(1)	18(1)*
C(2)	-1660(2)	4926(1)	436(1)	21(1)*
C(3)	-3092(2)	4476(1)	355(1)	22(1)*
C(4)	-3167(2)	4000(1)	1345(1)	22(1)*
C(5)	-2525(2)	4638(1)	2304(1)	19(1)*
C(6)	-3369(2)	5600(1)	2305(1)	22(1)*
C(7)	-3271(2)	6406(1)	1548(1)	22(1)*
C(8)	-1815(2)	6542(1)	1408(1)	20(1)*
C(9)	1807(2)	2940(1)	3826(1)	18(1)*
C(10)	3236(2)	3006(1)	4678(1)	22(1)*
C(11)	4452(2)	3373(1)	4324(2)	26(1)*
C(12)	4099(2)	4247(1)	3567(2)	25(1)*
C(13)	2664(2)	4182(1)	2720(1)	21(1)*
C(14)	2577(2)	3355(1)	1929(1)	23(1)*
C(15)	2653(2)	2291(1)	2344(1)	22(1)*
C(16)	1738(2)	2117(1)	3033(1)	21(1)*
C(17)	-86(2)	6168(1)	4000(1)	20(1)*
C(18)	1098(2)	6194(1)	4844(1)	22(1)*
C(19)	1891(2)	5382(1)	4737(1)	20(1)*
H(O)	-354	3433	2031	306(31)

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

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **6**

Atom	x	y	z	U(eq)
S	1122(1)	1812(1)	1898(1)	28(1)*
B(1)	512(2)	2182(1)	728(2)	21(1)*
B(2)	1462(2)	921(1)	1341(2)	21(1)*
N(1)	1088(1)	1735(1)	-14(1)	21(1)*
N(2)	1508(1)	1140(1)	264(1)	20(1)*
C(1)	-672(2)	2049(1)	744(2)	28(1)*
C(2)	-1137(2)	2396(1)	1614(2)	43(1)*
C(3)	-843(2)	3136(1)	1755(2)	44(1)*
C(4)	253(2)	3302(1)	1550(2)	40(1)*
C(5)	681(2)	2979(1)	653(2)	28(1)*
C(6)	187(2)	3266(1)	-243(2)	39(1)*
C(7)	-885(2)	3038(1)	-428(2)	43(1)*
C(8)	-1105(2)	2302(1)	-198(2)	41(1)*
C(9)	2484(2)	640(1)	1795(1)	23(1)*
C(10)	2768(2)	-38(1)	1342(2)	28(1)*
C(11)	1922(2)	-559(1)	1276(2)	35(1)*
C(12)	881(2)	-276(1)	1040(2)	35(1)*
C(13)	598(2)	383(1)	1552(2)	26(1)*
C(14)	466(2)	302(1)	2625(2)	35(1)*
C(15)	1432(2)	163(1)	3177(2)	34(1)*
C(16)	2341(2)	582(1)	2872(2)	29(1)*
C(17)	1186(2)	1780(1)	-956(2)	28(1)*
C(19)	1856(2)	829(1)	-512(1)	27(1)*
C(18)	1665(2)	1216(1)	-1295(1)	30(1)*
H(O)	1981	2095	1828	53(8)

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

cipitate was filtered and recrystallized from ethanol to give **9a**, 0.79 g (95%), m.p. 256–257°C. – ^{1}H-NMR (CDCl$_3$): δ = 8.2 (d, 4H); 6.1 (t, 2H); 1.7 (m, 24H); 1.4 (br, 4H). – ^{13}C-NMR (CDCl$_3$): δ = 136.6 (d); 103.4 (d); 33.2 (t); 23.0 (br, d); 21.2 (t). – ^{11}B-NMR (CDCl$_3$): δ = 3.4 ($h_{1/2}$ = 200 Hz). – MS (70 eV): *m/z* (%) = 376 (M$^+$, B$_2$, 20), 267 (25), 265 (30), 188 (45), 187 (75), 160 (70), 145 (70), 132 (70), 81 (100).

$C_{22}H_{34}B_2N_4$ (376.2)	Calcd.	C 70.25	H 9.11
	Found	C 70.38	H 8.98

X-Ray Single-Crystal Structure Determination of **2** *and* **6** *(General Procedure):* Data collection and calculations were carried out on a Syntex R 3 m/V four-circle diffractometer with Microvax II and SHELXTL-PLUS software[13]. The structure solutions were carried out by direct methods, and all but the oxygen- or sulfur-bound 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 (IDP's) of all the H atoms were refined without constraints. The oxygen- or the sulfur-bound hydrogen atom was located from the difference Fourier synthesis and refined with distance constraint of 0.90 Å and no constraints, respectively. Structural data for **2** and **6** are shown in Table 3, the atom coordinates in Tables 4 and 5[14].

CAS Registry Numbers

1: 74744-62-0 / **2**: 116928-36-0 / **Me-2**: 116928-41-7 / **benzo-2**: 116928-42-8 / **3**: 7318-84-5 / **4**: 116928-37-1 / **5**: 116928-43-9 / **6**: 116928-38-2 / **7**: 116951-81-6 / **8**: 116928-39-3 / **9a**: 116928-40-6 / **9b**: 14695-69-3 / 9-BBN: 280-64-8 / Pz: 288-13-1 / 3-MePz: 1453-58-3 / indazole: 271-44-3 / Et$_2$BOH: 4426-31-7

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[14] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53353, the names of the authors, and the journal citation.

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