Pyrazole-Organoboranes, VI[1]

Monomeric and Dimeric 9-Pyrazolyl-9-borabicyclo[3.3.1]nonanes

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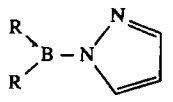
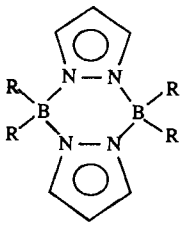
Bis(9*H*-9-borabicyclo[3.3.1]nonane) **(9H-9-BBN)$_2$** reacts with pyrazole (**Pz**) and its 4-bromo, 3-methyl, 3-phenyl, 3,5-dimethyl, 3-methyl-5-phenyl, 3,5-diphenyl, 3,5-di-*tert*-butyl, 3,5-diadamantyl, 3,5-di-*tert*-butyl-4-methyl, and 3,5-di-*tert*-butyl-4-ethyl derivatives [**brPz**, **mPz**, **pPz**, **m$_2$Pz**, **mpPz**, **p$_2$Pz**, **(tb)$_2$Pz**, **(ad)$_2$Pz**, **(tb)$_2$mPz**, and **(tb)$_2$ePz**, respectively] to give the 9-pyrazolyl-9-borabicyclo[3.3.1]nonanes with the dimeric structures **(1)$_2$**–**(3)$_2$** (X-ray, NMR, and MS analysis), and **4**–**11** with monomeric structures (X-ray, NMR, MS).

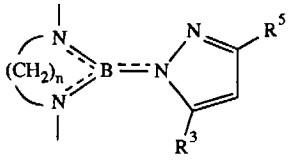
In a previous publication[2] we have shown that substituents in the 3- and/or 5-position of pyrazoles hinder the coordination of these N bases to the boron atom(s) of bis(1,5-cyclooctanediylboryl) oxide or sulfide. Dialkyl-pyrazolyl-boranes in the monomeric form **I** with a trigonal boron atom should become accessible by utilizing these steric interactions. This class of boron-nitrogen compounds has been extensively studied, and in all cases its members have been found to exist in the dimeric state **II**[3–5] (X-ray[6], NMR[7], and MS[8] analysis). The only monomeric pyrazolylborane species reported so far are the diamino-pyrazolylboranes **III**[9], in which the Lewis acidity of the trigonal boron atom can be assumed to be significantly reduced by π orbital interactions with the three neighbouring nitrogen atoms. In a preliminary account of this work[10] we have shown that pyrazoles with very bulky substituents in their 3- and 5-positions react with bis(9*H*-9-borabicyclo-[3.3.1]nonane) **(9H-9-BBN)$_2$** to form the corresponding monomeric 9-pyrazolyl-9-borabicyclo[3.3.1]nonanes. In this publication we show how the reaction of **(9H-9-BBN)$_2$** with a number of pyrazoles with progressively increased number and sizes of the substituents gradually decreases the stability of the dimeric form and eventually leads to stable monomeric diorgano-pyrazolyl-boranes.



I

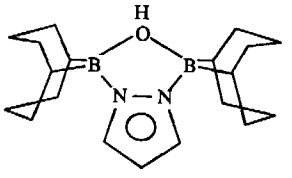


II



III

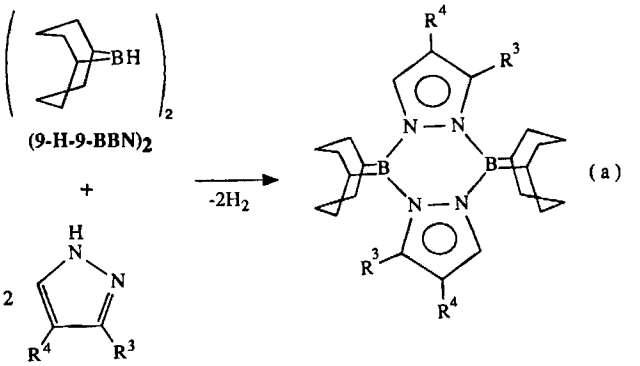
n = 2,3, R = Me
R^3, R^5 = H or Me



IV

Results and Discussion

The dimeric 9-pyrazolyl-9-borabicyclo[3.3.1]nonane **(1)$_2$** has previously been obtained in an indirect way by the reaction of the B_2ON_2 heterocycle **IV** with **(9H-9-BBN)$_2$**[11]. We have now found that **(1)$_2$** is more readily accessible by



(9-H-9-BBN)$_2$ + 2 **Pz**: R^3 = R^4 = H; **BrPz**: R^3 = H, R^4 = Br; **mPz**: R^3 = Me, R^4 = H

-2H$_2$

(1)$_2$: R^3 = R^4 = H; **(2)$_2$**: R^3 = H, R^4 = Br; **(3)$_2$**: R^3 = Me, R^4 = H

(a)

  0009–2940/90/0606–1275 $ 02.50/0

Table 1. NMR data for dimeric and monomeric 9-pyrazolyl-9-borabicyclo[3.3.1]nonanes. Unless otherwise denoted, measurements were carried in $CDCl_3$ as solvent and at room temperature (n.m. = not measured)

Compounds	δ ^{13}C (50.4 MHz)						δ ^{11}B (64.2 MHz)	δ ^{1}H (200 MHz)				
	Pyrazole moiety			9-BBN moiety				Pyrazole moiety			9-BBN moiety	
	C^3 R^3	C^4	C^5 R^5	αC(br)	βC	γC		H^3 R^3	H^4	H^5 R^5	αH	β and γH
$(1)_2$	136.6	103.4	136.6	24.0	32.3	21.2	3.4[a]	8.05	6.12	8.05	1.39(4H)	1.5–2.0(24H)
$(2)_2$	137.4	91.8	137.4	23.6	32.0	21.0	4.8[c]	8.0	–	8.0	1.36(br,4H)	1.76(16H);1.45(4H)
$(3)_2$	144.5 12.4(br)	104.5(br)	134.5	23.1	34.3; 32.2 31.2; 30.8	23.9 23.2	1.3[c]	– 2.12(6H)	5.96(br) –	7.56(br) –	1.21(4H)	1.5–2.0(24H)
4	158.4 132.7 128.4 126.2	107.6	136.8	25.2	33.6	23.0	61.8[c]	– 8.06(2H) 7.45(3H)	6.88	8.06	1.45(2H)	2.0(12H)
–50°C (CD_2Cl_2)	148.6 131.0 129.6 129.3 126.0	102.8	136.2	23.3	31.8(vbr)	25.0	n.m.		n.m.			n.m.
5	150.0(br) 13.6(q)	110.7	150.0(br) 13.6(q)	24.0	32.9	22.9	54.3[b]	– 2.27(3H)	5.88 –	– 2.27(3H)	2.15(2H)	1.80(10H);1.30(2H)
–50°C (CD_2Cl_2)	146.1 13.8(q)	107.2	144.7 12.9(q)	22.8	31.4	24.7	n.m.		n.m.			n.m.
6	143.8 11.7(q)	102.5	148.5 131.1 128.3 127.8 125.6	26.0	32.8	22.9	52.7[b]	– 2.20(3H)	6.20 –	– 7.6(2H) 7.3(3H)	1.1(2H)	1.7(10H);1.3(2H)
–50°C	155.5 14.8(q)	109.2	150.0 132.2 128.3 128.2 125.6	25.8 24.8	33.4(vbr) 33.2(vbr)	22.8	n.m.		n.m.			n.m.
7	152.4 132.3 128.3 128.0 127.2	108.8	152.4 132.2 128.3 128.0 127.2	25.8	33.1	22.8	59.6[c]	– 7.54(br,2H) 7.30(3H)	6.68	– 7.54(br,2H) 7.30(3H)	1.75(2H)	1.75(10H) 1.27(2H)
8	162.8 32.0(s) 30.5(q)	106.5	162.8 32.0(s) 30.5(q)	28.5	33.6	22.8	63.1[c]	– 1.26(9H)	6.09	– 1.26(9H)	2.33(2H)	1.88(12H) –
9	164.2 42.8 37.3 34.5 29.4	106.0	164.2 42.8 37.3 34.5 29.4	30.2	33.9	23.7	63.1[c]	– 12.0(9H) 1.78(6H)	6.21	– 2.0(9H) 1.78(6H)	2.45(2H)	2.00(10H) 1.42(2H)
10	158.4 32.9(s) 29.9(q)	115.9 12.7	158.4 32.9(s) 29.9(q)	30.1	33.8	22.8	64.2[c]	– 1.39(9H)	– 1.27(3H)	– 1.39(9H)	1.39(2H)	1.27(8H) 1.27(4H)
11	157.9 33.2(s) 30.8(q)	122.3 17.8(t) 16.5(q)	157.9 33.2(s) 30.8(q)	30.0	33.8	22.8	65.3[c]	– 1.36(9H)	– 2.67(2H) 1.14(3H)	– 1.36(9H)	1.95(2H)	1.88(12H) –

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

the direct reaction of pyrazole (**Pz**) with **(9H-9-BBN)$_2$** (Eq. a).

To avoid side-reactions[12] solutions of equal concentration of the two components are gradually and simultaneously mixed at 50–60°C. After quantitative hydrogen gas evolution, the solution is cooled to –60°C, and the crystalline **(1)$_2$** with m.p. 256–257°C (dec.) was obtained in >90% yield. The mass spectrum of **(1)$_2$** showed a molecular ion peak at *m/z* = 376 (B_2, 25%, ion source temperature 90°C) corresponding to the molecular formula $(C_{11}H_{15}BN_2)_2$. The spectrum also shows a peak with significant intensity (45%) at *m/z* = 188 ($M^+/2$), which is assigned to the molecular ion of the monomer **1**, and the base peak at *m/z* = 187 ($M^+/2-1$). (With increasing ion source temperature the intensity of the molecular ion at *m/z* = 376 progressively decreases, e.g. at 110°C it has an intensity of 5% relative to the $M^+/2-1$ ion.) Dimeric dialkyl-pyrazolyl-boranes generally do not show an $M^+/2$ ion[8]. In solution, the ^{11}B-NMR signal at δ = 3.4 (Table 1) indicates tetravalency of the boron atom[13] which is in agreement with the dimeric structure.

The structure of $(\mathbf{1})_2$ has been determined by X-ray diffraction (Figure 1). Selected bond lengths and bond angles are listed in Table 2.

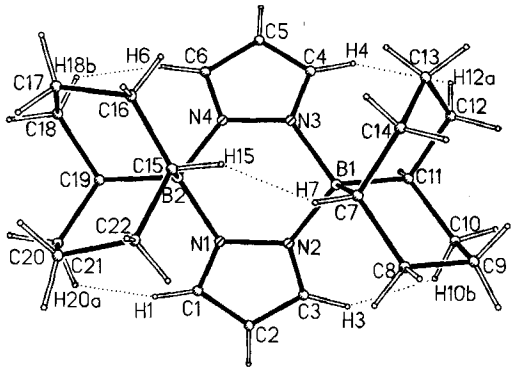


Figure 1. Molecular structure of $(\mathbf{1})_2$. Dotted lines show very short intramolecular non-bonded distances

Table 2. Selected bond lengths and angles for $(\mathbf{1})_2$

Bond lengths (Å)		Bond angles (°)	
B1 N2	1.597(2)	N3 B1 N2	98.6(1)
B1 N3	1.630(3)	B1 N2 N1	122.7(1)
B2 N1	1.610(3)	N2 N1 B2	122.6(1)
B2 N4	1.584(2)	N1 B2 N4	97.9(1)
N1 N2	1.370(2)	B2 N4 N3	120.8(2)
N3 N4	1.367(2)	N4 N3 B1	123.9(1)
B1 C7	1.616(3)	N1 B2 C15	116.7(2)
B1 C11	1.637(2)	N2 B1 C7	111.1(1)
B2 C15	1.618(3)	N4 B2 C15	111.3(1)
B2 C19	1.616(2)	N3 B1 C7	119.7(1)

The central B_2N_4 six-membered ring in $(\mathbf{1})_2$ has a boat conformation[6] with the interplanar angles N1B2N4/N1N2N3N4/N3B1N2 of 38.0 and 30.6°, respectively. As a result the two borabicyclic rings are bent upwards placing one of the α carbon atoms of each of these rings in an axial position on the central six-membered ring. In this conformation the molecule experiences considerable intramolecular crowding as seen by the very short non-bonded H7···H15 distances (d = 1.65 Å) (see Figure 1b, dotted lines). Interestingly, it appears that by becoming slightly twisted (torsional angle between the atoms N1N2N3N4 = 5.9°) an even shorter approach of the two hydrogen atoms has been avoided.

A further consequence of this crowding is the boat-chair conformation of one of the borabicyclic rings (ring incorporating B1), a single exception amongst the numerous examples involving [3.3.1]bicyclic structures. By adopting this unusual conformation the increased repulsive (eclipsed) 1,2-interactions of the bridgehead hydrogen atoms H7 and H11 with their neighbours is apparantly compensated for by avoiding an even closer intramolecular approach of the H4···H12a (d = 1.85 Å) hydrogen atoms.

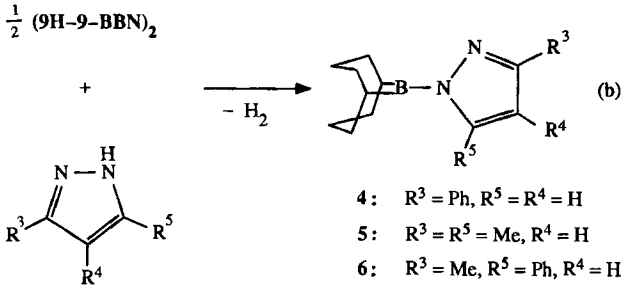
These internal strains obviously decrease the stability of the central six-membered ring, resulting in the relatively facile thermal dissociation in the gas phase, as compared with other dimers with less bulky substituents on the boron atoms[8]. Nevertheless, it is surprising that $(\mathbf{1})_2$ has such a high solid-state thermal stability [m.p. 256–257°C (dec.)].

Other derivatives of **1**, unsubstituted in the 3- and/or 5-positions of the pyrazole, should also be expected to be dimeric. Indeed, 9-(4-bromopyrazolyl)-9-borabicyclo-[3.3.1]nonane (**2**), prepared from 4-bromopyrazole and **(9H-9-BBN)$_2$**, has spectral characteristies (MS, NMR, see Table 1) which are in agreement with the dimeric structure $(\mathbf{2})_2$ (see Eq. a).

It could be expected that a substituent in the 3-position of the pyrazole would drastically increase the crowding and render the dimeric structure unstable. In fact, 9-(3-methylpyrazolyl)-9-borabicyclo[3.3.1]nonane $[(\mathbf{3})_2]$, obtained from the reaction of 3-methylpyrazole (**mPz**) and **(9H-9-BBN)$_2$** (see Eq. a) in crystalline form, m.p. 177–178°C, continues to be dimeric in solution as seen by the peak at δ = 1.3 in its ^{11}B-NMR spectrum (Table 1). The presence of only one type of boron peak is in agreement with the *anti*-configuration of the methyl groups in this dimer. The ^{13}C-NMR spectrum (Table 1) also shows the familiar[10,11] pattern of non-equivalence of the carbon skeleton of the borabicyclic rings. The broad signals for the methyl and the C^4 carbon atom of the **mPz** moiety indicate an exchange process, possibly a relatively slow boat-boat conformational interconversion.

The mass spectrum of $(\mathbf{3})_2$, even by chemical ionization technique, exhibits only a molecular ion peak at m/z = 202, which is assigned to the monomer **3** with the molecular formula $C_{12}H_{19}BN_2$. This shows that while in solution and probably also in the solid state the dimeric form $(\mathbf{3})_2$ prevails, in the gas phase it dissociates to the monomer **3**.

In the 3-phenylpyrazolylborane derivative **4** with the larger phenyl substituent the steric interactions have increased to an extent that even in solution only the monomer exists (Eq. b).



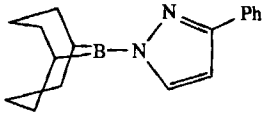
(b)

pPz: R^3 = Ph, R^5 = R^4 = H
m$_2$Pz: R^3 = R^5 = Me, R^4 = H
mpPz: R^3 = Me, R^5 = Ph, R^4 = H
p$_2$Pz: R^3 = R^5 = Ph, R^4 = H
(tb)$_2$Pz: R^3 = R^5 = t-Bu, R^4 = H
(ad)$_2$Pz: R^3 = R^5 = Ad, R^4 = H
(tb)$_2$mPz: R^3 = R^5 = t-Bu, R^4 = Me
(tb)$_2$ePz: R^3 = R^5 = t-Bu, R^4 = Et

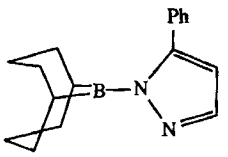
4: R^3 = Ph, R^5 = R^4 = H
5: R^3 = R^5 = Me, R^4 = H
6: R^3 = Me, R^5 = Ph, R^4 = H
7: R^3 = R^5 = Ph, R^4 = H
8: R^3 = R^5 = t-Bu, R^4 = H
9: R^3 = R^5 = Ad, R^4 = H
10: R^3 = R^5 = t-Bu, R^4 = Me
11: R^3 = R^5 = t-Bu, R^4 = Et

The ^{11}B-NMR spectrum of **4** shows a single peak at δ = 61.8 which is assigned to monomeric dialkyl-amino-

boranes[13]. Also the ^{13}C-NMR spectrum is significantly different from that of $(\mathbf{3})_2$. It shows in the high-field region only three peaks for the three types of α, β, and γ carbon atoms of the borabicyclic ring. The ^{13}C-NMR spectrum obtained at −50°C has basically the same features as that at room temperature, albeit with some shifts of the signals (see Tabe 1). The continued presence of only three signals for the three types of carbon atoms of the **9-BBN** moiety shows that even at −50°C only the monomeric species is present in solution. The slight broadening of the signals for the β and γ carbon atoms of the **9-BBN** group may indicate a tendency for dimerization at even lower temperatures. It may also indicate a decrease of the rate of rotation of the two rings about the connecting B−N bond. The occurrance of only a single set of three signals for the three carbon atoms of the pyrazolyl moiety of **4** suggests, furthermore, the presence of only one of two possible isomers **4a** and **4b**. On purely steric grounds **4a** should be the more stable isomer (see also discussion on the case of **5**, below).



4a

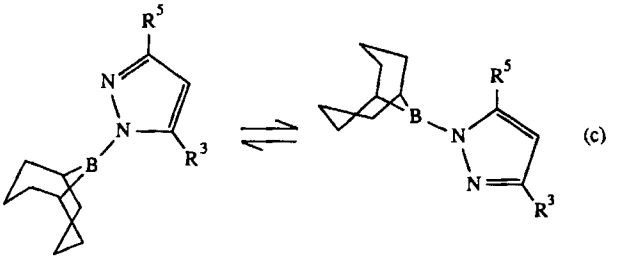


4b

The results discussed so far suggest that the presence of a further substituent in the 5-position of the pyrazoles employed should also lead to monomeric species. Indeed, the mass spectrum of 9-(3,5-dimethylpyrazolyl)-9-borabicyclo[3.3.1]nonane (**5**), obtained from 3,5-dimethylpyrazole (**m_2Pz**) and **(9H-9-BBN)$_2$** (see Eq. b), exhibits a molecular ion peak at $m/z = 216$, corresponding to that of the monomer. The ^{11}B-NMR spectrum shows a signal at $\delta = 54.3$. The ^{13}C-NMR spectrum shows only two signals for the three ring carbon atoms of the **m_2Pz** group and a single sharp signal for two equivalent methyl groups indicating a rapid positional exchange of the borane group between the two N^1 and N^2 atoms of the **m_2Pz** moiety[2].

This type of dynamic process has also been claimed for the case of the diamino-pyrazolyl-boranes **III**[9,14,15]. However, their ^{13}C-NMR data clearly show that in all of the cases cited, at least at room temperature, no dynamism of the borane group between the two nitrogen atoms of the pyrazole ring can be assumed. We suggest that in cases of **III** the electron donation by the lone pair electrons from the neighbouring nitrogen atoms to the Lewis acidic boron atom prevents the latter's further interaction with the second nitrogen atom of the pyrazolyl ring. In our sterically hindered monomer the electron deficiency of the latter cannot be reduced by the immediate neighbours, and therefore the boron atom seeks the additional participation of the nearest donor atom as shown by the equilibrium reaction (Eq. c). This would lead to the observed exchange process in the monomers.

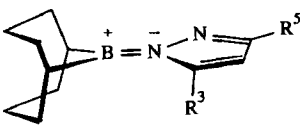
The rate of this exchange process becomes slow at low temperatures. Thus, for **5** at −50°C the ^{13}C-NMR spectrum



(c)

shows the expected two signals for the α carbon atoms as well as two signals for two chemically distinct methyl substituent of the **m_2Pz** moiety (see Table 1). Furthermore, while the signal of the γ carbon atoms of the **9-BBN** group is sharp, that of the β carbon atoms is slightly broadened and that of the α carbon atoms unusually broad ($h_{1/2} \approx 650$ Hz) at this temperature. These signal broadenings may be taken as evidence for the coalescence towards an unsymmetrical carbon skeleton of the **9-BBN** moiety as required by the low-temperature structure **5-LT**.

The next more bulky derivative investigated in this series, 9-(3-methyl-5-phenylpyrazolyl)-9-borabicyclo[3.3.1]nonane (**6**), shows a more pronounced low-temperature feature: Thus, while in the room-temperature ^{13}C-NMR spectrum of **6**, obtained from 3-methyl-5-phenylpyrazole (**mpPz**) and **(9H-9-BBN)$_2$** (see Eq. b), only three signals for the α, β, and γ carbon atoms of the 1,5-C_8H_{14} carbon skeleton can be observed, the spectrum at −50°C shows two broad peaks for the α-, two types of β-, and one signal for the two equivalent γ carbon atoms. Furthermore, except for the signals of the phenyl substituent, most of the signals for the **mpPz** moiety show a relatively large downfield shift, while for those of the 1,5-C_8H_{14} carbon skeleton a slight upfield shift is observed. This low-temperature spectrum is thus compatible with the "frozen" low-temperature structure **6-LT** in which, as a result of π BN overlap between the boron and the N^1 atom of the **mpPz** moiety, both the equilibration (Eq. c) and the free rotation about the B−N bond appear to have ceased. In this configuration the smaller methyl substituent comes to rest next to one of the α carbon atoms of the 1,5-C_8H_{14} moiety, rendering this bicyclic ring non-symmetrical. The development of a dipolar structure with a localized positive charge on the nitrogen atom N^1 and a negative one on the boron atom accounts for the observed changes of the chemical shifts.

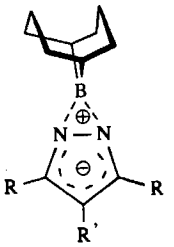


5-LT: $R^3 = R^5 = Me$
6-LT: $R^3 = Me$, $R^5 = Ph$

In view of the above results it has been expected and by the data presented in Table 1 confirmed that substitution of even more bulky groups on the pyrazoles employed will also yield only the monomeric species. Thus, we have obtained from 3,5-diphenyl- and 3,5-di-*tert*-butyl-, 3,5-diadamantyl-,

3,5-di-*tert*-butyl-4-methyl-, and 3,5-di-*tert*-butyl-4-ethylpyrazole [**p_2Pz**, **(tb)$_2$Pz**, **(ad)$_2$Pz**, **(tb)$_2$mPz**, and **(tb)$_2$ePz**, respectively] the corresponding pyrazolylboranes **7**–**11** (see Eq. b). The mass and the room-temperature NMR spectra (Tables 1 and 6) confirm their monomeric structure in the gas phase and in solution. The low-temperature ^{13}C-NMR spectra (75.5 MHz) of the 3,5-di-*tert*-butyl and 3,5-di-*tert*-butyl-4-methyl derivatives **8** and **10**[10] show that the fluctuation of the borane group continues to be very fast at very low temperatures. Thus, for **8** coalescence is observed at about −80°C. At −100°C resolved narrow peaks for two *tert*-butyl and for the C^3/C^5 carbon atoms of the pyrazole group are observed. The three signals for the α, β, and γ carbon atoms of the **9-BBN** moiety appear broadened. The spectrum of **8** at −100°C is therefore similar to that of the 3,5-dimethyl derivative **5** at −50°C. In contrast to **8**, fast fluctuation of the borane group in **10** continues at an even lower temperature. Thus, the ^{13}C-NMR spectrum (75.5 MHz) of **10** shows at −110°C sharp carbon signals for only one type of *tert*-butyl group, and also other signals remain unbroadened[10].

These observations indicate the presence of severe steric strains within those pyrazolylboranes containing very large substituents. As seen above, the activation barrier is so much reduced that speculation about the possible involvement of the intermediate symmetrical structure **A** in solution is warranted[10].



The crystal structure analyses performed on compounds **8**, **9**, and **11**[10] (Figure 2) show that the borane group is bound to only one nitrogen atom.

Table 3. Very short non-bonded intramolecular distances for compounds **8**, **9**, and **11**

8		**9**		**11**	
Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
H4 N2	2.37	H4 N2	2.33	H4 N2	2.53
B N2	2.39	B N2	2.39	B N2	2.34
H8 H18A	1.89	H8 H27A	1.94	H8 H18A	2.32
H8 H19A	1.97	H8 H30B	1.86	H8 H19A	1.79
H17B H2	2.27	H23B H2	2.23	H17A H20A	2.23
				H17B H20A	2.03
				H27B H21A	2.21
				H13C H20B	2.01
				H14B H20B	2.04

Intramolecular steric interactions are evident in all three structures. In Figure 2 the very short intramolecular non-bonded distances are shown by dotted lines. These distances are listed in Table 3.

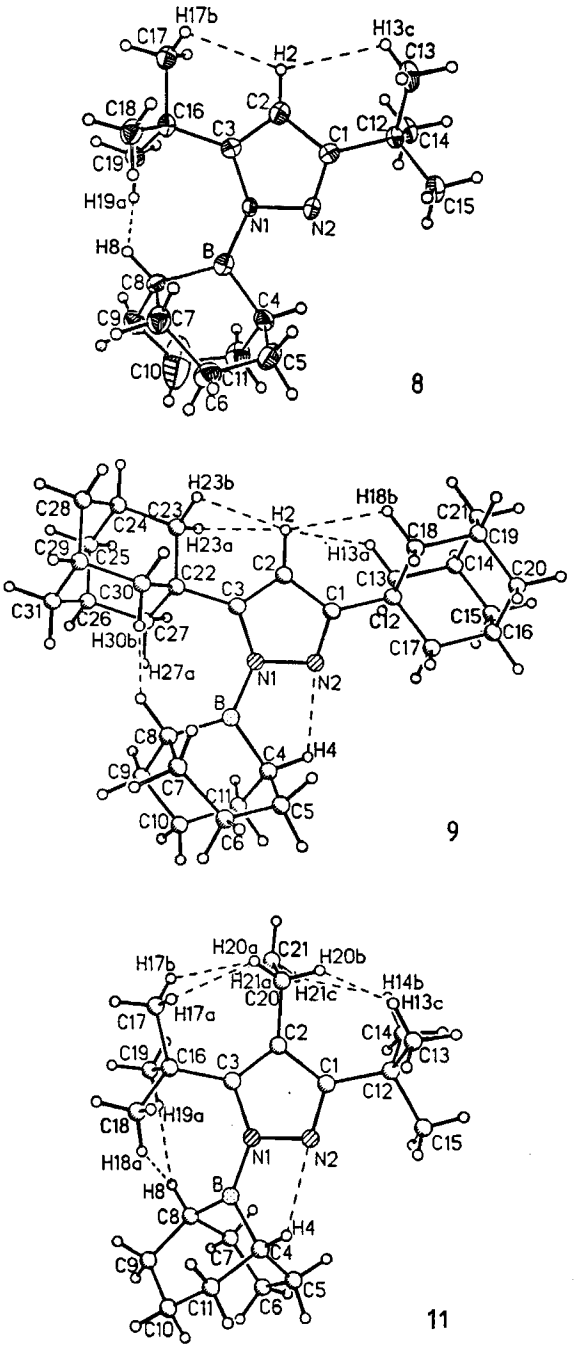


Figure 2. Molecular structure of **8**, **9**, and **11**. Dotted lines show very short intramolecular non-bonded distances

Table 4. Torsion and interplanar angles for compounds **8**, **9**, and **11**

Torsion/Interplanar angles (°)	**8**	**9**	**11**
C8 B N1 C3	-19.8	-22.0	44.1
C4 B N1 N2	-9.7	-20.9	37.3
B N1 C3 C16	1.3	-	10.7
B N1 C3 C22	-	-3.4	-
C16 C3 C2 C20	-	-	-3.0
C4 B C8 / N1 N2 C1 - 3	15.6	-17.9	44.3

Table 5. Selected bond lengths and angles for compounds **8**, **9**, and **11**

Bond lengsths (Å)				Bond angles (°)			
Bond	8	9	11	Angle	8	9	11
N1 B	1.450(6)	1.460(2)	1.466(4)	B N1 N2	113.6(3)	113.3(1)	110.3(2)
N1 N2	1.407(4)	1.404(2)	1.388(3)	B N1 C3	137.7(3)	137.9(1)	139.4(2)
N1 C3	1.396(5)	1.408(2)	1.387(4)	C3 N1 N2	108.7(3)	108.8(1)	110.1(2)
N2 C1	1.302(5)	1.312(2)	1.314(3)	N1 C3 C16	126.8(3)	-	121.1(2)
C1 C2	1.420(5)	1.421(2)	1.431(4)	N1 C3 C22	-	127.0(1)	-
C2 C3	1.352(5)	1.360(2)	1.384(3)	C16 C3 C2	126.3(3)	-	131.8(3)
B C4	1.573(6)	1.577(2)	1.569(4)	C22 C3 C2	-	126.2(1)	-
B C8	1.575(5)	1.576(2)	1.563(3)	C4 B C8	110.8(3)	110.4(1)	111.3(2)
				N1 B C4	119.9(3)	119.7(1)	119.4(2)
				N1 B C8	128.7(3)	137.9(1)	128.2(2)

The strains caused by these close contacts result in several important changes in bond lengths and angles. The foremost change, as the steric interactions increase, is the rotation of the two groups about the mutual B–N bond. The interplanar angle (see Table 4) between the plane made up of the atoms C4BC8 to the pyrazolyl ring plane increases from 15.6° in **8** to 44.3° in **11**. This is accompanied by an increase in the torsional angles as shown in Table 4.

In these conformations the optimal BN π overlap progressively decreases which leads to increased B–N bond lengths (see Table 5). In **11** the B–N bond length of 1.466 Å is significantly elongated compared to the $\geqslant B=N\leqslant$ bond found e.g. in Me_2BNMe_2[16], but is shorter than the $\geqslant B-N\leqslant$ single bond in $(\mathbf{1})_2$ (see Table 2). Another important feature of these three structures is a number of distortions of bond angles. Prominent among these are the changes in the N2N1B angle. With 113.6°, already very small in **8**, it decreases to 110.3° in **11** (see Table 5). This results in a close approach of the boron atom to N2 (non-bonded distance 2.34 Å, see Table 3).

Table 6. Experimental data for the preparation of pyrazolylboranes: dimeric $(\mathbf{1})_2-(\mathbf{3})_2$ and monomeric **4**–**11**; mass spectra and elemental analyses

Product	Reactants			Solvent	Temp. °C Time(h)	Yield g (%)	m.p. °C	MS m/z (%)	Elemental Analysis Mol.for. (mol.wt.)	Calcd C	H	B
	Pyrazole	g (mmol)	(9-H-9-BBN)$_2$ g (mmol)	(ml)						Found C	H	B
$(\mathbf{1})_2$	**Pz**	2.53 (37.2)	4.54 (18.6)	toluene (100)	50–60 (2)	6.5 (92)	256–7(d)	376(M^+, B2, 25), 267(5), 188(65), 187(100), 160(72), 159(80), 157(90)	$C_{22}H_{34}B_2N_4$ (376.2)	70.25 70.08	9.11 9.29	5.75 5.88
$(\mathbf{2})_2$	**BrPz**	1.95 (13.2)	1.62 (6.6)	toluene (100)	70–80 (2)	2.9 (81)	230(d)	536(M^+, trace), 427(trace), 268(M^+/2, 20), 267(40), 148(100)	$C_{22}H_{32}B_2Br_2N_4$ (533.9)	49.49 49.58	6.04 5.92	4.05 3.97
$(\mathbf{3})_2$	**mPz**	1.02 (6.4)	0.79 (3.2)	toluene (90)	70–80 (5)	1.4 (77)	177–8	202(M^+, B1, 70), 201(75), 174(70), 173(65), 159(68), 146(60), 95(75), 82(100)	$C_{24}H_{38}B_2N_4$ (404.2)	71.31 71.39	9.48 9.23	5.35 5.28
4	**pPz**	0.78 (5.4)	0.66 (2.7)	toluene (90)	90–100 (5)	1.0 (80)	152–4	264(M^+, B1, 64), 263(80), 236(30), 235(35), 221(50), 208(30), 144(100)	$C_{17}H_{21}BN_2$ (264.2)	77.29 77.17	8.01 8.20	4.09 4.17
5	**m$_2$Pz**	2.82 (29.4)	3.58 (14.7)	toluene (100)	90–100 (10)	4.6 (72)	68–70	216(M^+, B1, 100), 215(75), 188(35), 187(55), 173(50), 160(40), 109(65), 96(80)	$C_{13}H_{21}BN_2$ (216.1)	72.24 72.12	9.79 9.88	5.00 5.21
6	**mpPz**	0.87 (5.5)	0.67 (2.7)	heptane (20)	80–110 (10)	1.1 (71)	112–3	278(M^+, B1, 70), 277(100), 250(20), 249(40), 235(50), 169(45)	$C_{18}H_{23}BN_2$ (278.2)	77.71 77.88	8.33 8.19	3.89 3.80
7	**p$_2$Pz**	1.40 (6.4)	0.78 (3.2)	toluene (20)	100–110 (18)	1.6 (74)	130–1	340(M^+, B1, 70), 339(100), 311(25), 297(30), 231(50)	$C_{23}H_{25}BN_2$ (340.3)	81.18 81.02	7.41 7.53	3.18 3.29
8	**(tb)$_2$Pz**	1.17 (6.5)	0.81 (3.3)	heptane (20)	100–110 (18)	1.2 (63)	89–90	300(M^+, B1, 90), 285(45), 271(45), 257(65), 243(100), 217(75), 204(70), 41(100)	$C_{19}H_{33}BN_2$ (300.3)	75.99 75.86	11.08 11.21	3.60 3.49
9	**(ad)$_2$Pz**	1.09 (3.2)	0.40 (1.6)	toluene (20)	110 (18)	1.1 (75)	184–5(d)	456(M^+, B1, 100), 427(10), 413(15), 399(20), 336(50)	$C_{31}H_{45}BN_2$ (456.6)	81.56 81.24	9.94 9.89	2.37 2.48
10	**(tb)$_2$mPz**	0.84 (4.3)	0.53 (2.2)	heptane (15)	110 (24)	1.3 (94)	70–1	314(M^+, B1, 80), 299(20), 285(40), 271(70), 257(100), 231(100), 218(98), 205(65)	$C_{20}H_{35}BN_2$ (314.3)	76.43 76.80	11.22 11.29	3.44 3.53
11	**(tb)$_2$ePz**	1.36 (6.5)	0.84 (3.4)	toluene (25)	110 (24)	1.9 (88)	82–3	328(M^+, B1, 100), 313(40), 299(56), 285(65), 271(85), 245(85), 232(96)	$C_{21}H_{37}BN_2$ (328.3)	76.82 76.69	11.36 11.18	3.29 3.45

Even though the above results confirm the presence of an unsymmetrical structure, with the borane moiety bound to only one of the nitrogen atoms of the pyrazolyl group in the solid state, the severe strains, present in compounds **10** and **11**, tend to destabilize these structures in solution. It can be expected that the free fluctuating movement of the **9-BBN** group is radically restricted by the neighbouring groups. This should result in the relative stabilization of the symmetrical structure **A**, in which the boron atom is partially linked to both of the nitrogen atoms of the pyrazolyl group. The boron atom in this intermediate structure should carry a partial positive charge[10].

An additional indication for the presence of structure **A** in solution may be seen in the gradual shifts of the ultraviolet absorption maxima of compounds **5**, **8**–**11** [**5**: 220 nm ($\varepsilon = 1.5 \times 10^3$); **8**: 240 ($3.1 \times 10^3$); **9**: 244 ($5.4 \times 10^3$); **10**: 255 ($2.8 \times 10^3$); and **11**: 255 ($2.8 \times 10^3$)] to higher wavelengths. This points to an increase in the dipolar character of derivatives due to higher steric crowding. For compound **11** the structure found in the solid state requires a reduction of the BN double bond order and therefore a decrease of the molecular dipole.

These monomeric pyrazolylboranes constitute a novel type of donor/acceptor molecules. Some of their addition complexes are described in the following publication[12].

Experimental

Instruments: Büchi melting point apparatus, sealed capillary tubes. – IR: Perkin-Elmer 297. – MS: MAT CH 5. – ^1H, ^{11}B, ^{13}C NMR: Bruker AC 200 with $(CH_3)_4Si$ as internal and Et_2O-BF_3 as external standards. – Sources for the reagents are cited in ref.[2]. All operations were carried out under oxygen-free dry argon. Solvents were freshly dried and distilled.

General Procedure for the Preparation of Pyrazolylboranes **(1)$_2$**–**(3)$_2$**, **4**, *and* **5**: Equal molar quantities of the pyrazoles **Pz**, **BrPz**, **mPz**, **pPz**, or **m$_2$Pz** and **(9H-9-BBN)$_2$**, separately dissolved in toluene or heptane, were placed in two dropping funnels mounted on a three-necked round-bottomed flask equipped with a reflux condenser and gas inlet/outlet tubes. 20 ml of one of the above solvents, was placed into the flask, stirred magnetically and heated to 50–100°C. The dissolved reagents were added at approximately equal dropping rate maintaining a slow gas evolution. The gas evolved was collected in a manometer. On completion of the reaction (2–10 h, ≈100% gas evolution) the product solution was slowly cooled to −60°C. In cases where crystallization did not take place, the solution was concentrated by evaporating part of the solvent in vacuo and the cooling process repeated, or evaporated to dryness and the residue crystallized from hexane by cooling to −60°C. Yield and other relevant data are listed in Tables 1 and 6.

General Procedure for the Preparation of the Pyrazolylboranes **6**–**11**: Equal molar quantities of the solid pyrazoles **mpPz**, **p$_2$Pz**, **(tb)$_2$Pz**, **(ad)$_2$Pz**, **(tb)$_2$mPz**, or **(tb)$_2$ePz** and **(9H-9-BBN)$_2$** were dis-

Table 7. Crystallographic data for compounds **(1)$_2$**, **8**, **9**, and **11** and data collection procedures

	(1)$_2$	**8**	**9**	**11**
Formula	$C_{22}H_{30}B_2N_4$	$C_{19}H_{33}BN_2$	$C_{31}H_{45}BN_2$	$C_{21}H_{37}BN_2$
Crystal size (mm)	0.33 x 0.25 x 0.25	0.33 x 0.29 x 0.23	0.23 x 0.19 x 0.14	0.44 x 0.28 x 0.23
Space group	$P\bar{1}$	Pbca	$P\bar{1}$	$P2_1/n$
Z	2	8	2	4
a (Å)	10.088(2)	19.526(7)	6.456(1)	9.698(2)
b (Å)	10.299(2)	16.555(1)	10.916(1)	23.753(4)
c (Å)	10.710(3)	11.257(3)	18.426(2)	9.869(2)
α (deg)	104.35(2)		78.73(1)	
β (deg)	112.34(2)	90	90.08(1)	118.55(2)
γ (deg)	90.77(2)		85.69(1)	
T (K)	118	125	125	115
V (Å^3)	989.9(4)	3638(1)	1269.7(3)	1996.8(7)
d_{calcd} (g/cm^3)	1.259	1.096	1.194	1.092
μ (cm^{-1})	0.7	0.6	0.6	0.6
Radiation	M_o-K_α	M_o-K_α	M_o-K_α	M_o-K_α
$2\Theta_{max}$ (deg)	45	48	45	50
Total no. of unique reflections	2589	2200	4015	3532
Observed reflections	2387	1633	3476	2664
R	0.0414	0.058	0.039	0.059
R_w [$w=\sigma(F_o+gF^2)$]	0.0883	0.064	0.043	0.065
g	8.71×10^{-3}	1.04×10^{-4}	2.8×10^{-4}	2.7×10^{-3}
Residual electron density (e/Å^3)	0.169	0.325	0.22	0.429

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors [$Å^2 \times 10^3$] $(\mathbf{1})_2$

	x	y	z	U_{eq}
B(1)	3588(2)	7063(2)	11038(2)	17(1)*
B(2)	1455(2)	7199(2)	8077(2)	16(1)*
N(1)	1475(1)	5879(1)	8636(1)	15(1)*
N(2)	2439(1)	5816(1)	9933(1)	16(1)*
N(3)	4062(1)	7600(1)	9932(1)	15(1)*
N(4)	3144(1)	7535(1)	8577(1)	15(1)*
C(1)	814(2)	4628(2)	7911(2)	18(1)*
C(2)	1290(2)	3748(2)	8722(2)	22(1)*
C(3)	2307(2)	4528(2)	9971(2)	21(1)*
C(4)	5410(2)	7808(2)	10004(2)	18(1)*
C(5)	5387(2)	7888(2)	8731(2)	22(1)*
C(6)	3952(2)	7690(2)	7862(2)	19(1)*
C(7)	2890(2)	8052(2)	11992(2)	19(1)*
C(8)	2552(2)	7259(2)	12916(2)	24(1)*
C(9)	3878(2)	6828(2)	13949(2)	25(1)*
C(10)	4720(2)	5989(2)	13184(2)	22(1)*
C(11)	5040(2)	6675(2)	12179(2)	19(1)*
C(12)	6082(2)	7996(2)	13137(2)	22(1)*
C(13)	5469(2)	9335(2)	13017(2)	23(1)*
C(14)	3912(2)	9370(2)	12916(2)	24(1)*
C(15)	769(2)	8461(2)	8748(2)	18(1)*
C(16)	957(2)	9664(2)	8191(2)	23(1)*
C(17)	356(2)	9413(2)	6588(2)	24(1)*
C(18)	653(2)	8064(2)	5802(2)	21(1)*
C(19)	521(2)	6856(2)	6392(2)	19(1)*
C(20)	-1104(2)	6474(2)	6025(2)	20(1)*
C(21)	-1781(2)	7454(2)	6892(2)	25(1)*
C(22)	-813(2)	8007(2)	8447(2)	21(1)*

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

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors [$Å^2 \times 10^4$] for **8** (definition of U as in Table 8)

	x	y	z	U_{eq}
B	1753(3)	6076(2)	2015(3)	205(14)*
N(1)	2451(2)	6070(2)	1577(2)	170(9)*
N(2)	2610(2)	6735(2)	848(2)	204(10)*
C(1)	3243(2)	6645(2)	514(3)	185(11)*
C(2)	3530(2)	5941(2)	1031(3)	222(12)*
C(3)	3033(2)	5585(2)	1682(3)	182(11)*
C(4)	1292(2)	6845(2)	1834(3)	249(12)*
C(5)	777(2)	6619(2)	842(3)	332(14)*
C(6)	368(2)	5860(2)	1083(3)	295(13)*
C(7)	797(2)	5147(2)	1524(3)	301(13)*
C(8)	1320(2)	5354(2)	2531(3)	206(12)*
C(9)	954(2)	5611(2)	3692(3)	302(13)*
C(10)	691(4)	6437(3)	3745(5)	987(29)*
C(11)	941(2)	7088(2)	3018(3)	371(15)*
C(12)	3590(2)	7267(2)	-275(3)	200(12)*
C(13)	4093(2)	6844(2)	-1115(3)	312(14)*
C(14)	3983(2)	7862(2)	518(3)	284(13)*
C(15)	3055(2)	7731(2)	-992(3)	291(13)*
C(16)	3096(2)	4800(2)	2379(3)	208(12)*
C(17)	3849(2)	4537(2)	2415(3)	301(14)*
C(18)	2702(2)	4122(2)	1752(3)	274(13)*
C(19)	2866(2)	4916(2)	3686(3)	230(12)*

solved or suspended in toluene or heptane. The mixture was heated at 80–110°C for 10–24 h, until the calculated amount of H_2 gas had evolved. On cooling to −60°C generally a microcrystalline mass was obtained which was recrystallized from hexane by slow cooling to −60°C. Compounds **10** and **11** were purified by high-vacuum sublimation. Yields and other relevant data are listed in Tables 1 and 6.

Table 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors [$Å^2 \times 10^3$] for **9** (definition of U as in Table 8)

	x	y	z	U_{eq}
N(1)	1272(2)	3643(1)	2634(1)	150(4)*
N(2)	529(2)	2810(1)	2221(1)	165(4)*
B	2586(3)	3021(2)	3264(1)	175(5)*
C(1)	-615(2)	3492(1)	1679(1)	149(5)*
C(2)	-694(2)	4781(1)	1720(1)	163(5)*
C(3)	486(2)	4870(1)	2317(1)	152(5)*
C(4)	2623(2)	1556(1)	3528(1)	203(5)*
C(5)	4747(3)	995(1)	3308(1)	231(5)*
C(6)	6649(2)	1606(2)	3532(1)	244(5)*
C(7)	6364(2)	3035(2)	3450(1)	226(5)*
C(8)	4248(2)	3573(1)	3712(1)	190(5)*
C(9)	3939(3)	3191(2)	4556(1)	262(6)*
C(10)	3676(3)	1797(2)	4844(1)	274(6)*
C(11)	2191(3)	1260(2)	4367(1)	260(5)*
C(12)	-1771(2)	2899(1)	1141(1)	152(5)*
C(13)	-4126(2)	3091(2)	1263(1)	203(5)*
C(14)	-5339(2)	2490(2)	726(1)	249(5)*
C(15)	-4698(3)	1084(2)	852(1)	265(6)*
C(16)	-2372(3)	889(1)	721(1)	221(5)*
C(17)	-1162(3)	1481(1)	1263(1)	202(5)*
C(18)	-1328(2)	3506(1)	335(1)	182(5)*
C(19)	-2531(3)	2903(1)	-204(1)	231(5)*
C(20)	-1870(3)	1499(2)	-73(1)	248(5)*
C(21)	-4864(3)	3086(2)	-73(1)	283(6)*
C(22)	763(2)	6054(1)	2611(1)	154(5)*
C(23)	-808(2)	7113(1)	2208(1)	170(5)*
C(24)	-614(2)	8330(1)	2490(1)	191(5)*
C(25)	-1017(3)	8123(2)	3325(1)	213(5)*
C(26)	542(2)	7091(1)	3728(1)	200(5)*
C(27)	272(2)	5879(1)	3445(1)	175(5)*
C(28)	1576(3)	8758(1)	2341(1)	210(5)*
C(29)	3159(2)	7730(1)	2744(1)	193(5)*
C(30)	2957(2)	6517(1)	2453(1)	167(5)*
C(31)	2761(3)	7486(1)	3579(1)	210(5)*

X-ray Single-Crystal Structure Determination of $(\mathbf{1})_2$, **8**, **9**, *and* **11**: Data collection and calculations were carried out on a Syntex R3 m/V four-circle diffractometer with Microvax II and SHELXTL-PLUS software[17]. The structural data for the compounds investigated are compiled in Table 7. The structure determination was carried out by direct methods, and 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 or 120°). The isotropic displacement parameters (IDP's) of all the H atoms were refined without constraints.

The atom coordinates for $(\mathbf{1})_2$, **8**, **9**, and **11** are collected in Tables 8, 9, 10, and 11[18].

Table 11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors [$Å^2 \times 10^3$] for **11** (definition of *U* as in Table 8)

	x	y	z	U(eq)
B	2533(3)	6053(1)	7294(3)	165(11)
N(1)	1833(2)	6496(1)	7806(2)	151(8)
N(2)	2256(2)	7023(1)	7521(2)	165(8)
C(1)	1443(3)	7390(1)	7846(3)	151(9)
C(2)	512(2)	7120(1)	8427(3)	141(9)
C(3)	792(2)	6550(1)	8390(3)	132(9)
C(4)	4231(3)	6136(1)	7509(3)	196(10)
C(5)	4091(3)	6264(1)	5909(3)	269(11)
C(6)	2953(3)	5885(1)	4584(3)	298(11)
C(7)	1439(3)	5757(1)	4649(3)	256(10)
C(8)	1707(3)	5532(1)	6250(3)	204(10)
C(9)	2695(3)	4988(1)	6771(3)	260(11)
C(10)	4465(3)	5058(1)	7369(3)	302(12)
C(11)	5146(3)	5590(1)	8286(3)	251(11)
C(12)	1669(3)	8014(1)	7631(3)	184(10)
C(13)	2562(3)	8302(1)	9204(3)	249(11)
C(14)	83(3)	8303(1)	6654(3)	261(11)
C(15)	2635(3)	8078(1)	6786(3)	280(12)
C(16)	230(3)	6035(1)	8924(3)	164(10)
C(17)	-250(3)	6191(1)	10155(3)	211(10)
C(18)	1577(3)	5609(1)	9687(3)	208(10)
C(19)	-1198(3)	5766(1)	7566(3)	201(10)
C(20)	-522(3)	7422(1)	8961(3)	179(10)
C(21)	-2273(3)	7410(1)	7790(3)	236(11)

CAS Registry Numbers

(**1**)$_2$: 116928-40-6 / (**2**)$_2$: 125995-72-4 / (**3**)$_2$: 125995-73-5 / **4**: 125995-67-7 / **5**: 125995-68-8 / **6**: 125995-69-9 / 7: 125950-19-8 / **8**: 125303-72-2 / **9**: 125995-70-2 / **10**: 125281-22-3 / **11**: 125281-23-4 / **(9-H-9-BBN)$_2$**: 21205-91-4 / **Pz**: 288-13-1 / **(ad)$_2$Pz**: 125995-71-3 / **BrPz**: 2075-45-8 / **mPz**: 1453-58-3 / **m$_2$Pz**: 67-51-6 / **mpPz**: 3347-62-4 / **pPz**: 2458-26-6 / **p$_2$Pz**: 1145-01-3 / **(tb)$_2$Pz**: 1132-14-5 / **(tb)$_2$ePz**: 125282-21-2 / **(tb)$_2$mPz**: 18712-47-5

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