Preparation and Some Reactions of (Acylamino)diorganoboranes

Mohamed Yalpani*[a], Roland Köster[a], and Roland Boese[b]

Max-Planck-Institut für Kohlenforschung[a],
Kaiser-Wilhelm-Platz 1, W-4330 Mülheim an der Ruhr, F.R.G.

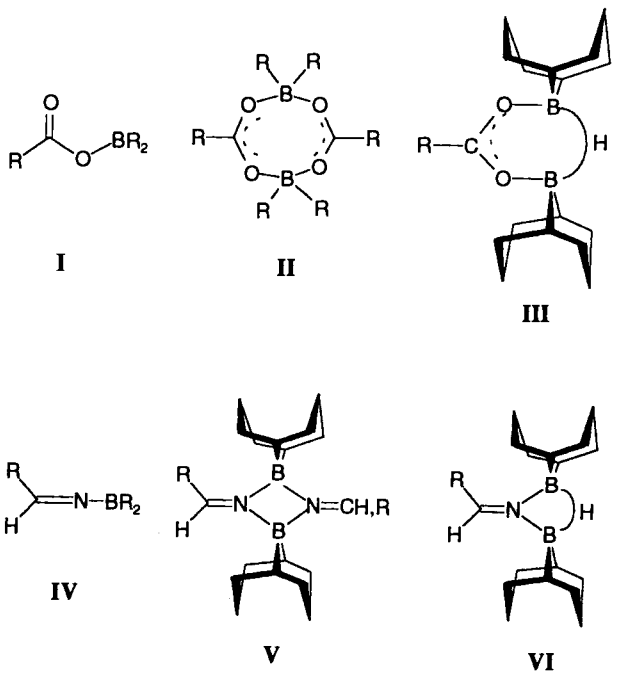
Institut für Anorganische Chemie der Universität Essen[b],
Universitätsstraße 5–7, W-4300 Essen, F.R.G.

Received August 13, 1992

Key Words: Amides / Boranes, trialkyl- / Boranes, dialkylhydro- / Boron-nitrogen heterocycles / Bis(9H-9-borabicyclo[3.3.1]nonane)

The carboxamides $RCONH_2$ [R = Ph (**1**), *t*Bu (**2**)] react with BEt_3 and with **(9H-9-BBN)$_2$** to give the (acylamino)diethylboranes **3**, **4** and the 9-acylamino-**9-BBN** **5**, **6**, respectively. Compounds **3** and **4** are largely monomeric (NMR) in solution and dimeric as crystalline solids [X-ray structure of (**4**)$_2$]. The **9-BBN** derivatives **5** and **6** are associated and probably polymeric in solution (NMR). The 1:1 adducts **7** and **8** containing the NCOBHB ring (X-ray structure of **7**) are formed on the reaction of **3** and **4** with **(9H-9-BBN)$_2$** by borane exchange. The former is also obtained directly by treating compound **1** or **2** with **(9H-9-BBN)$_2$**. Compound **7** reacts at 140–150°C to give the air-stable OBNCNC heterocycle **11** (X-ray structure).

The reactions of carboxamides with either trialkylboranes or ≥BH-borane reagents have in the past received only little attention[1]. Recently, we have begun to investigate the reactivity of carboxylic acids and some of their derivatives towards trialkylboranes[2] or their hydroboration with, e.g., bis(9H-9-borabicyclo[3.3.1]-borane) **(9H-9-BBN)$_2$**[3]. In particular, in the reactions of the parent carboxylic acids with BR_3 the mixed anhydrides (**I**) of the corresponding borinic acids are readily formed[2]. Undiluted, these normally exist in the dimeric form **II** and in solution in equilibrium with **I**. In the presence of an excess of a suitable ≥BH-borane reagent, they readily form the thermally labile 1:1 adducts **III**[3]. In an extension of this study we have also investigated the reaction of nitriles with either trialkylboranes or dialkylhydroboranes. In the former case, reactivity was only observed at about 200°C leading to the formation of various BN heterocycles[4]. In the reactions of nitriles with ≥BH-boranes, depending on the substituents, the monomeric and dimeric aldimino-diorganoboranes **IV** and **V**, respectively, are formed which in the presence of an excess of the borane reagent also give the corresponding 1:1 adducts **VI**[5]. The reactivity of amides, another group of carboxylic acid derivatives, towards trialkylboranes and dialkyl(alkylthio)-boranes and certain of their reactions have already been briefly investigated[6,7]. On the basis of infrared and ^{11}B-NMR results it has been reported that the initially formed (acylamino)dialkylborane products exist as an equilibrium monomer-dimer mixture. This communication deals with more structural details of these compounds and of their **9H-9-BBN** adducts.

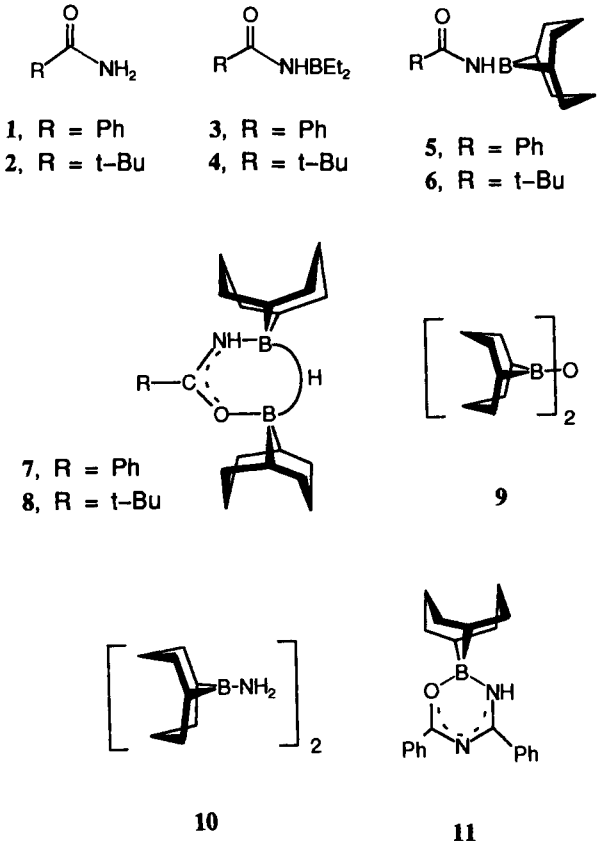


Result and Discussion

The reactions of benzo- and pivalamide (**1** and **2**), which have no α-hydrogen atoms, with BEt_3 or **(9H-9-BBN)$_2$** were investigated. The reactions can be carried out in a hydrocarbon solvent or, in the case of BEt_3, in an excess of the reagent. Generally, the reaction started at room temperature, in some cases in a slightly exothermic reaction, releasing quantitatively one equivalent of hydrogen or ethane gas. Secondary reactions occur on prolonged and excessive heating.

The (acylamino)diethylboranes **3** and **4** were obtained as pure solids with relatively low melting points. Compound **4** could even be vacuum-distilled (b.p. 56–60°C/0.001 Torr). The **9-BBN** derivatives **5** and **6** are obtained as powders which are difficult to purify. In all cases the infrared spectrum (nujol suspension) shows a carboxy group absorption band at about 1600 cm^{-1}. This suggests that the compounds

  0009–2940/93/0303–0565 $ 10.00+.25/0



3–6 exist as associates. As in the case of the (acyloxy)dialkylboranes, also with 3–5, depending on the substituents the spectra change between −25 and 150°C, and a carbonyl group frequency develops at about 1690–1720 cm^{-1}[2]. Figure 1 shows the changes observed in the carbonyl region for **4** when the sample is heated from −25 to 120°C. In the case of **5** the transformation begins above 140°C and with **6** no change is observed up to 150°C. These processes are fully reversible. The position of the carbonyl absorption at above 1700 cm^{-1} indicates that in the corresponding monomeric species formed at elevated temperatures the boryl group is suprisingly nitrogen-rather oxygen-bonded.

Earlier reports[6,7] on the preparation and properties of (acylamino)dialkylboranes, formed by treatment of acetamide with dialkyl(alkylthio)boranes or pivalamide with BPr_3 or $B(iPr)_3$, provide contradictory results with respect to the spectroscopic properties and therefore the structures of these compounds. Thus, in the case of (acetamido)dialkylboranes the presence of a carbonyl absorption band at 1620 cm^{-1} in their infrared spectra and the ^{11}B-NMR signal ($\delta = -2.2$) are indicative of an associated, probably dimeric form[6a]. In the (pivalamido)boranes (**4**, **6**) the strong carbonyl absorption at 1725 cm^{-1} and the ^{11}B-NMR signal ($\delta = 52-54$) are evidences of the presence of only the monomeric species in solution and at room temperature[6b]. In our cases, the ^{11}B-NMR signals for compounds **3** and **4** ($\delta \approx 55$) are in agreement with the above ones. The ^{11}B-NMR spectra of the **9-BBN** derivatives **5** and **6**, however, with very broad signals at about $\delta^{11}B = 10$ and also the broad ^{13}C-NMR lines indicate the existence of associated, probably polymeric, species from which during mass spectroscopic analysis the monomer is liberated into the gas phase. The greater ease of aggregate formation of the **9-BBN** derivatives is attributed to the higher boron Lewis acidity of this bicyclic group[8]. We have determined the molecular structure of dimeric $(4)_2$ by X-ray diffraction (see Figure 2). The eight-membered $(OBNC)_2$ heterocycle has a chair conformation similar to that of the dimeric (acyloxy)diorganoboranes **II**[2] and the dimeric diethylboryl-ζ-oenanthlactim[9]. The NB and OB bond lengths (see legend of Figure 2) of 1.585 and 1.541 Å, respectively, are normal. The BOC1 and BNC1

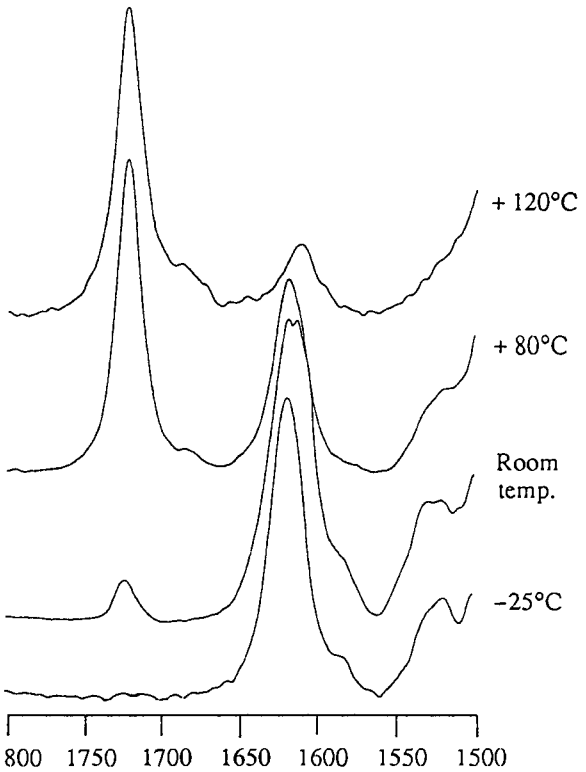


Figure 1. Changes in the carbonyl region of the infrared spectrum of $(4)_2$ between −25 and +120°C

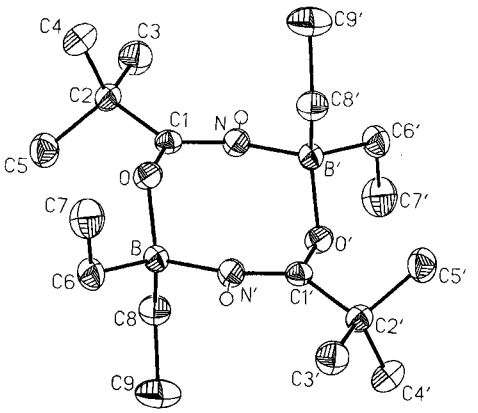


Figure 2. Molecular structure of $(4)_2$. Selected bond lengths [Å] and angles [°]: B–O 1.541(2), N′–B 1.585(2), O–C1 1.285(3), N–C1 1.294(3), C6–B 1.603(3), C8–B 1.608(4), C1–C2 1.517(2); N′–B–O 110.9(1), B–O–C1 129.1(2), O–C1–N 122.2(1), O–B–C6 104.5(2), O–B–C8 110.4(2), B–C6–C7 114.8(2), C6–B–C8 115.5(2), O–C1–C2 115.1(2), N–C1–C2 122.7(2)

angles inside the ring, 129.1 and 130.8°, respectively, are even wider than the analogous BOC angles in **II**. The exocyclic angles OBC6 and NBC6 of 104.5 and 105.9° are rather small.

Like the corresponding (acyloxy)diorganoboranes **II**[3], also these (acylamino)diorganoboranes form readily adducts with molar amounts of **(9H-9-BBN)$_2$** which are rather stable. In the case of the compound **(3)$_2$** and **(4)$_2$** the addition of only molar equivalents of **(9H-9-BBN)$_2$** leads to a ready borane exchange, and only the corresponding adducts **7** and **8** are formed. Both of these adducts are also formed in good yields when the amides **1** and **2** are allowed to react directly with two equivalents of **9H-9-BBN**. In both **7** and **8** there are two chemically non-equivalent **9-BBN** groups, as seen in their NMR spectra. Thus, there are two ^{11}B-NMR signals at about $\delta = 21$ and 10 for the boron atoms bound to the N and O atoms, respectively. There are also two sets of signals for two different C_8 rings in the corresponding ^{13}C-NMR spectra. Also the carbon skeleton of each of the C_8 rings is further differentiated in terms of the β and γ carbons facing the carboxamide group and those on the opposite side. The existence of an adduct structure was further indicated by the presence of a very strong and broad BHB IR band centered at about 1900 cm^{-1}.

The adduct structure was further confirmed by an X-ray diffraction investigation, carried out on **7**. As can be seen in Figure 3 the addition of the ≥BH group of the **9H-9-BBN** molecule across the functional atoms of a monomeric **5** results in a six-membered heterocycle, including the bridging hydrogen atom.

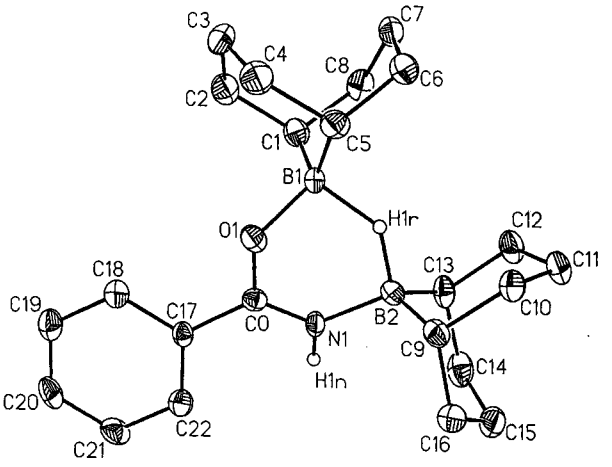


Figure 3. Molecular structure of molecule A of **7**. Selected bond lengths [Å] and angles [°]: B1–B2 2.471, B1–H1r 1.41(4), B2–H1r 1.24(4), O1–B1 1.520(5), O1–C0 1.301(5), N1–C0 1.293(5), N1–B2 1.550(5), C0–C17 1.474(5), C1–B1 1.577(5), C5–B1 1.583(7); B1–H–B2 138(3), B1–O1–C0 119.0(3), O1–C0–N1 118.8(3), C0–N1–B2 122.9(3), O1–C0–C17 117.3(3), N1–C0–C17 123.8(4)

Figure 4 shows the two independent molecules A and B of **7** present in the cell. The phenyl group in the molecule B is disordered. This is indicated by the rather large vibrational ellipsoids. The molecules A and B in the cell are packed differently. In the case of molecules A the phenyl groups are nearly staggered with an averaged distance of the C17–C22 plane to the neighboring C17′–C22′ plane of 3.51 Å. The molecules B with disordered nearly eclipsed phenyl groups are packed in a head-to-head fashion. In these, the average interlayer distance between the planes of two neighboring phenyl rings is with 3.37 Å considerably smaller. It appears that the phenyl groups decrease their overlap and thereby their adverse interactions by sideways deformation.

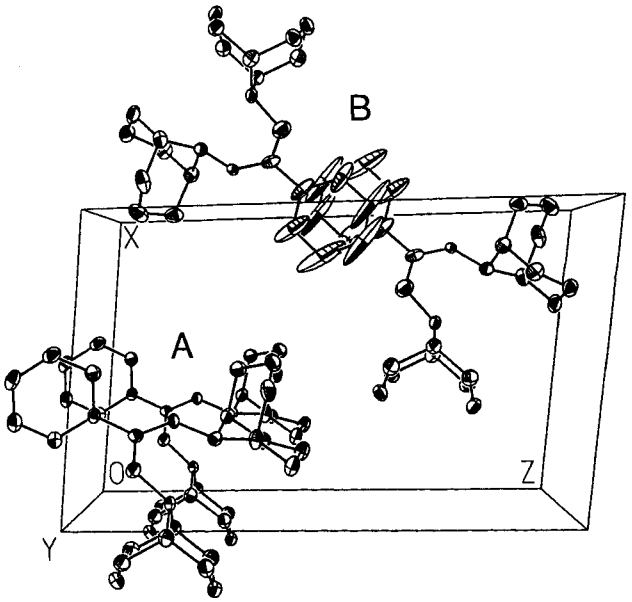


Figure 4. Packing of the two independent molecules A and B of **7** in the cell and ORTEP drawing displaying vibrational ellipsoids (50% probability levels), demonstrating the disordered packing of the phenyl group of molecule B

With the exception of the NB and the OB bonds all other bond lengths and angles in the molecules A and B are, within the accuracy of the data, identical. The N1B2 bond in molecule A, 1.550 Å, is by about 0.033 Å longer and the O1B1 bond, 1.520 Å, by about 0.012 Å shorter than the corresponding bonds in molecule B. Both NB bonds are by about 0.03 Å shorter than the analogous bonds in pyrazolyl boranes[10]. However, the OB bonds have similar lengths as in the adduct **III**[11].

Finally, in analogy to the facile thermal Cannizzaro-type reaction, observed in the case of **II**[3], a similar oxido-reduction should also be expected for **7**. In this case the reaction course can be expected to be more complex. A priori, the reduction could yield the **9-BBN** derivative of benzyl alcohol and/or that of benzylamine. The corresponding oxidation product(s) could be the borane derivative of benzoic acid and/or benzamide. Also in analogy, in this case **(9-BBN)$_2$O (9)** and/or **(9-H$_2$N-9-BBN)$_2$ (10)** could be formed as additional product(s). Compound **8** proved to be thermally rather stable. In the case of compound **7** a reaction commences only after heating its mesitylene solution to above 140°C[12]. During five hours hydrogen gas evolves, and a deep orange solution is formed from which upon cooling the air-stable, orange crystalline compound **11** sep-

arates in 70% yield (based on the assumed condensation of two molecules of **7**). The NMR spectra of **11** show a tetravalent boron atom, one **9-BBN** moiety, and two chemically distinct phenyl groups. The molecular structure of **11**, determined by X-ray crystallography, is shown in Figure 5[13]. Due to disordered packing only the overall atomic arrangement about the central OBNCNC ring[9] is significant. The conclusive assignment of structure **11** takes account also of the presence of two sets of β and γ carbon atoms for the **9-BBN** moiety in the ^{13}C-NMR spectrum of this compound which indicate the prevalence of different chemical environments on either side of this bicyclic residue[14].

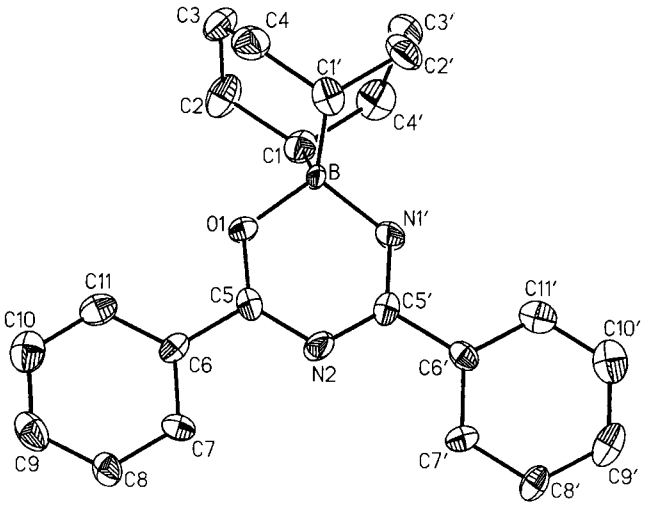


Figure 5. Molecular structure of **11**

The ^{11}B-NMR spectrum of the slightly yellow filtrate after separation of **11** exhibits a main peak (ca. 87%) at δ = 58.7 corresponding to **9**. The two smaller peaks at δ = 49.5 (ca. 8%) and −2.1 (ca. 5%) can be assigned to **9-PhCH$_2$NH-9-BBN** and to the dimeric **(9-H$_2$N-9-BBN)$_2$ (10)**[15]. For these, the corresponding molecular ion peaks at *m/z* 227 and 274, respectively, are found in the mass spectrum of the mixture, which also contains a small amount of **9-HO-9-BBN** (*m/z* 138[M$^+$]). These complex results show that the conversion of **7** to **11** is also accompanied by some other reactions.

Experimental

Melting points: Büchi apparatus, sealed capillary tubes. – IR: Perkin-Elmer 297 and Nicolet 7199 FT-IR system. – MS: MAT CH 5. – ^{1}H, ^{11}B, ^{13}C NMR: Bruker AC 200 with Me_4Si as internal and $Et_2O \cdot BF_3$ as external standards and unless otherwise mentioned $CDCl_3$ used as solvent and at room temperature. – All operation were carried out under dry oxygen-free argon. All solvents were freshly distilled under argon from the appropriate drying agents.

(Benzamido)diethylborane Dimer [(**3**)$_2$]: A suspension of 3.5 g (28.9 mmol) of **1** in 7.2 g (73.5 mmol) of BEt_3 was stirred at 50–60°C until gas evolution ceased (0.7 l, 100%). The resulting solution was stirred for an additional 2 h, and the volatile components were removed under reduced pressure. The residue, a yellow solid, was recrystallized from 25 ml of hexane to give 4.8 g (87%) of yellow (**3**)$_2$, m.p. 70–72°C. – MS, *m/z* (%): 189 (40) [M$^+$], 188 (45), 174 (5), 160 (10), 105 (60), 104 (100). – IR (nujol): ν(NH) 3375 cm^{-1}, ν(C=O) 1595 (at +80°C: 1700). – ^{1}H NMR: δ = 7.88 (d, 2H), 7.55 (m, 3H), 7.4 (br., 1H), 1.30 (br., 4H), 0.95 (t, 6H). – ^{11}B NMR: δ = 56.6 ($h_{1/2}$ = 500 Hz). – ^{13}C NMR: δ = 171.0 s, 134.8 s, 131.9 d, 128.4 d, 13.2 br. t, 7.8 q.

[$C_{11}H_{16}BNO$ (189.1)]$_2$ Calcd. C 69.88 H 8.53 B 5.72
Found C 69.93 H 8.43 B 5.98

Diethyl(pivalamido)borane Dimer [(**4**)$_2$]: To a solution of 3.9 g (38.2 mmol) of **2** at room temperature was added dropwise 7.7 g (78.6 mmol) of BEt_3. In a slightly exothermic reaction ethane gas evolved (0.9 l, 100%), and the resulting solution was heated for an additional 4 h at 70°C. Excess BEt_3 was removed under reduced pressure. The residue, a colorless suspension, was distilled in vacuo, b.p. 56–60°C/0.001 Torr. The distillate recrystallized on standing at room temp. and was recrystallized from 10 ml of hexane at −78°C to give 4.6 g (71% yield) of (**4**)$_2$, m.p. 41–42°C. – MS, *m/z* (%): 169 (15) [M$^+$], 140 (10), 112 (25), 84 (35), 69 (40), 57 (100). – IR (nujol): ν(NH) 3390 cm^{-1}, ν(C=O) 1600, at 90°C: 1718. – ^{1}H NMR: δ = 6.9 (br., 1H), 1.19 (s, 9H), 1.1 (br., 4H), 0.80 (t, 6H). – ^{11}B NMR: δ = 56.1 ($h_{1/2}$ = 200 MHz). – ^{13}C NMR: δ = 182.0 s, 26.7 q, 12.9 br. t, 7.5 q.

[$C_9H_{20}BNO$ (169.1)]$_2$ Calcd. C 63.94 H 11.93 B 6.39
Found C 64.11 H 12.14 B 6.21

9-(Benzamido)-9-borabicyclo[3.3.1]nonane Oligomer (**5**)$_n$: A mixture of 3.1 g (25.6 mmol) of **1** and 3.1 g (12.8 mmol) of **(9H-9-BBN)$_2$** in 50 ml of toluene was heated to 60–70°C for 8 h until the gas evolution ceased (0.63 l, 100%). The suspension formed was filtered to give 5.1 g (82%) of colorless solid **5**, m.p. 120–122°C. – IR (nujol): ν(NH) 3380 cm^{-1}, ν(C=O) 1610 (at 150°C: 1690). – MS, *m/z* (%): 241 (25) [M$^+$], 198 (20), 132 (30), 104 (100). – ^{1}H NMR: δ = 7.90 (m, 2H), 7.51 (m, 3H), 7.4 (br., 1H), 1.78 (m, 8H), 1.45 (m, 4H), 1.12 (br., 2H). – ^{11}B NMR: δ = 10.0 ($h_{1/2}$ = 2000 Hz). – ^{13}C NMR δ = 172.0 s, 132.2 d, 128.7 d, 127.7 d, 126.6 s, 31.8 br. t, 24.4 br. t, 24.0 br.

9-(Pivalamido)-9-borabicyclo[3.3.1]nonane Oligomer (**6**)$_n$: A mixture of 2.3 g (9.4 mmol) of **(9H-9-BBN)$_2$** and 1.91 g (18.9 mmol) of **2** in 80 ml of toluene was stirred for 18 h at room temp. until the gas evolution was completed (0.46 l, 100%). The solvent was removed under reduced pressure and the colorless solid residue recrystallized from hexane to give 2.6 g (62%) of **6**, m.p. 88–91°C. – IR: ν(NH) = 3400 cm^{-1}, ν(C=O) = 1695. – MS, *m/z* (%): 221 (25) [M$^+$], 164 (15), 138 (25), 57 (100). – ^{1}H NMR: δ = 7.45 (s, 1H), 1.86 (m, 10H), 1.48 (m, 2H), 1.25 (br., 2H), 1.06 (s, 9H). – ^{11}B NMR: δ = 10.0 ($h_{1/2}$ = 2000 Hz). – ^{13}C NMR: δ = 152.2 br. s, 37.3 s, 33.6 br. t, 26.8 q, 24.4 br. d, 24.1 br. t.

1:1 Addition Complex of **5** *and* **9H-9-BBN** (**7**): To a solution of 2.7 g (26.2 mmol) of **1** in 35 ml of toluene was added dropwise at 50–60°C a solution of 6.4 g (26.2 mmol) of **(9H-9-BBN)$_2$** in 35 ml of toluene. After the gas evolution had ceased (0.64 l, 100%) the volatile components were removed at reduced pressure, the residue was dissolved in 25 ml of pentane and the solution slowly cooled to −78°C to give 7.5 g (82%) of colorless crystals of **7**; m.p. 136–137°C. – IR (nujol): ν(NH) 3420 cm^{-1}, ν(BH) 1900 (v. br.), ν(C=O) 1600. – MS, *m/z* (%): 363 (5) [M$^+$], 241 (20), 198 (25), 105 (85), 104 (100). – ^{1}H NMR: δ = 7.82 (d, 2H), 7.52 (m, 3H), 2.0–1.5 (m, 25H), 0.97 (br., 2H), 0.89 (br., 2H), 0.3 (br., 1H). – ^{11}B NMR: δ = 21.6 ($h_{1/2}$ = 300), 10.1 ($h_{1/2}$ = 100). – ^{13}C NMR: δ = 168.5 s, 133.2 d, 128.8 d, 128.7 s, 127.4 d, 32.6 t, 32.5 t, 32.2 t, 31.7 t, 24.2 t, 24.1 t, 24.0 t, 23.9 t, 22.9 br. d.

$C_{23}H_{35}B_2NO$ (363.2) Calcd. C 76.07 H 9.71 B 5.95
Found C 75.90 H 9.73 B 5.98

1:1 Addition Complex of **6** *and* **9H-9-BBN** (**8**): To a solution of 2.6 g (25.7 mmol) of **2** in 40 ml of toluene was added dropwise at 50–60 °C a solution of 6.4 g (26.2 mmol) of **(9H-9-BBN)$_2$** in 40 ml of toluene. 0.63 l (100%) of hydrogen gas evolved. The solvent was removed under reduced pressure, the viscous residue dissolved in 20 ml of hexane and the solution slowly cooled to −60 °C to give 6.4 g (72%) of colorless crystalline **8**, m.p. 130 °C (dec.). – IR (nujol): $\tilde{\nu}$(NH) 3420 cm^{-1}, ν(BH) 1950 (v. br.), ν(C=O) 1590. – MS, *m/z* (%): 343 (70) [M$^+$], 233 (35), 232 (45), 57 (100). – ^{1}H NMR: δ = 6.9 (br., 2H), 1.8 (m, 16H), 1.4 (m, 8H), 1.21 (s, 9H), 0.8 (br., 4H). – ^{11}B NMR: δ = 21.3 ($h_{1/2}$ = 300 Hz), 9.4 ($h_{1/2}$ = 200 Hz). – ^{13}C NMR: δ = 181.4 s, 32.8 t, 32.5 t, 32.4 t, 32.0 t, 27.1 s, 26.9 q, 24.5 t, 24.3 t, 24.2 t, 24.1 t, 22.5 br.

$C_{21}H_{39}B_2NO$ (343.2) Calcd. C 73.50 H 11.43 B 6.30
Found C 73.31 H 11.22 B 6.05

Table 1. Crystallographic data for compounds $(4)_2$, **7**, and **11** and data collection procedures

	$(4)_2$	**7**	**11**
Formula	$(C_9H_{20}BNO)_2$	$C_{23}H_{35}B_2NO$	$C_{22}H_{25}BN_2O$
Crystal Size [mm]	0.57x0.41x0.36	0.27x0.23x0.20	0.32x0.11x0.10
Space group	$P2_1/c$	$P\bar{1}$	C2/c
Z	4	4	4
a [Å]	9.571(4)	10.288(1)	14.748(12)
b [Å]	10.719(4)	12.563(1)	19.480(16)
c [Å]	11.374(4)	16.463(2)	6.866(3)
α [°]	90	81.59(1)	90
β [°]	113.72(3)	82.03(1)	115.62(5)
γ [°]	90	78.49(1)	90
T [K]	191	120	120
V [Å^3]	1068.4(6)	2049.4(4)	593.5
d [g/cm^3]	1.051	1.177	1.286
μ [mm^{-1}]	0.07	0.06	0.07
Radiation	Mo-K$_\alpha$	Mo-K$_\alpha$	Mo-K$_\alpha$
$2\Theta_{max}$ [°]	50	45	45
Reflections unique			
Total no. of	1772	5388	1017
Observed	1468	4501	571
R	0.055	0.074	0.083
R$_w$	0.065	0.083	0.075
g	0.003	0.00055	0.0005
Residual electron density [e/Å^3]	0.17	1.052	0.33

Table 2. Atomic coordinates (· 10^4) and equivalent isotropic displacement factors (Å^2 · 10^3) of $(4)_2$. Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
N	9774 (2)	795 (1)	8577 (2)	25 (1)
O	8134 (1)	247 (1)	9463 (1)	27 (1)
B	8657 (2)	-979 (2)	10221 (2)	25 (1)
C(1)	8402 (2)	653 (2)	8511 (2)	22 (1)
C(2)	6998 (2)	1020 (2)	7336 (2)	26 (1)
C(3)	7384 (3)	1499 (2)	6238 (2)	37 (1)
C(4)	6187 (2)	2043 (2)	7761 (2)	37 (1)
C(5)	5944 (2)	-115 (2)	6876 (2)	35 (1)
C(6)	7403 (2)	-1241 (2)	10799 (2)	33 (1)
C(7)	7091 (3)	-148 (2)	11506 (2)	45 (1)
C(8)	8840 (2)	-2054 (2)	9315 (2)	33 (1)
C(9)	9245 (3)	-3330 (2)	9944 (3)	52 (1)

2,2-(1,5-Cyclooctanediyl)-2,3-dihydro-4,6-diphenyl-1,5,3,2-oxazaazoniaboratin (**11**): A solution of 2.1 g (5.8 mmol) of **7** was heated for 5 h in 15 ml of boiling xylene. The solution rapidly turned deep orange, and 60 ml (2.7 mmol) of hydrogen gas evolved. Upon cooling to room temp. the orange crystalline **11** formed was collected, 0.7 g, m.p. 220–222 °C. – IR: ν(NH) 3400 cm^{-1}, ν(C=N) 1595.

Table 3. Atomic coordinates (· 10^4) and equivalent isotropic displacement factors (Å^2 · 10^3) of **7**. Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
N(1)	3494 (3)	553 (2)	2082 (2)	19 (1)
N(2)	1318 (3)	6003 (2)	2702 (2)	14 (1)
O(1)	1958 (3)	261 (2)	1347 (2)	25 (1)
O(2)	2629 (3)	4959 (2)	3615 (2)	38 (1)
B(1)	920 (4)	289 (4)	2100 (3)	21 (1)
B(2)	2869 (4)	-46 (4)	2888 (3)	22 (2)
B(3)	3787 (4)	4708 (4)	2938 (3)	24 (2)
B(4)	2048 (4)	5406 (3)	1987 (3)	22 (1)
C(0)	3059 (4)	609 (3)	1374 (2)	19 (1)
C(1)	18 (4)	1458 (3)	2137 (2)	25 (1)
C(2)	-704 (4)	1693 (3)	1346 (2)	31 (1)
C(3)	-1425 (4)	805 (3)	1203 (3)	32 (2)
C(4)	-666 (4)	-377 (3)	1370 (3)	31 (2)
C(5)	23 (4)	-615 (3)	2163 (2)	24 (1)
C(6)	-950 (4)	-582 (3)	2962 (2)	28 (1)
C(7)	-1748 (4)	555 (3)	3118 (3)	29 (1)
C(8)	-917 (4)	1458 (3)	2949 (2)	28 (1)
C(9)	3470 (4)	-1310 (3)	3060 (2)	23 (1)
C(10)	2617 (4)	-1836 (3)	3794 (2)	25 (1)
C(11)	2332 (4)	-1254 (3)	4574 (2)	29 (1)
C(12)	2005 (4)	-8 (3)	4412 (2)	31 (1)
C(13)	2882 (4)	514 (3)	3690 (2)	26 (1)
C(14)	4358 (4)	377 (3)	3844 (3)	33 (2)
C(15)	5156 (4)	-792 (3)	3879 (3)	31 (2)
C(16)	4938 (4)	-1411 (3)	3191 (2)	27 (1)
C(18)	3023 (4)	1346 (3)	-101 (2)	25 (1)
C(19)	3617 (4)	1809 (3)	-834 (2)	28 (1)
C(20)	4904 (4)	1988 (3)	-893 (2)	27 (1)
C(21)	5612 (4)	1703 (3)	-216 (2)	28 (1)
C(22)	5022 (4)	1244 (3)	526 (2)	24 (1)
C(17)	3725 (4)	1068 (3)	587 (2)	18 (1)
C(50)	1553 (4)	5673 (3)	3454 (3)	23 (1)
C(51)	4512 (4)	3465 (3)	2980 (2)	26 (1)
C(52)	5143 (4)	3182 (3)	3804 (2)	30 (1)
C(53)	6035 (4)	3958 (3)	3945 (3)	31 (1)
C(54)	5495 (4)	5183 (3)	3715 (2)	30 (1)
C(55)	4870 (4)	5463 (3)	2891 (2)	27 (1)
C(56)	5893 (4)	5301 (3)	2125 (2)	28 (1)
C(57)	6521 (4)	4110 (3)	2034 (3)	29 (1)
C(58)	5546 (4)	3306 (3)	2214 (2)	28 (1)
C(59)	2338 (4)	6199 (3)	1170 (2)	27 (1)
C(60)	3236 (4)	5535 (3)	528 (2)	33 (2)
C(61)	2729 (4)	4528 (3)	353 (2)	31 (1)
C(62)	2189 (4)	3839 (3)	1127 (3)	31 (1)
C(63)	1313 (4)	4498 (3)	1783 (2)	26 (1)
C(64)	-39 (4)	5093 (4)	1509 (3)	36 (2)
C(65)	33 (4)	6034 (4)	810 (3)	40 (2)
C(66)	989 (5)	6784 (3)	908 (3)	37 (2)
C(67)	615 (5)	6105 (3)	4141 (3)	40 (2)
C(68)	964 (7)	6045 (5)	4909 (3)	73 (3)
C(69)	70(12)	6472 (8)	5516 (6)	167 (7)
C(70)	-1106(15)	6921 (7)	5432 (8)	150 (8)
C(71)	-1574 (8)	7021 (5)	4633 (7)	148 (5)
C(72)	-660 (6)	6619 (4)	4008 (5)	95 (3)
H(1R)	1691(34)	-3(27)	2767(21)	20 (9)
H(2R)	3269(33)	4935(27)	2236(20)	16 (9)

– MS, *m/z* (%): 344 (55) [M^+], 301 (25), 287 (35), 261 (30), 248 (35), 104 (100). – ^{1}H NMR: δ = 8.85 (d, 2H), 8.05 (d, 2H), 7.75 (br., 1H), 7.48 (m, 6H), 1.9 (m, 12H), 0.79 (br., 2H). – ^{11}B NMR: δ = 5.6 ($h_{1/2}$ = 300 Hz). – ^{13}C NMR: δ = 173.8 s, 166.7 s, 133.3 s, 133.1 s, 133.0 d, 132.7 d, 129.7 d, 128.6 d, 127.9 d, 127.1 d, 32.9 t, 30.9 t, 24.5 t, 24.2 t, 24.0 br.

$C_{22}H_{25}BN_2O$ (344.3) Calcd. C 76.76 H 7.32 B 3.14
Found C 76.41 H 7.22 B 3.05

The filtrate from above: ^{11}B NMR: δ = 58.7, 49.5 and −2.1 (integral ratio ≈ 20:2:1). – MS of the mixture: *m/z*: 258 [M^+, major component, **9**]; 227 [M^+, **9-PhCH$_2$NH-9-BBN**], 274 [M^+, **10**] and 138 [M^+, **9-HO-9-BBN**] (as minor components). – IR: Nearly identical with that of authentic **(9-BBN)$_2$O** (**9**).

Table 4. Atomic coordinates (· 10^4) and equivalent isotropic displacement factores (Å^2 · 10^3) of **11**. Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
B	0	3483 (6)	2500	26 (6)
N/O(1)	-923 (5)	3975 (3)	1670(10)	39 (3)
N(2)	0	4973 (4)	2500	43 (6)
C(1)	3 (6)	2991 (4)	4373(12)	30 (4)
C(2)	-962 (6)	2574 (4)	3489(11)	39 (4)
C(3)	-1164 (7)	2169 (4)	1445(13)	42 (4)
C(4)	-969 (7)	2550 (4)	-266(13)	40 (4)
C(5)	-857 (6)	4629 (3)	1764(10)	21 (3)
C(7)	-1778 (3)	5739 (2)	920 (6)	24 (4)
C(8)	-2666	6117	240	29 (4)
C(9)	-3582	5781	-348	37 (4)
C(10)	-3611	5066	-257	38 (4)
C(11)	-2723	4688	423	31 (4)
C(6)	-1807	5024	1011	22 (4)

X-Ray Single-Crystal Structure Determination of **(4)$_2$**, **7**, *and* **11**: Data collection and calculations were carried out on a Nicolet R 3 m/V four-cycle diffractometer with Microvax II and SHELXTL-PLUS software[16]. The structure solutions were performed by direct methods, and all hydrogen atoms except for H1 in **7** were included as rigid groups (C–H bond lengths 0.96 Å, C–C–H and H–C–H angles 109.5 and 120°, respectively). The IDP's of all the hydrogen atoms were refined without constraints. The N and O atoms of compound **11** were refined at equal positions with occupation factors 0.5. The structural data for compounds **(4)$_2$**, **7**, and **11** are compiled in Table 1 and the atom coordinates in Tables 2–4[17].

[1] [1a] R. Köster, *N*-Diorganobor-Carbonsäureamid(amidin)- und -Kohlensäureamid-Verbindungen in *Methoden Org. Chem. (Houben-Weyl) 4th Ed.*, **1983**, vol. XIII/3b (Ed: R. Köster), p. 87–99. – [1b] W. Maringgele, A. Meller, *Z. Anorg. Allg. Chem.* **1977**, *433*, 94–110, see also leading references herein.
[2] M. Yalpani, R. Boese, K. Seevogel, R. Köster, *J. Chem. Soc., Dalton Trans.*, in print.
[3] P. Idelmann, G. Müller, W. Scheidt, W. Schüßler, K. Seevogel, R. Köster, *Angew. Chem.* **1984**, *96*, 145–146; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 153–154.
[4] M. Yalpani, R. Köster, R. Boese, *Chem. Ber.* **1991**, *124*, 15–22.
[5] M. Yalpani, R. Köster, R. Boese, *Chem. Ber.* **1993**, *126*, 285–288.
[6] [6a] B. M. Mikhailov, V. A. Dorokhov, V. S. Bogdanov, I. P. Yakovlev, A. D. Naumov, *Doklady Akad. Nauk., SSSR* **1970**, *194*, 595–598, engl. 690–693. – [6b] V. A. Dorokhov, L. I. Lavrinovich, I. P. Yakovlev, B. M. Mikhailov, *Zh. Obshch. Chim.* **1971**, *41*, 2529–2534.
[7] W. Maringgele, A. Meller, *Z. Anorg. Allg. Chem.* **1978**, *443*, 148–158.
[8] M. Yalpani, J. Serwatowski, R. Köster, *Chem. Ber.* **1989**, *122*, 3–7.
[9] R. Köster, R. Kucznierz, W. Schüßler, D. Bläser, R. Boese, *Liebigs Ann. Chem.*, in press.
[10] M. Yalpani, R. Boese, R. Köster, *Chem. Ber.* **1990**, *123*, 1285–1291.
[11] G. Müller, C. Krüger, *Acta Crystallogr., Sect. C*, **1986**, *42*, 1856–1859.
[12] R. Köster, M. Yalpani, *Pure Appl. Chem.* **1991**, *63*, 387–394, see p. 392.
[13] [13a] R. Köster, Lewisbase-Amidino-diorgano-borane in *Methoden Org. Chem. (Houben-Weyl) 4th Ed.*, **1983**, vol. XIII/3b (Ed: R. Köster), p. 649–651. – [13b] W. Maringgele, A. Meller, *Chem. Ber.* **1979**, *112*, 1595–1605.
[14] M. Yalpani, R. Boese, R. Köster, *Chem. Ber.* **1989**, *122*, 1231–1236.
[15] R. Köster, G. Seidel, *Liebigs Ann. Chem.* **1977**, 1837–1846.
[16] G. M. Sheldrick, *SHELXTL-PLUS* (Version 2), *an Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, University of Göttingen, **1987**.
[17] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, quoting the depository numbers CSD-320550 [**(4)$_2$**], -320552 (**7**), -320551 (**11**), the names of the authors, and the journal citation.

[320/92]