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Reactions of Borazines with Pyrazole and Related Studies: (μ-Amido)(μ-pyrazolato)diboron Species, Novel Relatives of the Pyrazaboles[1]

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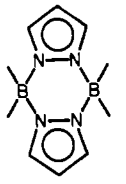
The reaction of borazines, $(-BRNR'-)_3$, with pyrazole, Hpz, gives (μ-pyrazolato)(μ-amido)diboron species of the type R(pz)B(μ-pz)(μ-NHR′)BR(pz) (**3**) containing a central B_2N_3 ring system. Four compounds of type **3** with R = C_2H_5 or C_6H_5 and R′ = H or CH_3, respectively, were prepared. Identical species can be obtained on interaction of bis((dimethylamino)boryl)amines of the type $R'N[BRN(CH_3)_2]_2$ with Hpz; they are closely related to the pyrazaboles, $R_2B(\mu\text{-pz})_2BR_2$, which contain a central B_2N_4 ring. A pathway for the formation of **3** is postulated and supported by NMR data. Conformational isomers of **3** could be identified but not separated. In contrast, $RB[N(CH_3)_2]_2$ (R = C_2H_5) reacts with Hpz at room temperature to give $(CH_3)_2HNBR(pz)_2$ and in refluxing toluene to yield the pyrazabole R(pz)B(μ-pz)$_2$BR(pz). The latter compound was also obtained from $(-BRNR'-)_3$ (R′ = H, CH_3) or **3** (R = C_2H_5, R′ = H) and boiling Hpz (at temperatures near 180–200 °C). The compound could be separated into conformational isomers. The lower melting one with the terminal pz groups in cis (equatorial) position crystallizes tetragonally in space group $I4_1/acd$, $a = b = 14.876$ Å, $c = 34.932$ Å, and $Z = 16$, with the central B_2N_4 ring in a boat conformation. The higher melting trans isomer crystallizes monoclinically in space group $P2_1/c$, $a = 8.156$ Å, $b = 14.720$ Å, $c = 7.501$ Å, $\beta = 95.58°$, and $Z = 2$, with the central B_2N_4 ring in a chair conformation.

Introduction

The pyrazaboles, dimeric 1-pyrazolylboranes of the general structure **1**, are heterocyclic four-coordinate boron compounds that exhibit considerable chemical and thermal stability, and a wide variety of boron- and/or carbon-substituted pyrazaboles is known.[2] A novel type of pyrazabole, **2**, was recently obtained by the interaction of tri-*B*-organylboroxins, $(-BRO-)_3$, with pyrazole, Hpz.[3] Compounds of type **2** were the first examples of neutral diboron compounds in which the two boron atoms are not only connected by two pz groups but also by a third linkage, in this case a O–BR–O unit. Thus, these compounds contain both three- and four-coordinate boron. Their seemingly unusual formation has prompted an investigation of the interaction of Hpz with other boron heterocycles; the present report describes the reaction of borazines, $(-BRNR'-)_3$, with Hpz and some related studies.



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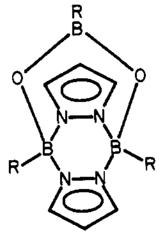

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Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block. All experiments were performed with strict exclusion of moisture.

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shift from the reference (internal Me_4Si for ^1H and ^{13}C, external $Et_2O{\cdot}BF_3$ for ^{11}B); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in Hz. Details for HOMCOR-2D NMR experiments have been given elsewhere.[4] Infrared spectra were recorded on a PE Model 621 or a BOMEM Model DA3 spectrometer under standard operating conditions; mass spectral data were obtained on a VG ZAB-2F spectrometer.

All solvents were dried by standard procedures. Pyrazole (=Hpz) (Aldrich Chemical Co., Milwaukee, WI) was distilled over sodium. Silazanes were obtained from Petrarch Systems, Inc., Bristol, PA; they were freshly distilled before use. Borazines, $(-BRNR'-)_3$, were prepared by a general method via reaction of a dihaloborane with a disilazane.[5] The procedure is detailed below for the preparation of $(-BC_2H_5NH-)_3$.

$(-BC_2H_5NH-)_3$. To 223 g (2.01 mol) of $C_2H_5BCl_2$[6] (cooled in an ice–ethanol bath) was added dropwise under argon cover and with stirring 366 g (2.2 mol) of $HN[Si(CH_3)_3]_2$ over a period of 4 h. The mixture was left standing overnight to reach room temperature. $(CH_3)_3SiCl$ was distilled off through a column under atmospheric pressure (bp 50–55 °C) and the residue was vacuum-distilled twice over a 25-cm silver-mantle column to yield 67.8 g (61.5%) of a main fraction of $(-BC_2H_5NH-)_3$: bp 92–95 °C (18 Torr); bp 56–57 °C (2 Torr) (lit.[7] bp 192–193 °C (760 Torr)).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 4.68* (1 H, s), 0.95 (1 H, q, $J = 6$), 0.84 (3 H, t, $J = 6$); $\delta(^{11}B)$ 36.2 (s, $h_{1/2} = 200$ Hz).

$(-BC_2H_5NCH_3-)_3$. The compound was prepared from $CH_3N[Si(CH_3)_3]_2$ and $C_2H_5BCl_2$ in a procedure analogous to that described above for $(-BC_2H_5NH-)_3$: yield, 90%; bp 83–85 °C (1 Torr) (lit.[8] bp 98 °C (1.8 Torr)).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 2.95 (3 H, s), 1.02 (5 H, m); $\delta(^{11}B)$ 36.2 (s, $h_{1/2} = 220$ Hz).

$(-BC_6H_5NH-)_3$. The compound was prepared from $HN[Si(CH_3)_3]_2$ and $C_6H_5BCl_2$[9] in a procedure analogous to that described above for $(-BC_2H_5NH-)_3$ with benzene as solvent: yield, 78%; mp 176–180 °C (lit.[10] mp 175–185 °C).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.78 (2 H, m), 7.46 (3 H, m) 5.90* (1 H, s); $\delta(^{11}B)$ 32.8 (s, $h_{1/2} = 580$ Hz).

$(-BC_6H_5NCH_3-)_3$. This compound was prepared from $C_6H_5BCl_2$ and $CH_3N[Si(CH_3)_3]_2$ in a similar fashion as described above with benzene as solvent: yield, 78%; mp 260–263 °C (lit.[11] mp 247–276 °C).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.39 (5 H, m), 2.56 (3 H, s); $\delta(^{11}B)$ 36.3 (s, $h_{1/2} = 500$ Hz).

$HN[BC_6H_5N(CH_3)_2]_2$.[12] NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.40 (4 H, m), 7.25 (6 H, m), 3.70* (1 H, s), 2.75 (12 H, s); $\delta(^{11}B)$ 32.8 (s, $h_{1/2} = 360$ Hz).

$(CH_3)_2NB(C_6H_5)Cl$.[13] NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.49

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(1) Boron–Nitrogen Compounds. 111 (K.N.). Part 110: See ref 17. Contributions to the Chemistry of Boron 178 (H.N.). Part 177: Nöth, H.; Rattay, W. *J. Organomet. Chem.*, in press.

(2) *Gmelin Handbuch der Anorganischen Chemie*; Springer-Verlag: West Berlin, 1975; Vol. 23, Supplement Boron Compounds 5, pp 1–8.

(3) Bielawski, J.; Niedenzu, K. *Inorg. Chem.* **1986**, *25* 85–87.

(4) Layton, W. J.; Niedenzu, K.; Smith, S. L. *Z. Anorg. Allg. Chem.* **1982**, *495*, 52–64.

(5) Nöth, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 618–620.

(6) Köster, R.; Grassberger, M. A. *Liebigs Ann. Chem.* **1968**, *719*, 169–186.

(7) Köster, R. *Angew. Chem.* **1958**, *70*, 413–414.

(8) Ryschkewitsch, G. E.; Harris, J. J.; Sisler, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 4515–4517.

(9) Gerwarth, U.; Weber, W. *Inorg. Synth.* **1983**, *22*, 207–208.

(10) *Gmelin Handbuch Der Anorganischen Chemie*; Springer-Verlag: West Berlin, 1978; Vol. 51, Supplement Boron Compounds 17, pp 79–80.

(11) Gerwarth, U.; Weber, W. *Inorg. Synth.* **1983**, *22*, 136.

(12) Jenne, H.; Niedenzu, K. *Inorg. Chem.* **1964**, *3*, 68–70.

(2 H, m), 7.30 (3 H, m), 2.98 (3 H, s), 2.82 (3 H, s); $\delta(^{11}B)$ 36.2 (s, $h_{1/2}$ = 150 Hz).

$CH_3N[BC_6H_5N(CH_3)_2]_2$. The compound was prepared from $(CH_3)_2NB(C_6H_5)Cl$ and $CH_3N[Si(CH_3)_3]_2$ in a fashion analogous to the preparation of $HN[BC_6H_5N(CH_3)_2]_2$:[13] yield, 41%; bp 141–143 °C (1 Torr). Anal. Calcd for $C_{17}H_{25}B_2N_3$ (M_r 293.1): C, 69.67; H, 8.60; B, 7.38; N, 14.34. Found: C, 69.13; H, 8.52; B, 7.26; N, 14.37.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.34 (10 H, m), 2.65 (12 H, s), 2.56 (3 H, s); $\delta(^{11}B)$ 35.6 (s, $h_{1/2}$ = 320 Hz).

The mass spectrum exhibited a strong parent ion near *m/z* 293; the most intense fragmentation peak was observed near *m/z* 248.

$(C_2H_5)(pz)B(\mu\text{-}pz)(\mu\text{-}NH_2)B(C_2H_5)(pz)$ (3, R = C_2H_5, R′ = H). A solution of 4.1 g (25 mmol) of $(-BC_2H_5NH-)_3$ and 5.1 g (75 mmol) of Hpz in 25 mL of $CHCl_3$ was stored at room temperature for 4 weeks. Solvent was then removed under reduced pressure (15 Torr) and the pasty residue was washed with 25 mL of petroleum ether. The remaining crystalline material was collected, washed with petroleum ether, and dried under vacuum to give 6.9 g (93% yield calculated for Hpz) of colorless product, mp 110–111 °C. Anal. Calcd for $C_{13}H_{21}B_2N_7$ (M_r 296.98): C, 52.58; H, 7.13; B, 7.28; N, 33.01. Found: C, 52.17; H, 7.01; B, 7.17; N, 32.81.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.67 (d, J = 2.4) + 7.63 (d, J = 1.6) + 7.60 (d, J = 1.6) + 7.56 (d, J = 2.2) (4 H), 7.50 (d, J = 2.3) + 7.34 (d, J = 2.3) (2 H), 6.48 (t, J = 2.3) + 6.43 (t, J = 2.3) (1 H), 6.30 (2 overlapping d) + 6.29 (2 overlapping d?) (2 H), 5.15* (2 H, s), 1.0–0.8 (10 H, m); $\delta(^{11}B)$ 2.7 (s, $h_{1/2}$ = 135 Hz). On the basis of the ^1H HOMCOR-2D data, the $\delta(^1H)$ signals 7.60/7.56/6.48 are assigned to the terminal pz groups and the pair 7.50/6.48 to the bridging pz group of the most abundant isomer; those at $\delta(^1H)$ 7.67/7.63/6.29 and 7.34/6.43 are assigned to the less abundant species (ratio ca. 6:1).

Mass spectral data: see text. IR: $\nu(NH)$ = 3210 cm^{-1} (with shoulders at 3145 and 3124 cm^{-1}).

$(pz)(C_2H_5)B(\mu\text{-}pz)_2B(pz)(C_2H_5)$. A solution of 2.0 g (12 mmol) of $(-BC_2H_5NH-)_3$ and 2.5 g (37 mmol) of Hpz in 20 mL of mesitylene was refluxed with stirring for 8 h. A colorless precipitate, 2.2 g, was collected and an additional 0.3 g were obtained on concentration of the filtrate to provide for a 78% yield of $(pz)(C_2H_5)B(\mu\text{-}pz)_2B(pz)(C_2H_5)$ as an isomer mixture. Isomer A, mp 152–153 °C, was obtained after two recrystallizations from cyclohexane. The cyclohexane-insoluble material was recrystallized from benzene to give pure isomer *B*, mp 210–212 °C (ratio of A:B = 1:1, i.e. ca. 1 g of each product). Anal. Calcd for $C_{16}H_{22}B_2N_8$ (M_r 348.1): C, 55.20; H, 6.38; B, 6.21; N, 32.20. Found for isomer A: C, 55.07; H, 6.47; B, 6.02; N, 31.99. Found for isomer B: C, 55.36; H, 6.53; B, 6.07; N, 32.26.

NMR data (solution in $CDCl_3$) for isomer A: $\delta(^1H)$ 7.64 (2 H, d, J = 2.5), 7.61 (1 H, d, J = 1.3), 7.17 (1 H, d, J = 2.5), 6.52 (1 H, t, J = 2.5), 6.14 (1 H, unresolved t = two overlapping d), 1.34 (2 H, q, J = 8), 0.71 (3 H, t, J = 8); $\delta(^{11}B)$ 2.2 (s, $h_{1/2}$ = 190 Hz). Data for isomer B: $\delta(^1H)$ 7.67 (2 H, d, J = 2.5), 7.64 (1 H, d, J = 1.4), 7.27 (1 H, d, J = 2.2), 6.55 (1 H, t, J = 2.5), 6.24 (1 H, unresolved t = two overlapping d), 0.91 (2 H, q, J = 8), 0.67 (3 H, t, J = 8); $\delta(^{11}B)$ 2.2 (s, $h_{1/2}$ = 190 Hz).

In the 13-eV mass spectrum of either isomer, only two major ion clusters at *m/z* 319 (parent ion P – 29) and 281 (P – 67), respectively, are observed in about 10:1 relative intensity.

Alternate Procedure. A mixture of 3.0 g (18 mmol) of $(-BC_2H_5NH-)_3$ and 7.5 g (110 mmol) of Hpz was heated to reflux with stirring for 3 h. After the mixture was allowed to stand overnight, the crude solid material was recrystallized from benzene to give isomer B (above) and a small amount of an insoluble residue (which was discarded). After evaporation of the benzene from the filtrate, the resultant residue was recrystallized from cyclohexane to give isomer A (above). The two isomers were obtained in an A:B = 2:1 ratio, i.e. ca. 4 and 2 g, respectively.

The same two isomers were obtained when $(-BC_2H_5NCH_3-)_3$ was reacted with Hpz in a manner as described above.

Alternate Procedure. A solution of 3.2 g (25 mmol) of $C_2H_5B[N(CH)_3)_2]_2$[14] in 15 mL of toluene was heated to reflux and a solution of 5.5 g (81 mmol) of Hpz in 55 mL of toluene was added dropwise with stirring. The mixture was refluxed for 6 h. When the mixture was cooled to room temperature, 1.15 g (26.5%) of a colorless precipitate of essentially pure isomer B formed and was collected, washed with petroleum ether and dried. The filtrate was evaporated, and the residue was washed with petroleum ether (to remove excess Hpz) to give a mixture of A and B, which was worked up as described above. An overall yield of about 60% of pure A and B in about 2:3 molar ratio was obtained.

Table I. Summary of Crystallographic Data and Data Collection Procedures[a] for $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$

	isomer A	isomer B
formula	$C_{16}H_{22}B_2N_8$	$C_{16}H_{22}B_2N_8$
fw	335.9	335.9
cryst size, mm	0.27 × 0.30 × 0.31	0.18 × 0.34 × 0.57
cryst syst	tetragonal	monoclinic
space group	$I4_1/acd$[b]	$P2_1/c$[c]
a, Å	14.876 (6)	8.156 (3)
b, Å	14.876 (7)	14.720 (5)
c, Å	34.932 (22)	7.501 (2)
α, deg	90	90
β, deg	90	95.58 (3)
γ, deg	90	90
Z	16	2
V, Å^3	7730.3	896.3
d_{calcd}, g/cm^3	1.154	1.244
μ, cm^{-1}	0.71	0.60
$F(000)$	2943	344
2θ, deg	2–45	2–45
scan speed, deg/min	4–29.3	4–29.3
scan width, deg	0.6	0.7
total no. of reflcns	1607	2075
no. of unique reflcns	997	1166
no. of variables used	159	151
R	0.0744	0.047
R_w	0.0616	0.049
g	0.000 30	0.000 68
highest residual electron density, e/Å^3	0.266	0.147

[a] In this and all subsequent tables esd's are given in parentheses. [b] Origin choice 2 of ref 22; twofold axis at $^1/_2$, $^1/_4$, $\bar{z}$. The molecule shows crystallographically imposed C_2 symmetry. [c] The molecule possesses a crystallographic inversion center at 010 = 000.

Alternate Procedure. A mixture of **3** (R = C_2H_5, R′ = H, CH_3) was heated with excess Hpz to 180–200 °C for 4 h. After the mixture was cooled to room temperature excess Hpz was removed and the residue was worked up as described above to give an essentially quantitative yield of A and B in about 2:1 molar ratio.

Crystal data on the two isomers A and B of $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$ were obtained on a Syntex P3 automated diffractometer by using graphite-monochromated Mo Kα radiation and standard operating techniques. Unit cell parameters were obtained from the least-squares refinement of the diffracting positions of 18 and 22 high-angle reflections, respectively. Intensity data were collected in the ω-scan technique in the range $2° < 2\theta < 45°$. Scattering factors for neutral atoms were taken as implemented in the SHELXTL structure solution package. The structures were solved by direct methods, and the *E* maps revealed the positions of all non-hydrogen atoms. Parameters were refined by using the blocked-cascade method. After convergence was achieved in further refinement with anisotropic temperature factors, all hydrogen positions were revealed from a difference Fourier map. Refinement of their positions was included with use of isotropic temperature factors in the final refinement. Definitions are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R = \sum(w^{1/2}||F_o| - |F_c||)/\sum(w^{1/2}|F|)$, where $w^{-1} = \sigma^2(F_o) - g(F_o)^2$. A summary of the crystallographic data and data collection procedures is given in Table I.

$(CH_3)_2HN{\cdot}B(C_2H_5)(pz)_2$. A mixture of 3.2 g (25 mmol) of $C_2H_5B[N(CH_3)_2]_2$,[14] 3.2 g (47 mmol) of Hpz, and 30 mL of hexane was stirred at room temperature for 24 h. The precipitate was collected, washed with hexane, and dried under vacuum to give 3.8 g (70%) of colorless crystals of the desired compound, mp 86–90 °C dec. The material can be recrystallized from hexane or cyclohexane.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.69 (2 H, d, J = 1.5), 7.53 (2 H, d, J = 2.2), 6.7* (1 H, s), 6.26 (2 H, unsym t = two overlapping d), 2.39* (6 H, s; at –44 °C, unsym d, $J \simeq 6.5$), 1.07 (2 H, q, J = 7.5), 0.72 (3 H, t, J = 7.5); $\delta(^{11}B)$ 2.7 (s, $h_{1/2}$ = 120 Hz).

$(C_2H_5)(pz)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(C_2H_5)(pz)$ (3, R = C_2H_5, R′ = CH_3). A solution of 4.25 g (62.5 mmol) of Hpz and 5.2 g (25 mmol) of $(-BC_2H_5NCH_3-)_3$ in 30 mL of $CHCl_3$ was stored at room temperature for 4 weeks. Solvent was removed under reduced pressure, and the residue was washed with petroleum ether to give 6.0 g (93% yield) of the desired product, mp 104–108 °C. Anal. Calcd for $C_{14}H_{23}B_2N_7$ (M_r 311.01): C, 54.07; H, 7.45; B, 6.95; N, 31.53. Found: C, 53.92; H, 7.38; B, 6.93; N, 31.31.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.75–7.61 (m) + 7.55 (d) + 7.35 (d) + 7.15 (d) (6 H), 6.54 (t, J = 2.4) + 6.38 (t, J = 2.3) + 6.30

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(13) Niedenzu, K.; Seelig, S. S.; Weber, W. *Z. Anorg. Allg. Chem.* **1981**, *483*, 51–62.

(14) Nöth, H.; Fritz, P. *Z. Anorg. Allg. Chem.* **1963**, *322*, 297–309.

(m = overlapping d?) + 6.23 (m) (3 H), 2.22 (d, $J = 6.2$) + 2.02 (d, $J = 6.3$) (ratio 1:1, 3 H), 1.2–0.5 (10 H, m); $\delta(^{11}B)$ 3.0 (s, $h_{1/2}$ = 190 Hz).

A very weak parent ion P – 1 was observed in the low-voltage mass spectrum of the material. In the infrared spectrum, ν(NH) = 3152 cm^{-1} (with shoulders at 3208 and 3090 cm^{-1}).

$(C_6H_5)(pz)B(\mu\text{-}pz)(\mu\text{-}NH_2)B(C_6H_5)(pz)$ (3, R = C_6H_5, R′ = H). A solution of 3.7 g (55 mmol) of Hpz on 20 mL of diethyl ether was added with stirring to a mixture of 7.4 g (27 mmol) of $HN[BC_6H_5N(CH_3)_2]_2$ and 20 mL of ether. A colorless precipitate formed immediately, and dimethylamine was evolved. The mixture was heated with stirring to reflux for 20 h. After the mixture was cooled to room temperature, the precipitate was collected, washed with ether and then petroleum ether, and dried in vacuum to give 4.3 g of product (60% yield calculated for Hpz), mp 168–172 °C. (An additional crop of much less pure material, mp 144–158 °C, can be obtained on concentration of the filtrate.) The initial material was recrystallized (with considerable losses) from cyclohexane/benzene; no change in the mp of 168–172 °C was observed. Anal. Calcd for $C_{21}H_{21}B_2N_7$ (M_r 393.07): C, 64.17; H, 5.39; B, 5.50; N, 24.94. Found: C, 63.51; H, 5.40; B, 5.54; N, 24.46.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.7–7.0 (16 H, series of ill-resolved multiplets with major peaks at 7.57, 7.49, 7.37, 7.24, and 7.08 and minor peaks at 7.72, 7.52, 7.20, 6.98), 6.56 (1 H, t, $J = 2.3$ Hz), 6.23 (2 H, unsymmetrical t = two overlapping d), 5.9* (2 H, s); $\delta(^{11}B)$ 2.1 (s, $h_{1/2}$ = 220 Hz).

The major ion observed in the low-voltage mass spectrum is at m/z 248. IR: ν(NH) = 3294, 3169, 3147, 3096 cm^{-1}.

An identical material was obtained from the reaction of excess of $(-BC_6H_5NH-)_3$ with Hpz as described below for the reaction $(-BC_6H_5NCH_3-)_3$ with Hpz.

$(C_6H_5)(pz)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(pz)(C_6H_5)$ (3, R = C_6H_5, R′ = CH_3). A slurry of 3.5 g (10 mmol) of $(-BC_6H_5NCH_3-)_3$ and 2.1 g (31 mmol) of Hpz in 100 mL of hexane was refluxed with stirring for 12 h. The solid material (4.6 g) was collected and washed with ether. It was recrystallized from cyclohexane/benzene to give 2.4 g (58%) of material, mp 186–191 °C. Anal. Calcd for $C_{22}H_{23}B_2N_7$ (M_r 407.10): C, 64.91; H, 5.69; B, 5.31; N, 24.08. Found: C, 64.81; H, 5.81; B, 5.56; N, 23.95.

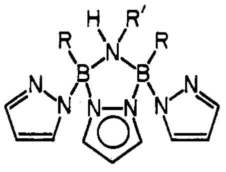
NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.42* (1 H, s), 7.8–7.0 (16 H, m with d at 7.42, 7.18, and 7.08), 6.54 (1 H, 2 overlapping t of different intensity), 6.30 (2 H, m), 2.27 (d, $J = 5.6$) + 2.04 (d, $J = 6.0$) (ratio 4:1, 3 H); $\delta(^{11}B)$ 3.2 (s, $h_{1/2}$ = 250 Hz). IR: ν(NH) = 3117 cm^{-1} (with shoulders at 3139 and 3098 cm^{-1}).

Alternate Procedure. A solution of 4.85 g (71.3 mmol) of Hpz in 20 mL of ether was added to a solution of 7.3 g (25 mmol) of $CH_3N[BC_6H_5N(CH_3)_2]_2$ in 40 mL of ether. An immediate exothermic reaction occurred with concurrent precipitation of a colorless material. The mixture was refluxed with stirring for 25 h, and the insoluble material was collected, washed with ether and then petroleum ether and dried under vacuum to give 7.23 g (74.8% calculated for Hpz) of product, mp 190–192 °C, identical (spectroscopic data) with the material as described above.

Results and Discussion

Formation and Identification of the (μ-Amido)(μ-pyrazolato)diboron Species 3. When $(-BC_2H_5NH-)_3$ and Hpz (in a molar ratio not to exceed 1:4) were mixed at room temperature in $CHCl_3$ solution, a slightly exothermic reaction initiated with simultaneous generation of ammonia. The formation of a species containing four-coordinate boron was readily evidenced by the appearance of a broad ^{11}B NMR signal near 1 ppm, and signals for different pyrazolyl groups were observed in the ^1H NMR spectrum (evidenced best by the pz 4-H signals). However, even after 3 days at room temperature the spectra were not static and continued to change slowly. After 1 week minor additional changes were still observed, but there were no noteworthy additional changes after 2 weeks at room temperature. After 4 weeks the reaction had come to complete rest, and no further changes in the NMR spectra were observed. At this time the solution contained (besides unreacted borazine) two isomeric species in about 6:1 molar ratio. On the basis of HOMCOR-2D ^1H NMR spectral data, the structure of a (μ-pyrazolato)(μ-amido)diboron compound, $R(pz)B(\mu\text{-}pz)(\mu\text{-}NH_2)BR(pz)$ (3, R = C_2H_5, R′ = H), could be assigned to the isomers.

A mixture of the two isomers not contaminated by an excess of borazine was obtained by evaporating the solvent under reduced pressure. The resultant pasty residue was then washed with petroleum ether in order to dissolve the excess of borazine and to leave the crystalline material 3 in essentially quantitative yield (calcd for Hpz). The formation of the (μ-amido)(μ-pyrazolato)diboron species 3 can be illustrated by eq 1.



3

$$2(-BRNR')_3 + 9Hpz \rightarrow 3(\mathbf{3}) + 3R'NH_2 \qquad (1)$$

The more abundant isomer of 3 with R = C_2H_5 and R′ = H had the following ^1H NMR data for the pz region: δ 7.60/7.56/6.30 for the two terminal pz groups and δ 7.50/6.48 for the bridging pz group. The NH_2 signal for both isomers was evidenced by a broad singlet at 5.15 ppm; $\delta(^{11}B)$ for both isomers was 2.7 (s, $h_{1/2}$ = 135 Hz). In conjunction with the observation of only one and reasonably sharp ^{11}B NMR signal for the material, the ^1H NMR data clearly dispute the existence of a pyrazabole structure, i.e., $(H_2N)RB(\mu\text{-}pz)_2BR(pz)$. Hence, it is worth noting that compounds of this latter (isomeric) type, which are true pyrazaboles, containing a central $B(\mu\text{-}pz)_2B$ unit and a B_2N_4 ring, have previously been described as products of the interaction of Hpz with (monoboron) aminoboranes (see below).[13]

The predominant ion cluster observed in the low-voltage mass spectrum of the freshly isolated material 3 with R = C_2H_5 and R′ = H was observed in the m/z 200 region, corresponding to a composition $B_2(pz)_2(C_2H_5)(NH) = C_2H_{21}B_2N_5$, which was confirmed by the calculated and observed relative fractional abundances (fa):

m/z	198	199	200	201	202
fa(calcd)	0.035	0.289	0.606	0.064	0.003
fa(obsd)	0.041	0.294	0.621	0.059	0.002

A very minor peak was observed for the parent ion P – 1 (calculated for monoisotopic P, 297) and a fairly strong peak at m/z 68 (=Hpz). The general appearance of the mass spectral fragmentation does not follow the usual fragmentation pattern of pyrazaboles,[15,16] thus supporting the assumed lack of a pyrazabole structure, i.e. a central $B(\mu\text{-}pz)_2B$ moiety, in the material.

The initial steps of the reaction between $(-BC_2H_5NH-)_3$ and Hpz were best observed when the borazine was added to a large excess of Hpz. In that case, initially only a fairly broad ^{11}B NMR signal for four-coordinate boron was observed with δ 0.4, exhibiting a shoulder at δ 5.5. After the reaction mixture was allowed to stand for 2 days, an additional signal near 2.5 ppm became evident. On prolonged standing, this latter shoulder emerged as the dominant and finally sole peak (δ 2.7). Similar changes were observed in the ^1H NMR spectrum. For example, after mixing of the reactants, the quartet/triplet (δ 0.95/0.84) pattern of the ethyl groups of the borazine was not observed. Rather, the mixture exhibited a broad singlet (δ 1.12) and two triplets (δ 0.80 and 0.58, respectively), the latter appearing in 2:1 ratio. On standing, the signals became more and more complex until (after about 2 weeks at room temperature) the multiplet of the final product emerged. Furthermore, initially the signals of unreacted Hpz at δ 7.54 (2 H, d) and 6.36 (1 H, t) as well as a signal pair δ 7.72(2 H, d)/6.30(1 H, t) were observed. Constant changes occurred until, ultimately, the signals of the final product and of Hpz remained.

It has been shown that the initial product of the interaction of equimolar amounts of a tri-*B*-organylboroxin, $(-BRO-)_3$ with Hpz is an adduct containing one three-coordinate and two four-coordinate boron atoms.[17] It seems reasonable to assume that a similar species, 4 ($\delta(^{11}B)$ ca. 0.4 for the four-coordinate B atoms?), is formed on interaction of $(-BRNR'-)_3$ with Hpz.

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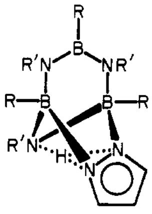
(15) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1662–1666.

(16) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 220–223.

(17) Bielawski, J.; Niedenzu, K. *Inorg. Chem.* **1986**, *25*, 1771–1774.



4

However, the third boron atom of the borazine may coordinate with the excess of Hpz to cause the observed signal $\delta(^{11}B)$ 5.5. Such an initial intermediate would account for the observation of two types of boron-bonded ethyl group signals in the ^1H NMR spectrum in 2:1 ratio as described above. The singly coordinated Hpz group may rapidly exchange with free Hpz, thus giving rise to only one common set of ^1H signals for noncoordinated and monocoordinated Hpz. The second (and much less abundant) set of pz signals as discussed above can then be assigned to the doubly coordinating Hpz group as shown in **4**. Significantly, **4** contains the B(μ-pz)(μ-NHR')B skeleton of the ultimate product.

After adduct formation, the next step in the (–BRO–)$_3$/Hpz interaction is the elimination of water and formation of two terminal B-pz bonds with retention of the bridging O–BR–O moiety to give the triply bridged pyrazabole **2**.[17] In the (–BRNR'–)$_3$/Hpz case, however, the two terminal B–pz bonds are seemingly formed by attack at the B–NR'–BR–NR'–B linkages of **4** to give the observed product **3** with the elimination of amine. In this process, however, no RB(NHR')$_2$ is generated, since this latter should react with Hpz to give R'H$_2$N·BR(pz)$_2$ (see below), which was not observed.

Unfortunately, the isomers of **3** could not be separated, although it was noted that one (the less abundant) isomer seems to hydrolize quite readily to yield the pyrazabole **2** (which also could not be separated from **3** but was clearly identified by mass spectral and NMR data). The hydrolysis of **3** may proceed as is illustrated by eq 2; this would suggest that even the pyrazolyl-bridge between the two boron atoms of **3** is attacked (in order to generate a O–BR–O moiety).

$$3(\mathbf{3}) + 4H_2O \rightarrow 3NH_3 + 5Hpz + 2(\mathbf{2}) \qquad (2)$$

Complete hydrolysis of **3** to yield **2** was achieved when the former compound was stirred with water at room temperature. The progress of the hydrolysis is readily observed by the changes in the ^1H NMR spectrum of the material. It has not been possible to separate **2** from **3**; hence the preparation of **3** must be performed under strict exclusion of moisture. Also, it is difficult to completely separate an excess of Hpz from **3**. Therefore it is recommended to use an excess of (–BRNR'–)$_3$ in the preparation of **3**.

The ^{11}B NMR and elemental analysis data substantiated the formation of compound **3** with R = C_2H_5 and R' = CH_3 in the reaction of (–$BC_2H_5NCH_3$–)$_3$ with Hpz. Also, the overall ^1H NMR data were in agreement with the suggested structure, but even on the basis of a ^1H HOMCOR-2D study, the spectrum could not be completely assigned. For example, despite the fact that the signal at δ 6.54 is a clean 1:2:1 triplet and thus should be assigned to a bridging pz 4-H, it is coupled with two doublets (rather than the expected one) at δ 7.45 and 7.65, respectively. On the other hand, the triplet at δ 6.38 is coupled only to the doublet at δ 7.35. The multiplet at δ 6.30 is coupled to two doublets at δ 7.15 and 7.68, respectively, but the multiplet at δ 6.23 is coupled to at least four signals in the δ 7.55–7.75 region. Moreover, the isomer distribution (as observed by the ^1H NMR signals of the (N)CH_3 group) differed slightly from one experiment to another although they were performed under seemingly similar conditions. Furthermore, occasionally there were indications for the formation of an additional isomer, as was shown by the appearance of another ^1H NMR signal for the methyl group. In the low-voltage mass spectrum of the material, a very weak parent ion P was observed; in the 70 eV spectrum, *m/z* 296 (parent ion P – 15) appeared instead in addition to major fragments at *m/z* 282, 243, and (the base peak) 214. It must be noted that traces of higher molecular weight species were also observed but did not recognizably affect the NMR or elemental analysis data.

The compounds were found to be thermally stable and could be sublimed under vacuum, although this procedure was not useful for purification. All attempts to promote an intermolecular condensation of **3** to yield a species of the type R'N[BR(μ-pz)$_2$BR(pz)]$_2$ by thermal treatment failed.

The existence of species of type **3** is surprising. First of all, the reaction of tris(dimethylamino)borane with pyrazole has previously[13] been found to give either the monoboron species $(CH_3)_2HNB(pz)_3$ = H[$(CH_3)_2NB(pz)_3$] or true pyrazaboles with a central B(μ-pz)$_2$B unit, including the species [$(CH_3)_2N$](pz)B(μ-pz)$_2$B(pz)$_2$ and [$(CH_3)_2N$](pz)B(μ-Pz)$_2$B[$N(CH_3)_2$](pz). Similar products were obtained on reaction of $C_6H_5B[N(CH_3)_2]_2$ with Hpz. Similarly, in the present study the room-temperature reaction of $C_2H_5B[N(CH_3)_2]_2$ with Hpz was found to yield $(CH_3)_2HN{\cdot}B(C_2H_5)(pz)_2$. In refluxing hexane, however, the reaction yielded the pyrazabole (C_2H_5)(pz)B(μ-pz)$_2$B(C_2H_5)[$N(CH_3)_2$] ($\delta(^{11}B)$ 4.8 and 1.7), and in refluxing toluene the species (C_2H_5)(pz)B(μ-pz)$_2$B(C_2H_5)(pz) was formed (see below).

Since **3** contains terminal boron–bonded pz groups that are available for coordination and, hence, could prompt the formation of a B(μ-pz)$_2$B skeleton, there must be some inherent reason for the preferred bridging of the two boron atoms by only one pyrazolyl group and an amido group rather than two pyrazolyl groups. In this conjunction it may be noted that an analogous preferred bridging function for an $N(CH_3)_2$ group (as compared to a pz group) has recently been observed in two molybdenum poly(1-pyrazolyl)borate complexes, where this event was thought to be due to a greater compactness of the species B(μ-pz)(μ-NMe_2)Mo as compared to B(μ-pz)$_2$Mo.[18] Furthermore, the B_2N_3 ring system of **3** has also been observed in other pyrazole derivatives of boron, i.e. in the low-temperature dimerization of 1,3-dimethyl-2-(1-pyrazolyl)diazaboracyclopentane[19] and the low-temperature interaction of the latter compound with a (dimethylamino)dialkylboranes.[20]

In the present case, the availabilty of a preexisting B–N–B linkage (from the starting borazine) seems to be the prerequisite that leads to the preferential formation of **3** rather than a true pyrazabole. This assumption was supported by the fact that bis((dimethylamino)boryl)amines of the type R'N[$BRN(CH_3)_2$]$_2$ (and containing the N–B–N–B–N arrangement) also reacted with Hpz to give the same compounds of type **3**, which were obtained from the corresponding borazines. This was shown by the reaction of the two bis((dimethylamino)boryl)amines with R = C_6H_5 and R' = H or CH_3, respectively, as illustrated in eq 3.

$$R'N[BRN(CH_3)_2]_2 + 3Hpz \rightarrow \mathbf{3} + 2(CH_3)_2NH \qquad (3)$$

Although the aromatic region from δ 7.7 to 7.0 of the ^1H NMR spectra of the species of type **3** with R = C_6H_5 was quite complex, it was readily established that two of the three pz groups of the molecules were terminal rather than bridging. For example, in the case of R' = H, the signal of the pz 4-H proton $\delta(^1H)$ 6.23 was not only an unsymmetrical triplet equivalent to two overlapping doublets (1 H), but irradiation of this signal led to the collapse of two doublets at δ 7.37 and 7.49 (1 H each), respectively. On the other hand, the signal $\delta(^1H)$ 6.56 was a clear triplet (1 H), irradiation of which led to the collapse of only one doublet (2 H) at δ 7.57 ppm, and, hence, must be assigned to a bridging pz group.

No principal differences were observed when the reaction between (–BRNR'–)$_3$ and Hpz was carried out in the presence of a large excess of Hpz or in refluxing $CHCl_3$, benzene, or toluene rather than at room temperature. In those latter cases, the reaction was completed within several hours and there were small differences with respect to the distribution of the isomers of **3**. On the other hand, minor variations with respect to the isomer distribution were also observed when the reactions were run under

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(18) Niedenzu, K.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 4222–4223.
(19) Weber, W.; Niedenzu, K. *J. Organomet. Chem.* **1981**, *205*, 147–156.
(20) Alam, F.; Niedenzu, K. *J. Organomet. Chem.* **1982**, *240*, 107–119.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Isomer A of $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$

atom	*x*	*y*	*z*	U^a
N1	5411 (2)	1648 (2)	378 (1)	45 (1)
N2	5954 (2)	2385 (2)	352 (1)	44 (1)
N5	4404 (2)	1526 (2)	−184 (1)	44 (1)
N6	3604 (2)	1508 (2)	−372 (1)	59 (1)
B	4408 (3)	1646 (3)	258 (1)	42 (1)
C1	5937 (3)	936 (3)	451 (1)	55 (2)
C2	6817 (3)	1207 (3)	475 (1)	61 (2)
C3	6806 (3)	2113 (3)	411 (1)	54 (2)
C7	5083 (3)	1411 (2)	−436 (1)	50 (1)
C8	4737 (3)	1319 (2)	−793 (1)	54 (1)
C9	3822 (3)	1386 (3)	−738 (1)	58 (2)
C10	3825 (3)	907 (3)	471 (1)	54 (2)
C11	3814 (3)	948 (3)	905 (1)	80 (2)
H1	5652 (22)	380 (22)	478 (9)	51 (10)
H2	7308 (27)	823 (27)	500 (11)	90 (14)
H3	7296 (22)	2576 (22)	393 (8)	56 (10)
H7	5678 (21)	1406 (20)	−344 (8)	43 (10)
H8	5062 (23)	1207 (21)	−1039 (8)	70 (10)
H9	3362 (24)	1366 (22)	−909 (11)	65 (13)
H10a	4024 (22)	325 (23)	386 (9)	59 (11)
H10b	3177 (28)	897 (25)	373 (10)	84 (13)
H11a	4434 (27)	867 (27)	1004 (11)	90
H11b	3473 (23)	443 (24)	1039 (10)	90
H11c	3567 (24)	1501 (25)	1013 (10)	90

[a] Equivalent isotropic *U* for non-hydrogen atoms defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for the Cis (A) and Trans (B) Isomers of $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$

atoms	A	B
	Distances	
B1–N1	1.550 (5)	1.577 (3)
B2–N2	1.574 (5)	1.557 (3)
N1–N2	1.365 (4)	1.356 (2)
N1–C1	1.341 (5)	1.334 (3)
N2–C3	1.346 (5)	1.340 (3)
C1–C2	1.373 (6)	1.366 (3)
C2–C3	1.366 (6)	1.362 (3)
B1–C10	1.585 (6)	1.597 (3)
B1–N5	1.554 (5)	1.548 (3)
	Angles	
N1–B1–N4	105.8 (3)	106.6 (1)
B1–N1–N2	123.6 (3)	126.0 (2)
B2–N2–N1	123.2 (3)	125.0 (1)
N1–B1–C10	113.6 (3)	110.7 (2)
N4–B1–C10	110.6 (3)	112.2 (2)
N1–B1–N5	105.8 (3)	107.6 (1)
N4–B1–N5	108.1 (3)	107.0 (1)
C10–B1–N5	112.6 (3)	112.5 (1)

seemingly similar conditions at room temperature. However, in no case was the formation of a triply bridged pyrazabole of either the type $RB(\mu\text{-}pz)_2(\mu\text{-}NR'BRNR')BR$ or $RB(\mu\text{-}pz)_2(\mu\text{-}NR')BR$ observed.

Formation of Pyrazaboles. The bis(amino)borane $RB[N(CH_3)_2]_2$ ($R = C_2H_5$) reacted with excess Hpz in refluxing toluene to yield the pyrazabole $R(pz)B(\mu\text{-}pz)_2BR(pz)$. As noted above, $(-BRNR'-)_3$ reacted with Hpz under the same conditions to give the (μ-amido)(μ-pyrazolato)diboron compound **3**. However, **3** reacted with Hpz in refluxing Hpz to form the same pyrazabole, which was also obtained directly on reaction of $(-BRNR'-)_3$ in refluxing Hpz. Similarly, *B*-phenylborazines as well as compounds of type **3** with $R = C_6H_5$ were transformed to the corresponding pyrazaboles by heating in refluxing Hpz. All of these reactions are essentially quantitative, and materials of high purity were obtained quite readily.

X-ray Crystal and Molecular Structure of $R(pz)B(\mu\text{-}pz)_2BR(pz)$ ($R = C_2H_5$). The pyrazabole $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$ could be separated into two isomers melting at 152–153 °C and 210–212 °C, respectively. This is the first known case that a pyrazabole of the type $RR'B(\mu\text{-}pz)_2BRR'$ could be separated into two isomers, and the crystal and molecular structures of both isomers were determined by single-crystal X-ray diffraction analysis.

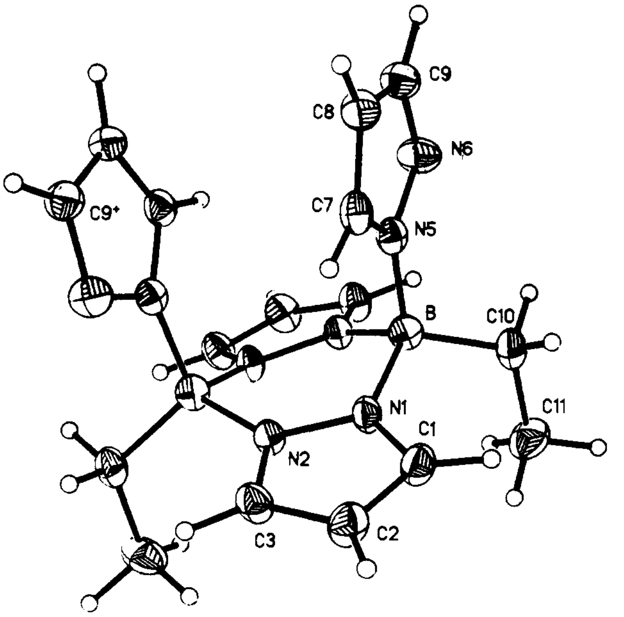

Figure 1. ORTEP plot of the isomer A of 4,8-diethyl-4,8-bis(1-pyrazolyl)pyrazabole, $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$.

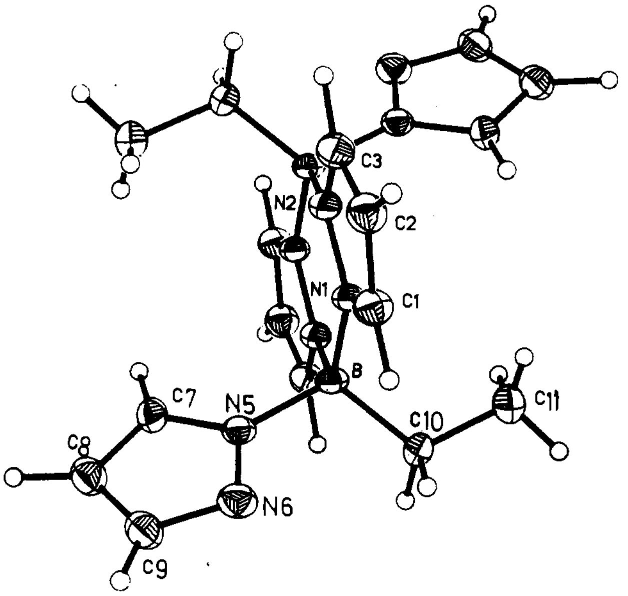

Figure 2. ORTEP plot of the isomer B of 4,8-diethyl-4,8-bis(1-pyrazolyl)pyrazabole, $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$.

The lower melting isomer (A) crystallizes in the tetragonal space group $I4_1/acd$ with 16 molecules in the unit cell. The central B_2N_4 ring has boat conformation and the terminal boron substituents are in cis orientation whereby the pz groups occupy the axial positions. The BN_2 plane of the boat forms an angle of 23.5° with the central N_4 plane, of which the bridging pz rings are deflected by 11.1°. The terminal pz groups are tilted by 86.3° with respect to the central N_4 plane. The structure of isomer A is illustrated in Figure 1, atomic coordinates are listed in Table II, and selected bond distances and bond angles are given in Table III.

The higher melting isomer (B) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell. Here, the central B_2N_4 ring has the chair conformation (rare for a pyrazabole, see below) with the terminal boron substituents in trans orientation. The two terminal pz groups again are in the axial positions, their planes being oriented by 82.2° with respect to the

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for Isomer B of $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$

atom	*x*	*y*	*z*	*U*[a]
N1	411 (2)	10495 (1)	1606 (2)	34 (1)
N2	−1171 (2)	10216 (1)	1247 (2)	34 (1)
N5	2824 (2)	9422 (1)	1642 (2)	35 (1)
N6	3930 (2)	9637 (1)	3058 (2)	44 (1)
B	1912 (2)	10199 (1)	564 (3)	33 (1)
C3	−2013 (2)	10494 (1)	2594 (3)	42 (1)
C2	−987 (3)	10949 (1)	3829 (3)	45 (1)
C1	518 (3)	10931 (1)	3173 (3)	45 (1)
C9	4436 (3)	8846 (2)	3762 (3)	49 (1)
C8	3690 (3)	8120 (2)	2831 (3)	48 (1)
C7	2671 (2)	8510 (1)	1505 (3)	42 (1)
C10	3083 (2)	11046 (1)	283 (3)	42 (1)
C11	2268 (3)	11833 (2)	−744 (4)	64 (1)
H1	1506 (24)	11136 (12)	3645 (26)	50
H2	−1218 (23)	11238 (12)	4892 (24)	50
H3	−3103 (23)	10344 (12)	2579 (25)	50
H7	1925 (24)	8270 (14)	535 (28)	50
H8	3837 (23)	7467 (16)	3091 (25)	50
H9	5232 (26)	8835 (12)	4759 (28)	50
H10a	3534 (25)	11275 (14)	1429 (29)	50
H10b	4021 (26)	10853 (14)	−305 (25)	50
H11a	1766 (26)	11655 (15)	−1881 (29)	50
H11b	3016 (24)	12298 (15)	−958 (27)	50
H11c	1351 (27)	12077 (14)	−206 (26)	50

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

N_4 plane. The N–B–N plane of the ring forms an angle of 13.6° with the N_4 plane, with which the bridging pz rings are almost coplanar. The structure of isomer B is shown in Figure 2, atomic coordinates are listed in Table IV, and selected bond distances and bond angles are given in Table III.

Corresponding B–N distances of isomers A and B are essentially identical with a surprisingly long bond to the terminal pz groups. Interestingly, the B–N bonds within the central B_2N_4 ring differ by 0.02 Å, perhaps signaling the construction of the pyrazabole skeleton by two monomeric 1-pyrazolylborane units. The B–C distance of 1.593 Å is in excellent agreement with the sum of the covalent radii.

In conjunction with previous X-ray data on pyrazaboles,[21] some structural trends are now quite apparent. Firstly, terminal pz groups have a distinct preference for the axial positions. They are found to be orthogonal to the N_4 plane, and the NN vector includes angles with the BB vector ranging from 100 to 120°. This arrangement seems to impair interaction with the H atoms of the bridging pz groups. Also, the boat conformation of the central B_2N_4 ring is quite predominant. The chair conformation is observed only if the two terminal substituents at each boron atom are different and trans to one another. In addition, the predominance of isomer A suggests that the boat conformation is energetically favored.

Conclusion. The present study illustrates that only the first steps of the interaction of pyrazole with boroxins or borazines, respectively, are comparable by forming adducts such as **4**. Subsequently, different condensations occur to yield either **2** or **3**, respectively, and this difference may be due to the electronic environment of the three-coordinate boron of the heterocycle as illustrated in **4**. Still, the ready conversion of B–O bonds to B–N bonds in the $(\text{–BRO–})_3$/Hpz case is somewhat surprising, as is the lack of a NR′–BR–NR′-bridged analogue of **2**. Also, it must be emphasized that formation of **3** requires a B–N–B bond in the starting material, which may be a borazine or a diborylamine. A substantial difference between **2** and **3** resides in the fact that **2** does not react with refluxing Hpz. In contrast, under these same conditions **3** is readily converted to a pyrazabole of the type $R(pz)B(\mu\text{-}pz)_2BR(pz)$, which may exist in conformational isomers, as was documented for $R = C_2H_5$.

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Supplementary Material Available: Complete listings of bond angles and distances and anisotropic thermal parameters for the two isomers of 4,8-diethyl-4,8-bis(1-pyrazolyl)pyrazabole (5 pages); structure factor tables for both isomers (13 pages). Ordering information is given on any current masthead page.

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(21) Brock, C. P.; Niedenzu, K.; Hanecker, E.; Nöth, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1458–1463 and references cited therein.

(22) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.

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Reactions of 2-Substituted Ethylamines with Hexachlorocyclotriphosphazene

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The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with 2-substituted ethylamines have been investigated. In the case of 2-haloethylamines the following compounds have been prepared: $N_3P_3Cl_5NHCH_2CH_2X$ (X = Cl, Br), 2,2-$N_3P_3Cl_4(NHCH_2CH_2X)_2$ (X = Cl, Br), and 2,2,4,4-$N_3P_3Cl_2(NHCH_2CH_2Cl)_4$. Traces of 2,2,4-$N_3P_3Cl_3(NHCH_2CH_2Cl)_3$ were observed. In acetonitrile nongeminal as well as geminal bis derivatives were obtained. A reaction with 2-chloroethanol led to 2,2-$N_3P_3Cl_4(OCH_2CH_2Cl)_2$ while the use of 2-methoxyethylamine gave 2,4-$N_3P_3Cl_4(NHCH_2CH_2OCH_3)_2$. The mono- and bis((2-chloroethyl)amino) derivatives have been converted to their dimethylamino derivatives, $N_3P_3[N(CH_3)_2]_{6-n}[NHCH_2CH_2N(CH_3)_2]_n$ ($n = 1, 2$). All compounds were characterized by mass spectrometry and NMR (^{31}P, ^1H) spectroscopy. The regioselectivity observed in these reactions is discussed in terms of substituent and incoming-group effects.

Introduction

The reactions of primary and secondary amines with halocyclophosphazenes are among the most widely studied processes in phosphazene chemistry.[1] The reasons for the intensive study of these reactions are twofold. Kinetic studies and product analysis have allowed for a detailed understanding of the mechanisms by which these reactions occur.[2,3] At the stage of disubstitution in the reaction of primary amines with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, the relative amount of the geminal (2,2) isomer increases with the steric bulk of the amine. Thus, while the nongeminal (2,4) bis isomers predominate in the reactions of methyl[4,5] and ethylamine,[6] the geminal isomer is produced ex-

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(1) Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.

(2) Gabay, Z.; Goldschmidt, J. M. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1456.

(3) Katti, K. V.; Krishnamurthy, S. S. *J. Chem. Soc., Dalton Trans.* **1985**, 285.

(4) Lehr, W. *Z. Anorg. Allg. Chem.* **1967**, *352*, 27.

0020-1669/86/1325-4628$01.50/0