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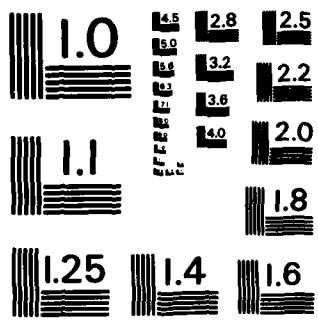

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Syntheses and Reactions of Pyrazaboles

by

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The unsymmetrical pyrazabole $(C_6H_5)_2B(\mu\text{-pz})_2BH_2$ (pz = $N_2C_3H_3$ = pyrazolyl) was prepared by the reaction of $K[(C_6H_5)_2Bpz_2]$ with $(CH_3)_2NBH_2I$; subsequent halogenation with Br_2 yielded $(C_6H_5)_2B(\mu\text{-pz})_2BBr_2$. Similarly, $(C_2H_5)_2B(\mu\text{-pz}')_2BH_2$ (Hpz' = 3,5-dimethylpyrazole) was converted to

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$(C_2H_5)_2B(\mu\text{-}pz')_2EBr_2$. Reaction of $H_2B(\mu\text{-}pz')_2EH_2$ with (even an excess of) BBr_3 gave a mixture of cis and trans isomers of $HBrB(\mu\text{-}pz')_2BHBr$, whereas reaction with Br_2 afforded $Br_2B(\mu\text{-}pz')_2BBr_2$. Reaction of the latter compound with Kpz yielded $pz_2B(\mu\text{-}pz')_2Bpz_2$, the first characterized pyrazolylpyrazabole containing different pyrazolyl moieties bonded to the same boron atom. A second, polymeric modification of $Hpz'B(\mu\text{-}pz')_2BHpz'$ was identified; it appears to be the one reacting with additional Hpz' to form $pz'_2B(\mu\text{-}pz')_2Bpz'_2$. The latter forms a monohydrate in a reversible reaction, but no similar interaction occurs with NH_3.

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506; and the Polymer Products Department, E. I. DuPont de Nemours & Co., Parkersburg, West Virginia 26101

Syntheses and Reactions of Pyrazaboles[1]

W. J. Layton,[a] K. Niedenzu,[a] P. M. Niedenzu,[a] and S. Trofimenko[b]

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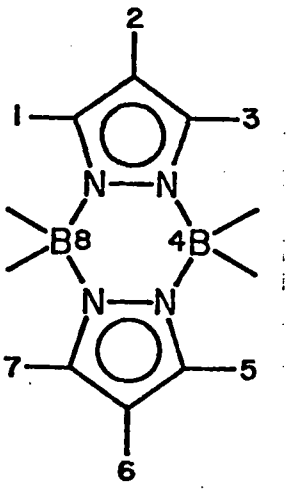
The unsymmetrical pyrazabole $(C_6H_5)_2B(\mu\text{-}pz)_2BH_2$ (pz = $N_2C_3H_3$ = pyrazolyl) was prepared by the reaction of $K[(C_6H_5)_2Bpz_2]$ with $(CH_3)_3NBH_2I$; subsequent halogenation with Br_2 yielded $(C_6H_5)_2B(\mu\text{-}pz)_2BBr_2$. Similarly, $(C_2H_5)_2B(\mu\text{-}pz')_2BH_2$ (Hpz' = 3,5-dimethylpyrazole) was converted to $(C_2H_5)_2B(\mu\text{-}pz')_2BBr_2$. Reaction of $H_2B(\mu\text{-}pz')_2BH_2$ with (even an excess of) BBr_3 gave a mixture of cis and trans isomers of $HBrB(\mu\text{-}pz')_2BHBr$, whereas reaction with Br_2 afforded $Br_2B(\mu\text{-}pz')_2BBr_2$. Reaction of the latter compound with Kpz yielded $pz_2B(\mu\text{-}pz')_2Bpz_2$, the first characterized pyrazolylpyrazabole containing different pyrazolyl moieties bonded to the same boron atom. A second, polymeric modification of $Hpz'B(\mu\text{-}pz')_2BHpz'$ was identified; it appears to be the one reacting with additional Hpz' to form $pz'_2B(\mu\text{-}pz')_2Bpz'_2$. The latter forms a monohydrate in a reversible reaction, but no similar interaction occurs with NH_3.

Introduction

The pyrazaboles of the general structure 1 (with positional numbering) are a chemically and thermally remarkably stable class of heterocycles containing four-coordinate boron.[2]



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Surprisingly, their chemistry has been studied only to a relatively small extent. However, the discovery of isolable symmetrical cleavage products of pyrazaboles, i.e., pyrazol-1-ylboranes containing trigonal boron,[3] has led to a renewed interest in pyrazabole chemistry and brought about new features, especially with respect to electrophilic attack at B-H bonds of pyrazaboles.[4] Moreover, it was found that methylation at the 1,3,5 and 7 sites of a pyrazabole skeleton imposes significant differences in chemical behavior.[5]

The present work is concerned with a further exploration of syntheses and the reactivity of pyrazaboles.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorr.) were determined on a Mel-Temp block.

Mass spectral data (unless otherwise noted: 70 eV) were obtained from the University of Kentucky Mass Spectrometry Center and were recorded on a PE-Hitachi RMU-7 or VG ZAB-2F instrument. Data are listed for ions of 5% or higher relative abundances only. NMR spectra were recorded on a Varian XL-200 spectrometer. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H and ^{13}C, external Et_2OBF_3 for ^{11}B). Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = unresolved multiplet. An asterisk denotes a broad signal. Coupling constants J are given in Hz. Details for HOMCOR and HETCOR NMR experiments have been given elsewhere.[6] Infrared spectra were recorded on a PE Model 621 instrument under standard operating conditions.

Ammine-triphenylborane. To 2.5 L of commercially available (E. I. DuPont de Nemours & Co.) aqueous solution of $Na[HOB(C_6H_5)_3]$ (ca. 7% plus 3% excess NaOH) was added 1 L of conc. aqueous ammonia solution (large excess). The resultant colorless precipitate was collected, washed with water until the washings were no longer basic, and pressed dry. The still moist material was stirred with 1.2 L ethyl acetate. The lower (aqueous) layer of the resultant mixture was discarded. The upper (organic)

layer was stirred with Celite and anhydrous $MgSO_4$ and filtered. The filtrate was concentrated until a thick paste remained. Sufficient toluene was added to make a stirrable slurry. The desired compound was collected as fine needles that were dried in vacuum (ca. 80 % yield); it begins to decompose near 180°C and is completely molten/decomposed near 225°C. Anal. Calcd. for $C_{18}H_{18}BN$ (259.16): C, 83.42; H, 7.00; B, 4.17; N, 5.40. Found: C, 83.20; H, 7.29; B, 3.98; N, 5.29. $\delta(^{11}B)$ (solution in $CDCl_3$) = -2.7 ($h_{\frac{1}{2}}$ = 200 Hz).

Potassium diphenyl-dipyrazol-1-yl-borate. A 500-mL flask equipped with a small Vigreaux column was charged with 150 g (2.2 mole) of pyrazole and 22.4 g (0.4 mole) KOH pellets. The mixture was heated until all water distilled out and pyrazole started to distil. Heating was stopped immediately and the liquid was allowed to cool to 110-120°C. Then 103.5 g (0.4 mole) of $H_3NB(C_6H_5)_3$ was added in small portions, and heating was resumed at such a rate that benzene distilled out slowly. A total of 35 mL was collected. The melt was then poured into 600 mL of rapidly stirred toluene. The precipitated $K[(C_6H_5)_2Bpz_2]$ was collected and washed with hot toluene and was then dried under vacuum to yield 101 g (75 %) of the desired compound. An additional 15 g (11 %) of slightly less pure material could be recovered from the filtrate (excess pyrazole being removed by distillation). Anal. Calcd. for $C_{18}H_{16}BKN_4$ (338.26): C, 63.91; H, 4.77; B, 3.20; K, 11.56; N, 16.56. Found: C, 63.88; H, 5.10; B, 2.94; N, 16.89.

NMR data (solution in DMSO-d_6): $\delta(^1H)$ = 7.43 (1H, d, J = 2.4), 7.16 (1H, unresolved), 7.03 + 7.00 (4H, unresolved), 5.99 (1H, unsymm. t = 2 overlapping d, J ca. 2); $\delta(^{11}B)$ = 1.3 ($h_{\frac{1}{2}}$ = 325 Hz); $\delta(^{13}C)$ = 153.9*, 137.8 (d, J = 178, of t, J = 7), 134.0 (d, J = 157), 133.7 (d, J = 192), 125.6 (d, J = 155, of d, J = 5), 124.0 (d, J = 157, of t, J = 7), 101.5 (d, J = 171, of t, J = 11). Solution in D_2O: $\delta(^{11}B)$ = 0.5 ($h_{\frac{1}{2}}$ = 260 Hz); $\delta(^{13}C)$ (proton-decoupled) = 133.1, 130.6, 126.2, 124.2, 104.1.

Trimethylamine-monoiodoborane.[8] NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 2.87 (9H, s), ca. 2.6 (2H, very very broad); $\delta(^{11}B)$ = -9.5 (t, J = 131). Literature data: $\delta(^1H)$ (in CH_2Cl_2) = 2.82;[9] $\delta(^{11}B)$ (in benzene) = -8.9 (t, J = 142).[10]

4,4-Diphenylpyrazabole. A mixture of 18.7 g (55 mmole) potassium diphenyldipyrazol-1-ylborate, 11.3 g (57 mmole) of trimethylamine-monoiodoborane[8] and 300 mL toluene was stirred and slowly heated to 80°C. This temperature was maintained for 6 h and was then raised to reflux for 35 h. The hot mixture was filtered and the solvent was evaporated. The remaining crystals were crushed and washed with two 50-mL portions of water. After drying, they were stirred twice with 50-mL portions of petroleum ether.The crystals were then dissolved in chloroform and the clear filtrate was evaporated to give 14.62 g (82 %) of the crude product, mp 158-162°C. After recrystallization from toluene the compound melted at 168-170°C. Anal. Calcd. for $C_{18}H_{18}B_2N_4$ (311.99): C, 69.30; H, 5.82; B, 6.93; N, 17.96. Found: C, 69.06; H, 5.93; B, 7.08; N, 17.82.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.66 (1H, d, J = 2.0), 7.37 (1H, d, J = 2.3), 7.24-7.21 (3H, m), 6.99-6.94 (2H, m), 6.31 (1H, t, J = 2.2), 3.4* (2H); $\delta(^{11}B)$ (proton-decoupled) = +1.7 (1B, $h_{\frac{1}{2}}$ = 610 Hz), -8.4 (1B, $h_{\frac{1}{2}}$ = 220 Hz; broadens in the proton-coupled spectrum but could not be resolved); $\delta(^{13}C)$ = 145*, 136.3 (d, J = 190, of t, J = 7), 135.7 (d, J = 189, of t, J = 7), 133.6 (d, J = 156, of unresolved m), 127.3 (d, J = 161, of unresolved m), 126.8 (d, J = 159, of t, J = 8), 105.3 (d, J = 180, of t, J = 9).

Pyrazabole.[7] $\delta(^{11}B)$ (solution in DMSO-d_6) = -8.2 ($h_{\frac{1}{2}}$ = 250 Hz, proton-decoupled; $h_{\frac{1}{2}}$ = 350 Hz, proton-coupled). Additional NMR data have been reported elsewhere.[6] - First ionization potential: 12.24 eV (from CNDO calculations estimated by Koopmans theorem); 9.0 $\pm$ 0.2 eV (from mass spectrometry).

4,4,8,8-Tetraphenylpyrazabole.[4] NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.48 (2H, d, J = 2.5), 7.03 + 7.00 (3H, m), 6.81 + 6.78 (2H, m), 6.41 (1H, t, J = 2.5); $\delta(^{11}B)$ = +1.7 ($h_{\frac{1}{2}}$ = 320 Hz); $\delta(^{13}C)$ = 145.5*, 137.3 (d, J = 190, of t, J = 7), 133.2 (d, J = 154, of m), 127.0 (d, J = 157, of m), 126.4 (d, J = 159, of t, J = 7.5), 105.5 (d, J = 181, of t, J = 8.5). Suggested assignments (based on HOMCOR and HETCOR experiments and on coupling constant data): $\delta(^1H)/\delta(^{13}C)$ = 7.03 + 7.00/126.4, 127.0, o- and p-phenyl; = 6.80/133.2, m-phenyl; = 7.48/137.3, N-bonded CH of pyrazolyl groups; = 6.41/105.5, central CH of pyrazolyl groups.

4,4-Diphenyl-8,8-dibromopyrazabole. A solution of Br_2 in CH_2Br_2 was slowly added to a solution of 3.12 g (10 mmol) of 4,4-diphenylpyrazabole in CH_2Br_2 until the color of free Br_2 remained. The mixture was refluxed for 15 min and solvent was stripped off under reduced pressure until a volume of ca. 30 mL remained. On cooling to room temperature, 3.0 g (64%) of the desired compound precipitated. The latter was collected, washed with 5 mL portions each of toluene, chloroform and petroleum ether. The resultant colorless crystals had a mp 220°C (after drying in vacuum at 60°C). Anal. Calcd. for $C_{18}H_{16}B_2Br_2N_4$ (469.78): C, 46.02; H, 3.43; B, 4.60; Br, 34.02; N, 11.93. Found: C, 45.53; H, 3.68; B, 4.46; Br, 33.61; N, 11.76.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.48 (1H, d, J = 2.5), 7.57 (1H, d, J = 2.4), 7.28-7.21 (3H, m), 6.98-6.94 (2H, m), 6.61 (unsymmetrical t, J = 2.5); $\delta(^{11}B)$ = +1.9 ($h_{\frac{1}{2}}$ = 300 Hz), -6.6 ($h_{\frac{1}{2}}$ = 40 Hz), area ratio 1:1; $\delta(^{13}C)$ (proton-decoupled) = 145*, 139.5, 139.1, 133.2, 127.6, 127.5, 107.9.

1,3,5,7-Tetramethyl-4,4-diethyl-8,8-dibromopyrazabole. A solution of Br_2 in CH_2Br_2 was added dropwise with stirring to a solution of 3.37 g (12.5 mmole) of 1,3,5,7-tetramethyl-4,4-diethylpyrazabole[11] in CH_2Br_2. Once the color of free bromine remained, the mixture was refluxed for 15 min. The volume of the solution was then reduced under vacuum to ca. 20 mL and, on cooling to room temperature, the desired compound precipitated. It was collected, washed with CH_2Br_2 and then hexane and dried under vacuum to yield 3.33 g (63%) of colorless crystals, mp

236°C (decomp.). Anal. Calcd. for $C_{14}H_{24}B_2Br_2N_4$ (429.80): C, 39.12; H, 5.63; B, 5.03; Br, 37.18; N, 13.04. Found: C, 39.21; H, 5.72; B, 4.69; Br, 37.31; N, 13.25.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 6.20 (1H, s), 2.84 (3H, s), 2.48 (3H, s), 0.82 (2H, q, J = 7.7), 0.34 (3H, t, J = 7.6); $\delta(^{11}B)$ = +4.8 (1B, $h_{\frac{1}{2}}$ = 200 Hz), -6.7 (1B, $h_{\frac{1}{2}}$ = 30 Hz).

1,3,5,7-Tetramethyl-4,4,8,8-tetraethylpyrazabole.[7] NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 6.00 (1H, s), 2.41 (6H, s), 0.77 (4H, q, J = 7.5), 0.39 (6H, t, J = 7.5); $\delta(^{11}B)$ = 3.5 ($h_{\frac{1}{2}}$ = 150 Hz); $\delta(^{13}C)$ = 145.4 (s), 111.8 (d, J = 175), 16.4*, 15.4 (q, J = 129), 10.2 (q, J = 124). Literature:[7] $\delta(^1H)$ = 5.70 (1H, s), 2.40 (6H, s), 0.92-0.25 (m); $\delta(^{11}B)$ = 4.4.

1,3,5,7-Tetramethyl-4,8-dibromopyrazabole. A solution of 5.4 g (25 mmole) of 1,3,5,7-tetramethylpyrazabole[7] in 150 mL CH_2Br_2 was added dropwise with stirring to a solution of 50 g (0.2 mole) of BBr_3 in 50 mL CH_2Br_2. A precipitate formed immediately with slight warming of the reaction mixture. The mixture was stirred for 3 h at ambient temperature and the precipitate was collected. It was washed with CH_2Br_2 and then a small amount of $CHCl_3$ and dried under vacuum to give 7.9 g (84.5%) of the moisture-sensitive title compound, mp 298-305°C (with slight decomp). Anal. Calcd. for $C_{10}H_{16}B_2Br_2N_4$ (373.70): C, 32.14; H, 4.32; B, 5.79; Br, 42.76; N, 14.99. Found: C, 31.70; H, 4.32; B, 6.15; Br, 43.00; N, 14.84.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 6.11(s) + 5.84(s) (1H, ratio 2:1), 2.54(s) + 2.38(s) (6H, ratio 2:1); $\delta(^{11}B)$

(proton-decoupled) = -8.3*, -10.3* ($h_{\frac{1}{2}}$ ca. 600 Hz); $\delta(^{13}C)$ (proton-decoupled) = (148.6), 145.0, 106.5, 93.2, (12.6), (12.1), 11.0. - IR: ν(BH) = 2510 cm^{-1}. - Mass spectrum (20 eV, probe temperature: 180°C): M/z (relative abundance) = 296 (10), 295 (94), 294 (58), 293 (100), 292 (48), 291 (6), 214 (10), 213 (71), 212 (35), 211 (6). In addition, numerous peaks of lower than 5% relative abundances were observed. In particular, these include a low-intensity ion cluster in the parent ion region (M/z = 376 to 369).

1,3,5,7-Tetramethyl-4,4,8,8-tetrabromopyrazabole. A solution of 12 mL Br_2 in 50 mL CH_2Br_2 was added dropwise with stirring to a solution of 10.8 g (50 mmol) of 1,3,5,7-tetramethylpyrazabole[7] in 300 mL CH_2Br_2. The mixture was refluxed for 3 h and was then reduced to 50 mL volume by distillation. After cooling to room temperature, the precipitate was collected, washed with CH_2Br_2 and then with petroleum ether. The slightly yellow crystals were slurried with 15 mL $CHCl_3$, filtered and dried to give 11.0 g (83%) of colorless crystals, mp 336-338°C (decomp). Calcd. for $C_{10}H_{14}B_2Br_4N_4$ (531.49): C, 22.60; H, 2.65; B, 4.07; Br, 60.14; N, 10.54. Found: C, 22.62; H, 2.47; B, 3.92; Br, 60.33; N, 10.74.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 6.31 (s, 1H), 2.87 (s, 6H); $\delta(^{11}B)$ = -7.5 ($h_{\frac{1}{2}}$ = 30 Hz); $\delta(^{13}C)$ = 152.1 (s), 114.3 (d, J = 182), 15.8 (q, J = 131). - Mass spectrum: M/z (relative abundance) = 455 (31), 454 (25), 453 (95), 452 (57), 451 (100), 450 (49), 449 (37), 448 (16), 293 (21), 292 (27), 291 (32), 290 (27), 289 (11), 187 (8), 186.5 (5), 186 (15),

185.5 (15), 185 (9), 117 (5). Numerous additional ion peaks of lower than 5% relative abundances include a parent ion cluster M/z = 536 to 526.

1,3,5,7-Tetramethyl-4,4,8,8-tetrakis(pyrazol-1'-yl)pyrazabole. A mixture of 5.32 g (10 mmole) of 1,3,5,7-tetramethyl-4,4,8,8-tetrabromopyrazabole, 5.30 g (12.5 mmole) of potassium pyrazolyl-1-ate and 125 mL toluene was refluxed with stirring for 50 h. The hot mixture was filtered and the residue was washed with hot toluene. Solvent was evaporated from the combined toluene solutions. The crystalline residue was dissolved in chloroform and the solvent was evaporated from the clear filtrate. The solid residue was redissolved in 30 mL hot toluene. On standing (and slow evaporation of the solvent), several crystalline fractions were collected. The first one was essentially pure compound which was further purified by sublimation (material subliming under vacuum and at a bath temperature up to 150°C was discarded) to give ca. 2 g of product, mp 235-240°C. Based on mass spectral data the product contained a very minor impurity od $B_2pz_3pz'_3$ (M/z 508) and even $B_2pz_2pz'_4$ (M/z 536) which could, however, not be detected in the ^1H NMR spectrum. Anal. Calcd. for $C_{22}H_{26}B_2N_{12}$ (480.16): C, 55.03; H, 5.46; B, 4.50; N, 35.01. Found: C, 54.61; H, 5.63; B, 4.56; N, 35.06.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.63 (2H, d, J = 1.45), 6.65 (2H, d, J = 2.5), 6.10 (1H, s), 6.04 (2H, unsymmetrical t = 2 overlapping d), 1.63 (6H, s); $\delta(^{11}B)$ = -0.2 ($h_{\frac{1}{2}}$ = 40 Hz); $\delta(^{13}C)$ (proton-decoupled) = 151.3, 142.6, 133.9, 112.2, 105.8, 11.3.

4,4,8,8-Tetrakis(pyrazol-1'-yl)pyrazabole.[12] NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.57 (2H, d, J = 2.3), 7.51 (2H, d, J = 1.5), 6.75 (2H, d, J = 2.2), 6.65 (1H, t, J = 2.4), 6.07 (2H, t, J = 1.7); $\delta(^{11}B)$ = 0.7 ($h_{\frac{1}{2}}$ = 35 Hz); $\delta(^{13}C)$ (proton-decoupled) = 143.6, 141.1, 134.9, 109.5, 107.0. In DMSO-d_6: $\delta(^{11}B)$ = 0.2 ($h_{\frac{1}{2}}$ = 120 Hz). Additional NMR data have been reported elsewhere.[6] - Infrared spectrum (KBr pellet): 3100 (sh), 3090 (w), 1770 (vw), 1721 (vw), 1507 (m), 1493 (sh), 1411 (s, b), 1382 (vs), 1342 (m), 1326 (ms), 1291 (vs, b), 1247 (sh), 1233 (s), 1219 (s), 1213 (s), 1202 (s), 1186 (m), 1143 (m), 1095 (s), 1082 (vs), 1060 (m), 1045 (m), 1037 (m), 1023 (m), 971 (vw), 946 (sh), 943 (m), 933 (vw), 918 (m), 889 (sh), 883 (sh), 873 (s), 859 (sh), 851 (sh), 838 (sh), 833 (vs), 816 (m), 811 (s), 786 (s), 782 (sh), 772 (s), 760 (sh), 755 (vs), 673 (sh), 668 (w), 658 (w), 650 (vw).

1,3,5,7-Tetramethyl-4,8-bis(3',5'-dimethylpyrazol-1'-yl)-pyrazabole, second modification. A mixture of 20.2 g (0.05 mole) od 1,3,5,7-tetramethylpyrazabole and 9.6 g (0.1 mole) of 3,5-dimethylpyrazole was heated in an oil-bath of 180°C for 12 h and the temperature was then slowly increased to 220°C for 2 h. The melt now contained a considerable amount of precipitate and was cooled to room temperature. The product was washed with copious amounts of hot benzene and approximately 6 g of a powdery material remained. It did not melt at temperatures up to 350°C, where it began to decompose. The elemental analysis as well as NMR and mass spectral data of the material were identical to

those of the previously described 1,3,5,7-tetramethyl-4,8-bis-(3',5'-dimethylpyrazol-1'-yl)pyrazabole,[5] although this latter material had a sharp mp 286-288°C. However, the infrared spectra of the two modifications showed several significant differences (see below).

In an alternate experiment, one molar equivalent of the previously described[5] 1,3,5,7-tetramethyl-4,8-bis(3',5'-dimethylpyrazol-1'-yl)pyrazabole was heated for 8 h with two molar equivalents of 3,5-dimethylpyrazole to 180°C. At that time, again a considerable amount of precipitate had formed and the reaction mixture was worked up as above. The benzene-insoluble portion showed an identical IR spectrum to the one of the second modification of the title compound as prepared above, whereas the ^{1}H NMR spectrum was again identical to that of the previously described[5] modification. After evaporation of the solvent from the NMR solution, the remaining crystals had the mp 286-288°C, i.e., that of the normal modification.

IR spectral data: Previously described[5] modification (KBr pellet, 3200 to 600 cm^{-1} region only): 3218(m), 3082(w), 2980(sh), 2960(m), 2922(ms), 2900(sh), 2860(w), 2735(w), 2631(vw), 2462(vs), 2355(w), 2220(w), 2130(vw), 1625(w, br), 1562(sh), 1550 (vs), 1539(m), 1502(w), 1460(sh), 1452/1435/1415 (vs), 1390(vs), 1374(sh), 1368(w), 1348/1338(vs), 1264(s), 1204(sh), 1198(vs), 1155(vs), 1130(sh), 1070(vs), 1050(m), 1038(wm), 1020(wm), 1008(ms), 975(sh), 905(sh), 898(s), 812(vs), 802(s), 765(sh), 758(m), 685(w), 660 (m), 640(s). The spectrum of the second modification as prepared above was essentially identical to the preceding data, with the exception of the

following differences: The ν(BH) band had now shifted from 2462 cm^{-1} to 2495 cm^{-1}; the medium-intensity band at 975 cm^{-1} had become a very weak peak but a new band appeared at 852 cm^{-1} (m); the very strong absorption at 812 cm^{-1} had shifted to 770 cm^{-1}; and the 660 cm^{-1} band (m) was missing from the spectrum of the second modification.

Results and Discussion

Preparation and Characterization of Unsymmetrically Substituted Pyrazaboles

Recently,[5] the reaction of $K[Bpz_4]$ (pz = $N_2C_3H_3$ = pyrazolyl) with $(CH_3)_3NBH_2I$ has been described as a new approach for the preparation of unsymmetrically substituted pyrazaboles of the type $R_2B(\mu\text{-}pz)_2BR'_2$. The basic reaction is not limited to the cited case as is now documented by the reaction of $K[R_2Bpz_2]$ ($R = C_6H_5$) with $(CH_3)_3NBH_2I$ according to eq (1).

$$K[R_2Bpz_2] + (CH_3)_3NBH_2I \longrightarrow KI + (CH_3)_3N + R_2B(\mu\text{-}pz)_2BH_2 \quad (1)$$

The ^1H and ^{13}C NMR spectra of the resultant 4,4-diphenylpyrazabole were readily assigned on the basis of the observed fine structure, coupling constants, HETCOR and HOMCOR-2D NMR experiments, and relevant NMR data of the two related compounds $H_2B(\mu\text{-}pz)_2BH_2$ and $(C_6H_5)_2B(\mu\text{-}pz)_2B(C_6H_5)_2$. Thus the $\delta(^1H)/\delta(^{13}C)$ signals 7.23/127.3, 6.97/133.6, and 7.23/126.8 ppm are those of the o-, m- and p-CH moieties, respectively, of the phenyl groups;

whereas those at 7.66/135.7 ppm are those of the pyrazoyl-CH closest to the $B(C_6H_5)_2$ group ($\delta(^{11}B)$ = +1.8 ppm) and those at 7.37/136.3 ppm of the ones closest to the BH_2 group ($\delta(^{11}B)$ = -8.6 ppm). The $\delta(^1H)/\delta(^{13}C)$ signals of the central CH unit of the pyrazolyl rings are at 6.31/105.3 ppm.

4,4-Diphenylpyrazabole reacts with elemental bromine to yield 4,4-diphenyl-8,8-dibromopyrazabole according to eq (2).

$$R_2B(\mu\text{-pz})_2BH_2 + 2\ Br_2 \longrightarrow 2\ HBr + R_2B(\mu\text{-pz})_2BBr_2 \qquad (2)$$

The reaction proceeds in good yield and neither of the aromatic rings is attacked by Br_2 or HBr.

In a corresponding reaction, 1,3,5,7-tetramethyl-4,4-diethylpyrazabole was converted to 1,3,5,7-tetramethyl-4,4-diethyl-8,8-dibromopyrazabole in good yield. Thus, in contrast to the reaction with BBr_3,[4] reaction with Br_2 displaces only boron-bonded hydrogen but no organic substituents. However, it should be noted that, based on mass spectral and ^1H NMR data of the crude reaction products, small amounts of $R_2B(\mu\text{-pz}')_2BR_2$ ($R = C_2H_5$) and $Br_2B(\mu\text{-pz}')_2BBr_2$ were also formed. This observation suggests at least some opening of the central B_2N_4 ring of the original pyrazabole during the course of the reaction!

As based on mass spectral and ^1H NMR data, the reaction of $K[R_2Bpz_2]$ ($R = C_6H_5$) with two molar equivalents of $(C_2H_5)_2OBF_3$ gave some of the expected $R_2B(\mu\text{-pz})_2BF_2$. However, a small amount of $F_2B(\mu\text{-pz})_2BF_2$ was also observed and $R_2B(\mu\text{-pz})_2BR_2$ was the major product; only the latter

could be isolated in pure state! Also, the reaction of $K[Bpz_4]$ with R_2BBr did not yield the desired $R_2B(\mu\text{-}pz)_2Bpz_2$; rather, as based on ^1H NMR data, a mixture was obtained containing at least two different pyrazaboles. Furthermore, all attempts to prepare $pz_2B(\mu\text{-}pz)_2BF_2$ from the interaction of $K[Bpz_4]$ with $(C_2H_5)_2OBF_3$ failed. The only identified product of this latter reaction was $F_2B(\mu\text{-}pz)_2BF_2$.

These cited observations suggest a fairly complex path for the interaction of poly(pyrazol-1-yl)borates with trigonal boranes or Lewis base adducts thereof. This is in consonance with the previous[5] report that even in the reaction of $K[Bpz_4]$ with $(CH_3)_3NBH_2I$ substantial quantities of $H_2B(\mu\text{-}pz)_2BH_2$ were formed. Hence, the few observed cases to yield the desired products in reasonable quantity[5,11] seem to be fortuitous and a more detailed study is mandated before final conclusions about the general utility of the interaction of poly(pyrazol-1-yl)-borates with trigonal boranes for the formation of pyrazaboles can be drawn.

Chemical Studies on 1,3,5,7-Tetramethylpyrazaboles. The condensation of 3,5-dimethylpyrazole, Hpz', with trimethylamine-borane proceeds readily to yield $H_2B(\mu\text{-}pz')_2BH_2$.[7] The latter compound reacts with additional Hpz' to yield $Hpz'B(\mu\text{-}pz')_2BHpz'$ in a smooth reaction, but subsequent formation of $pz'_2B(\mu\text{-}pz')_2Bpz'_2$ requires excessive reaction times at high temperatures.[5] Even when a clear melt of $Hpz'B(\mu\text{-}pz')_2BHpz'$ and Hpz' was kept at temperatures near 180°C for six hours,

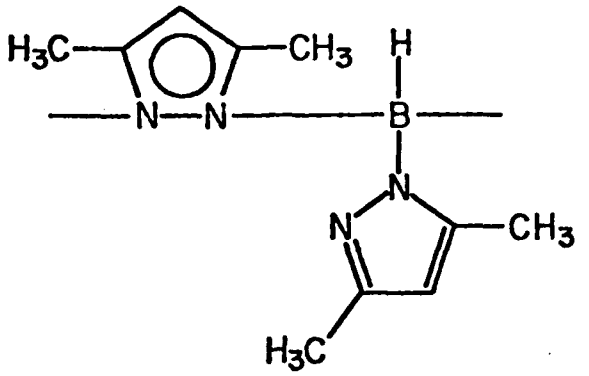
no formation of $pz'_2B(\mu\text{-}pz')_2Bpz'_2$ was observed as indicated by a mass spectrum of the product. However, at that time some solid material slowly precipitated from the melt and the amount of precipitate increased within two more hours of heating. In contrast to the other components of the reaction mixture, this precipitate was essentially insoluble in hot benzene and could thus be separated. It was identified by elemental analysis as well as NMR and mass spectroscopic data as $Hpz'B(\mu\text{-}pz')_2BHpz'$. However, although the cited analytical data were in complete agreement with those of the previously described material,[5] the melting behavior was distinctly different: It did not melt at temperatures up to 350°C where decomposition began. This contrasts with the normal modification of the compound which melts at 286-288°C without decomposition. Also, there were few but significant differences in the infrared spectra of the two materials. It should be noted that on evaporation of a solution of the high melting material (which was used for the NMR spectroscopic studies), the resultant crystalline residue showed the melting point of the previously known modification of the compound, i.e., 286-288°C.

Based on these observations, the high melting material is assumed to be a second modification of $Hpz'B(\mu\text{-}pz')_2BHpz'$. It is noteworthy that only when this second modification has been formed, reaction with additional Hpz' initiates and slowly leads to the formation of $pz'_2B(\mu\text{-}pz')_2Bpz'_2$ (as indicated by mass spectral data). This observation suggests that the

boron-bonded hydrogen atoms of the normal modification of $Hpz'B(\mu\text{-}pz')_2BHpz'$ are much less reactive than those of the second modification.

The crystal structure of $Hpz'B(\mu\text{-}pz')_2BHpz'$ has been shown to involve a B_2N_4 ring in chair conformation and the two terminal pyrazolyl groups were found to be in trans configuration and in axial position.[13] (Presumably, the sample involved was that of the previously described[5] modification of mp 286-288°C; unfortunately, no crystals suitable for a X-ray structure determination could be obtained from the second modification as described above.) Thus, the remaining B-H bonds of the molecule are in equatorial position. In this context it is of interest to note that the axial B-H bonds of $H_2B(\mu\text{-}pz)_2BH_2$[14] and $H_2B(\mu\text{-}pz)_2Bpz_2$[15] have been found to be longer, and hence weaker, than the equatorial ones. This difference in bond length ≈ reactivity seems to be also borne out by the interaction of $H_2B(\mu\text{-}pz')_2BH_2$ with BBr_3 (see below).

Considering all of the preceding data it appears that the second modification of $Hpz'B(\mu\text{-}pz')_2BHpz'$ is macromolecular in nature. This could be explained by assuming that one of the bridging B-N bonds of the pyrazabole is cleaved on prolonged heating to high temperatures to yield the structural unit 2.



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The species then could exist in a cyclic arrangement of several such units or even in a linear polymer containing trigonal boron in chain-terminating groups. In any case, the macromolecular nature would explain the lack of melting prior to thermal decomposition. It would also explain the differences in the infrared spectra of the two modifications and, of course, would influence the reactivity of the B-H bonds: The latter appear to be more reactive (in a condensation process) in the polymer. The identity of the NMR spectra of both modifications suggests that, once in solution, the macromolecule breaks down to the normal pyrazabole structure. (Note: Indeed, the polymer is considerably less readily soluble in $CHCl_3$ as compared to the normal modification of the compound.)

In a previous study it has been shown that the condensation of pyrazabole with pyrazoles at high temperatures must involve

at least partial cleavage of the central B_2N_4 ring of the pyrazabole.[5] The present findings seem to be in consonance with that observation. Apparently, 4,8-disubstitution at BH_2 sites of pyrazaboles occurs quite readily in a condensation process; however, a second such step may more readily proceed through polymeric intermediates formed by ring opening, although these have not been observed previously. This interpretation would readily account for the product mixture which was obtained on reacting $H_2B(\mu\text{-pz})_2BH_2$ with C-substituted pyrazoles.[5]

In this connection it is of interest to note that the boat conformation of the central B_2N_4 ring seems to be the preferred structural arrangement of pyrazaboles.[4] It seems possible that, even in low-temperature electrophilic-induced substitution processes, the arrangement of terminal substituents at the boron sites of pyrazaboles governs the reactivity to a major extent. This is already suggested by the pattern of B-disubstitution of a preformed pyrazabole, which always leads to a 4,8-disubstituted product rather than a geminal species. Furthermore, it is apparent that C-substitution at bridging pyrazolyl groups of pyrazaboles also induces specific features. For example, the parent pyrazabole reacts readily with an excess of either BBr_3 or Br_2 to form $Br_2B(\mu\text{-pz})_2BBr_2$.[8] In contrast, 1,3,5,7-tetramethylpyrazabole reacts with excess BBr_3 to form only the corresponding 4,8-dibromo derivative. The latter exists as a mixture of cis and trans isomer, as was

the case with the corresponding derivative of the parent compound, i.e., $HBrB(\mu\text{-}pz)_2BHBr$.[14] On the other hand, reaction of 1,3,5,7-tetramethylpyrazabole with excess Br_2 affords the 4,4,8,8-tetrabromo derivative, $Br_2B(\mu\text{-}pz')_2BBr_2$, in essentially quantitative yield.

In another experiment, Kpz was reacted with $Br_2B(\mu\text{-}pz')_2BBr_2$ in refluxing toluene to yield $pz_2B(\mu\text{-}pz')_2Bpz_2$. This latter compound is the first example of an isolated and characterized pyrazolylpyrazabole where a boron atom is bonded to two chemically different pyrazole moieties. Remarkably, mass spectral data on the crude reaction product indicated the formation of the pyrazaboles of the composition $B_2pz_3pz'_3$ and $B_2pz_2pz'_4$ as minor byproducts. Their formation suggests again opening of the central B_2N_4 ring of the starting material during the course of the reaction. Even though this seems to occur only to a small extent, it is apparent that such pyrazabole-ring opening may be much more common than heretofore assumed. This is in consonance with the various observations described above.

The observed $\delta(^1H)/\delta(^{13}C)$ data of $pz_2B(\mu\text{-}pz')_2Bpz_2$ are readily assigned on comparison with those of $pz_2B(\mu\text{-}pz)_2Bpz_2$.[6] The shifts 7.63/142.6, 6.04/105.8, and 6.65/133.9 of the former belong to the 3, 4, and 5 position, respectively, of the terminal pyrazolyl groups. They are essentially identical to those of the terminal pyrazolyl groups in $pz_2B(\mu\text{-}pz)_2Bpz_2$ with 7.70/142.6, 6.16/105.7, and 6.81/133.6, respectively. Also, the values for the 2,6 positions of the pyrazabole

skeleton of $pz_2B(\mu\text{-}pz')_2Bpz_2$ with 6.10/112.2 compare well with the corresponding data[5] of $pz'_2B(\mu\text{-}pz')_2Bpz'_2\cdot H_2O$ with 5.91/111.7 (and 5.88/111.1 in the anhydrous compound).

The compound $pz'_2B(\mu\text{-}pz')_2Bpz'_2\cdot H_2O$ can be dehydrated, though with some difficulty.[5] The anhydrous material is readily reconverted to the monohydrate by stirring the compound with water for a few minutes. However, anhydrous $pz'_2B(\mu\text{-}pz')_2Bpz'_2$ does not interact with liquid anhydrous ammonia, not even at room temperature in a sealed tube. Also, no reaction occurred when a solution of the anhydrous compound in $CHCl_3$ was mixed with a saturated solution of NH_3 in the same solvent and the mixture was subsequently evaporated. The starting material was recovered unchanged in all cases.

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