results for the Cu(II), Ni(II), UO_2^{2+}, Zn^{2+}, and several heterotrinuclear[2,3] complexes of H_3DBAA in which no oxidation is observed lead us to conclude that the oxidation to the 1,3,4,5,7-pentaketonate is metal ion dependent rather than due to unusual ligand susceptibility. The binuclear $Mn_2(DBAA)_2$ complex is also oxidized to what appears to be $Mn_2(O{=}DBAA)_2$,[16] i.e. the compound analogous to $Co_2(O{=}DBAA)_2$. Thus, the oxidation of the ligand does not appear to be simply a function of the 4-carbon reactivity but a selective reaction initiated by specific metal ions.

Acknowledgment is made to the National Science Foundation, Grant CHE 8300251, for support of this research.

Registry No. $Co_2(HDBAA)_2(py)_4$, 94499-12-4; $Co_2(O{=}DBAA)_2(py)_4{\cdot}4py$, 94499-14-6.

Supplementary Material Available: Complete listings of hydrogen atom parameters and listings of final positional and thermal parameters, bond lengths and angles, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

(16) Unpublished results.

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Bromination of Pyrazabole[1]

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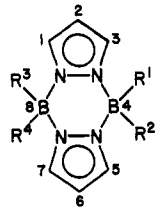
Received March 21, 1984

The stepwise B-bromination of pyrazabole with either BBr_3 or Br_2 has been studied. Both 4-bromo- and 4,8-dibromopyrazabole have been isolated and characterized. The former is a thermally unstable species; the latter is formed as a mixture of cis and trans isomers. 4,4,8-Tribromopyrazabole could not be obtained in the pure state but exists in a mixture with the dibromo and tetrabromo derivatives. The X-ray crystal and molecular structures of pyrazabole and 4,4,8,8-tetrabromopyrazabole have been determined. The central B_2N_4 ring of the former exists in boat conformation whereas this same unit of the latter compound is planar. Crystals of pyrazabole, $C_6H_{10}B_2N_4$, belong to space group *Pbca* with a = 7.645 (2) Å, b = 8.391 (2) Å, c = 27.372 (5) Å, and Z = 8. 4,4,8,8-Tetrabromopyrazabole, $C_6H_6B_2Br_4N_4$, crystallizes in space group $C2/m$ with a = 6.684 (3) Å, b = 15.557 (9) Å, c = 6.538 (3) Å, β = 114.45 (3)°, and Z = 2.

Introduction

The reaction of excess elemental bromine with pyrazabole, **1** (R^1 to R^4 = H) = $H_2B(\mu\text{-pz})_2BH_2$ (pz = $N_2C_3H_3$ = pyrazolyl), has been reported to yield 4,4,8,8-tetrabromopyrazabole, $Br_2B(\mu\text{-pz})_2BBr_2$, in a clean reaction.[2] It has also been found that



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pyrazabole reacts with boron tribromide at temperatures as low as −40 °C to form B-brominated pyrazaboles.[3] Isotopic labeling experiments have shown that this latter process of replacing boron-bonded H by Br does not involve an exchange of boron atoms; i.e., the reaction seems to proceed without opening of the central B_2N_4 ring of the pyrazabole. Furthermore, the existence of the partially brominated species $HBrB(\mu\text{-pz})_2BH_2$, $HBrB(\mu\text{-pz})_2BBrH$, and $Br_2B(\mu\text{-pz})_2BBrH$ was suggested by NMR data. On that basis it seemed reasonable to attempt the isolation and characterization of partially B-brominated pyrazaboles.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block. Mass spectral data were obtained from the University of Kentucky Mass Spectrometry Center (recorded on a Perkin-Elmer Hitachi RMU-7 instrument). NMR spectra were recorded on a Varian XL-200 or a Bruker WP-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference (internal Me_4Si for ^1H and ^{13}C, external Et_2OBF_3 for ^{11}B); coupling constants are given in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet; an asterisk denotes a broad signal. Pyrazabole was prepared by the literature procedure[4] and was recrystallized from methanol. Crystals of 4,4,8,8-tetrabromopyrazabole were obtained from a solution in CH_2Br_2. Crystal data were obtained on a Syntex P3 au-

Table I. Summary of Crystallographic Data and Data Collection Procedures[a]

compd	pyrazabole	4,4,8,8-tetrabromopyrazabole
formula	$C_6H_{10}B_2N_4$	$C_6H_6B_4Br_4N_4$
fw	159.80	475.38
cryst size, mm	0.30 × 0.28 × 0.42	0.30 × 0.22 × 0.35
space group	*Pbca*	$C2/m$
a, Å	7.645 (2)	6.684 (3)
b, Å	8.391 (2)	15.557 (9)
c, Å	27.371 (5)	6.538 (3)
α, deg	90	90
β, deg	90	114.45 (3)
γ, deg	90	90
Z	8	2
V, Å^3	1755.9 (1)	618.9 (5)
d_{calcd}, g/cm^3	1.21	2.55
μ, cm^{-1}	0.71	128.6
$F(000)$	671.76	439.89
2θ, deg	2-45	2-52
scan speed, deg/min	1.2-29.3	2-29.3
scan width, deg	0.9	0.9
total no. of reflcns	1446	1073
no. of unique reflcns	1385	1073
no. of variables used	149	44
R	0.039	0.064
R_w	0.0377	
g	0.0003	

[a] In this and all subsequent tables esd's are given in parentheses.

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(1) (a) Boron–Nitrogen Compounds. 100 (K.N.). Part 99: Niedenzu, K.; Niedenzu, P. M. *Inorg. Chem.* **1984**, *23*, 3713. (b) Contributions to the Chemistry of Boron. 147 (H.N.). Part 146: Kumpfmüller, F.; Nölle, D.; Nöth, H.; Pommerening, H.; Staudigl, R. *Chem. Ber.*, in press.
(2) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948.
(3) Niedenzu, K.; Nöth, H. *Chem. Ber.* **1983**, *116*, 1132.
(4) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165.

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tomated diffractometer 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 22 high-angle reflections. Intensity data were collected by using the ω-scan technique in the range $2.5° < 2\theta < 45°$ for pyrazabole and $2.5° < 2\theta < 50°$ for 4,4,8,8-tetrabromopyrazabole. The data for pyrazabole were corrected for Lorentz and polarization effects; those for the tetrabromo derivative were also corrected for absorption (empirical method using ψ scans, transmission factor 0.047–0.010). 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. The position of Br was ascertained by Patterson methods. The data for the tetrabromopyrazabole refined best for the space group *C2/m*. Atomic parameters were refined isotropically in six cycles 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: $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum(w^{1/2}||F_o| - |F_c||)/\sum(w^{1/2}|F_o|)$, where $w^{-1} = \sigma^2(F_o) - g(F_o)^2$. A summary of crystallographic data and data collection procedures is given in Table I.

4-Bromopyrazabole. A 250-mL flask was equipped with a pressure-equalizing dropping funnel topped with a P_4O_{10} drying tube. The flask was charged with 6.0 g (38 mmol) of pyrazabole and 100 mL of methylene chloride, and the solution was cooled to −15 °C. A dilute solution of BBr_3 in CH_2Cl_2 (75.0 mL of CH_2Cl_2 containing 9.98 mmol BBr_3) was added dropwise to the reaction flask over a period of 1 h while a temperature of approximately −12 °C was maintained. After the addition of the BBr_3 solution was complete, the reaction mixture was warmed to room temperature and stirred at ambient temperature for about 8 h. A small amount of gelatinous material was filtered off, and the clear liquid was then concentrated at room temperature under reduced pressure to a volume of about 50 mL. This produced a colorless precipitate of about 1.5 g of (impure) 4,8-dibromopyrazabole, which was filtered off. The filtrate was evaporated to dryness and consisted of 6.5 g of a mixture of unreacted pyrazabole and the desired compound. The former (1.75 g) was sublimed off under vacuum at a bath temperature of about 30 °C, and 4.75 g of solid (52% as calculated for the employed pyrazabole) remained. This residue was purified by sublimation under vacuum at bath temperatures below 50 °C. Anal. Calcd for $C_6H_9B_2BrN_4$ (mol wt 238.7): Br, 33.48. Found: Br, 33.52.

NMR data (solution in THF): $\delta(^1H)$ 7.80 (1 H, d, J = 2.4 Hz), 7.69 (1 H, d, J = 2.1 Hz), 6.35 (1 H, 2 overlapping d, J = 2.4 Hz); $\delta(^{11}B)$ +0.9 (d, J = 120 Hz, $h_{1/2}$ = 100 Hz), −8.9 (t, J = ca. 96 Hz, $h_{1/2}$ = 170 Hz); $\delta(^{13}C)$ 135.8 (d, J = 189 Hz, of t, J = 7.0 Hz), 134.5 (d, J = 190 Hz, of t, J = 7.1 Hz), 105.8 (d, J = 180 Hz, of t, J = 8.8 Hz). Mass spectral data (50 eV; more than 5% relative abundance (in parentheses) only): *M/z* 239 (8), 238 (6), 237 (12), 236 (7), 195 (10), 194 (8), 193 (35), 192 (19), 191 (9), 166 (6), 164 (6), 160 (6), 159 (62), 158 (56), 157 (88), 156 (48), 155 (8), 141 (12), 132 (6), 131 (8), 130 (24), 129 (10), 106 (7), 105 (6), 104 (10), 103 (8), 97 (6), 80 (13), 79 (41), 78.5 (9), 76 (12), 71 (8), 69 (10), 68 (100), 67 (8), 57 (19), 56 (41), 55 (16), 53 (8), 52 (51), 51 (16), 41 (11), 40 (15), 39 (10), 38 (13), 36 (15), 28 (13).

The melting behavior of the material is unusual. It melted to a large extent between 112 and 118 °C but then gave an apparently crystalline material, which subsequently melted over a range from 134 to 154 °C. Subsequent reheating of the material produced similar results, except that melting ranges were even broader and somewhat lower than in the initial determination. Proton NMR data on the melted samples indicated partial decomposition with the formation of pyrazabole and 4,8-dibromopyrazabole besides unidentified material.

Alternate procedure (product in mixture): A solution of Br_2 in CCl_4 (23 mL containing 3.07 mmol Br_2) was added slowly to a stirred solution of 490 mg (3.07 mmol) of pyrazabole in 5 mL of CCl_4. A precipitate formed with gas evolution. After 2 h of stirring, insoluble material (0.19 g of 4,8-dibromopyrazabole, $\delta(^{11}B)$ (in CH_2Br_2) = −5.5) was filtered off and the remaining solvent was evaporated to leave a mixture of pyrazabole and 4-bromopyrazabole. NMR data (in CCl_4/C_6D_6): $\delta(^1H)$ 7.54 (2 H, d, J = 2.2 Hz), 6.24 (1 H, t, J = 2.2 Hz) for pyrazabole; δ (^1H) 7.9 (1 H, unsym d), 7.8 (1 H, unsym d), 6.3 (1 H, unsym t = 2 overlapping d) for 4-bromopyrazabole; $\delta(^{11}B)$ −7.5 (t, BH_2), −6.5 (d, BHBr), −2.2 (d, BHCl from some halogen exchange during preparation).

Essentially identical results are obtained by performing the reaction at −20 or −78 °C, respectively.

4,8-Dibromopyrazabole. A solution of 4.7 g (29.4 mmol) of pyrazabole in 35 mL of CH_2Cl_2 was placed in a 100-mL flask and cooled to 0 °C. A 0.399 M solution of BBr_3 in CH_2Cl_2 (50 mL = 19.9 mmol of BBr_3) was added dropwise over a period of 1 h. Subsequently, the mixture was stirred for 8 h at ambient temperature. The solvent was removed under reduced pressure, and 8.8 g (94% yield based on pyrazabole) of crude material, mp 190–208 °C, was obtained. It could be purified by recrystallization from $CHCl_3$ (mp 208–213 °C) or benzene (mp 210–217 °C) or by sublimation under vacuum (mp 207–212 °C). Anal. Calcd for $C_6H_8B_2Br_2N_4$ (mol wt 317.59): C, 22.69; H, 2.54; B, 6.81; Br, 50.32; N, 17.64. Found: C, 22.95; H, 2.84; B, 6.69; Br, 48.55; N, 17.49.

NMR data: $\delta(^1H)$ (solution in THF) 7.81 (2 H, 2 overlapping d, J = 2.3 Hz each), 6.39 (1 H, t, J = 2.5 Hz); $\delta(^1H)$ (solution in $CDCl_3$) 8.06 (d, J = 2.5 Hz), 7.96 (d, J = 2.6 Hz), 6.62/6.57 (2 overlapping t, J = 2.6 Hz); $\delta(^1H)$ (solution in CD_3CN) 8.22 (d, J = 2.6 Hz), 8.15 (d, J = 2.6 Hz), 6.74 (t, J = 2.6 Hz), 6.71 (t, J = 2.6 Hz) (on the basis of the integration data, the cis and trans isomers (see text) are present in approximately 2:1 molar ratio); $\delta(^{11}B)$ (solution in THF) +0.3 (d, J = ca. 110 Hz, $h_{1/2}$ = 120 Hz); $\delta(^{11}B)$ (solution in CD_3CN) −0.8 (d, J = 143 Hz, $h_{1/2}$ = 30 Hz), −1.7 (d, J = 143 Hz, $h_{1/2}$ = 30 Hz). $\delta(^{13}C)$ (solution in THF) 135.7 (d, J = 190 Hz, of t, J = 7.1 Hz), 134.4 (d, J = 189 Hz, of t, J = 7.2 Hz), 106.1 (d, J = 181 Hz, of t, J = 8.7 Hz), 106.0 (d, J = 181 Hz, of t, J = 8.7 Hz). Mass spectral data (70 eV; more than 5% relative abundance (in parentheses) only): *M/z* 319 (8), 318 (6), 317 (17), 316 (9), 315 (9), 240 (7), 239 (87), 238 (51), 237 (100), 236 (51), 235 (19), 234 (7), 159 (6), 158 (11), 157 (79), 156 (41), 155 (7), 131 (7), 130 (19), 129 (11), 119 (8), 118.5 (6), 118 (12), 104 (9), 103 (7), 79 (55), 78.5 (13), 77 (12), 76 (10), 75 (7), 52 (16), 51 (9).

Alternate procedure: A solution of Br_2 in CCl_4 (40 mL of CCl_4 containing 6.76 mmol of Br_2) was added to a stirred solution of 540 mg (3.38 mmol) of pyrazabole in 10 mL of CCl_4. The resultant precipitate (510 mg) of 4,8-dibromopyrazabole (cis and trans isomer in about 7:5 molar ratio), mp 199–218 °C, was slightly contaminated by the presence of BHCl groups (via halogen exchange during the preparation). NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.07 (2 H, d, J = 2.4 Hz), 6.59 (1 H, t, J = 2.4 Hz) for the cis isomer; $\delta(^1H)$ 7.97 (2 H, d, J = 2.7 Hz), 6.64 (1 H, t, J = 2.7 Hz) for the trans isomer. IR data: ν(BH) 2510, 2490 cm^{-1}.

4,4,8-Tribromopyrazabole (in Mixture). A 250-mL flask was charged with 3.19 g (20.0 mmol) of pyrazabole and 100 mL of CH_2Cl_2, and the resulting clear solution was cooled to −10 °C. A dilute solution of BBr_3 in CH_2Cl_2 (100 mL of CH_2Cl_2 containing 20 mmol of BBr_3) was added dropwise to the stirred pyrazabole solution over a period of 2 h. The mixture was stirred for 8 h at ambient temperature. A small amount of gelatinous material was filtered off, and the volume of the filtrate was reduced to 100 mL under vacuum at room temperature. The resultant colorless precipitate (1.3 g) consisted primarily of 4,8-dibromopyrazabole as shown by ^1H NMR data. The filtrate was evaporated to dryness to give 5.85 g of a material that was identified by ^1H NMR data (solution in THF) to be a mixture of 4,8-dibromopyrazabole (δ 7.81, 6.39), 4,4,8-tribromopyrazabole (δ 8.47, 8.11, 6.69), and 4,4,8,8-tetrabromopyrazabole (δ 8.77, 6.99) in approximately 1:1:2 molar ratio. The mixture could not be separated by fractional crystallization or sublimation. Boron-11 chemical shift data for 4,4,8-tribromopyrazabole (in mixture) have been reported previously, with $\delta(^{11}B)$ −6.6 (d, J = 139 Hz) and −7.1 (s) (solution in CH_2Cl_2).[3]

Alternate experiment: A solution of Br_2 in CH_2Br_2 (60 mL of CH_2Br_2 containing 9.39 mmol of Br_2) was added to a solution of 500 mg (3.13 mmol) of pyrazabole in 40 mL of CH_2Br_2. After the gas evolution had ceased, the volume of the solution was reduced by half to give 1.5 g of precipitate. The remaining solution exhibited ^{11}B NMR signals indicating the presence of a mixture of di-, tri-, and tetrabromopyrazabole.

4,4,8,8-Tetrabromopyrazabole. A 250-mL flask was charged with a solution of 4.80 g (30.1 mmol) of pyrazabole in 50 mL of CH_2Cl_2 and cooled to 0 °C. A 0.399 M solution of BBr_3 in CH_2Cl_2 (150 mL = 60 mmol of BBr_3) was added dropwise with stirring over a period of 2–3 h. The cooling bath was removed, and the mixture was stirred for 8 h at ambient temperature. Insolubles were filtered off to give 5.18 g of fairly pure 4,4,8,8-tetrabromopyrazabole, mp 280–286 °C. Volatiles were removed from the filtrate under vacuum at room temperature to give a second crop of less pure material of the desired compound (5.17 g). Recrystallization from chlorobenzene yielded a pure material, mp 298–301 °C (lit. data[3,4] range from 291 to 305 °C).

NMR data (solution in THF): $\delta(^1H)$ 8.77 (2 H, d, J = ca. 2.4 Hz), 6.99 (1 H, t, J = 2.7 Hz); $\delta(^{11}B)$ −2.6 ($h_{1/2}$ = 20 Hz); $\delta(^{13}C)$ 142.8 (d, J = 196 Hz, of unresolved m), 111.4 (d, J = 187 Hz, of d, J = 4 Hz). Mass spectral data (70 eV; more than 5% relative abundance (in parentheses) only): *M/z* 399 (29), 398 (21), 397 (91), 396 (52), 395 (100), 394 (51), 393 (40), 392 (17), 315 (6), 237 (37), 236 (21), 235 (44), 234 (19), 159 (15), 158.5 (6), 158 (21), 157.5 (10), 157 (22), 156 (8), 155 (8), 132 (15), 131 (8), 130 (17), 129 (9), 118 (6), 51 (7).

The compound is soluble in THF or Me_2SO. It is only slightly soluble in aromatic solvents (benzene, chlorobenzene, toluene), chloroform, or dioxane.

Alternate procedure: A solution of 5.4 mmol of Br_2 in 30 mL of CCl_4 was added to a solution of 240 mg (1.5 mmol) of pyrazabole in 30 mL of CCl_4. A slightly yellow precipitate formed with the evolution of a gas (HBr). The mixture was refluxed for 2 h, and 300 mg (42%) of insoluble 4,4,8,8-tetrabromopyrazabole, mp 310 °C, was collected.

Alternate preparation: A solution of 2.55 g (7.5 mmol) of bis(ethylenedithio)pyrazabole[5] in 25 mL of CH_2Cl_2 was added with stirring to 75 mL of a 0.4 M solution of BBr_3 in CH_2Cl_2 (30 mmol). A precipitate formed immediately. The mixture was refluxed for 30 min, and the volume was then reduced to 35 mL by distillation. The solid residue was collected and washed with several 5-mL portions of CH_2Cl_2 and, subsequently, pentane. The product was then dried to yield 3.1 g (87%) of the desired 4,4,8,8-tetrabromopyrazabole, mp 298–301 °C.

Results and Discussion

Reaction of Boron Tribromide with Pyrazabole. In theory, all three Br atoms of BBr_3 may be exchangeable with boron-bonded hydrogens of pyrazabole according to eq 1. However, the previous

$$BBr_3 + 3H_2B(\mu\text{-pz})_2BH_2 \rightarrow 3HBrB(\mu\text{-pz})_2BH_2 + {}^1/_2B_2H_6 \quad (1)$$

studies had evidenced the formation of brominated diborane(6) in the cited reaction.[3] Under these circumstances, the potential ease of separation of mixtures was used as a guideline for the employed stoichiometry. For example, it was hoped that by using a stoichiometric deficiency of BBr_3 in the preparation of $HBrB(\mu\text{-pz})_2BH_2$, only unreacted pyrazabole would appear as a by-product. However, even under these circumstances, some 4,8-dibromopyrazabole was always formed. Nevertheless, 4-bromopyrazabole could be obtained as a solid material that was characterized by mass spectral and NMR spectroscopic data. The latter showed the expected two ^1H and ^{13}C signals for the pyrazole CH groups in positions 1,7 and 3,5, respectively, as well as two different ^{11}B signals of equal intensity. In contrast to all other known pyrazaboles, 4-bromopyrazabole is extremely moisture sensitive. Moreover, at temperatures near 90 °C it undergoes rearrangement and/or decomposition. Thus, the ^1H NMR spectrum of a sample that was heated to melting gave clear evidence for the presence of pyrazabole and 4,8-dibromopyrazabole in the previously pure material.

When BBr_3 and pyrazabole were reacted in 1:1.5 molar ratio, the major product was found to be $HBrB(\mu\text{-pz})_2BBrH$. The material obtained in this reaction is a mixture of cis and trans isomers (configuration of the Br atoms with respect to the central B_2N_4 ring). This is already suggested by the melting range of the compound but is clearly documented when the ^1H and ^{11}B NMR spectra are recorded in different solvents:

$\delta(^1H)$	in THF	7.81	6.39
	in $CDCl_3$	8.06, 7.96	6.62, 6.57
	in CD_3CN	8.22, 8.15	6.74, 6.71
$\delta(^{11}B)$	in THF	+0.3	
	in CD_3CN	−1.7, −0.8	

Moreover, the proton-decoupled ^{13}C NMR spectrum of the compound (in THF) shows four lines with $\delta(^{13}C)$ 135.7, 134.4, 106.1, and 104.1, respectively. On the basis of the integration of the ^1H and ^{11}B NMR signals, the ratio of the two isomers is about 2:1.

All attempts to isolate pure 4,4,8-tribromopyrazabole failed. However, it was possible to obtain a mixture of the desired compound with $HBrB(\mu\text{-pz})_2BBrH$ and $Br_2B(\mu\text{-pz})_2BBr_2$ in approximately 1:1:2 molar ratio, respectively. From the ^1H NMR spectrum of such a mixture, the chemical shifts of $Br_2B(\mu\text{-pz})_2BHBr$ could be deduced with $\delta(^1H)$ 8.47, 8.11, and 6.69. These findings are clearly supported by the following trends of the ^1H chemical shift data of the pyrazole groups in the various species (THF solutions):

	$\delta(^1H)$ in pyrazole ring positions	
compd	3,5	4
$H_2B(\mu\text{-pz})_2BH_2$	7.69	6.32
$HBrB(\mu\text{-pz})_2BH_2$	7.80, 7.69	6.35
$HBrB(\mu\text{-pz})_2BBrH$	7.81	6.39
$Br_2B(\mu\text{-pz})_2BBrH$	8.47, 8.11	6.69
$Br_2B(\mu\text{-pz})_2BBr_2$	8.77	6.69

Reaction of BBr_3 with pyrazabole in 2:1 molar ratio leads to the formation of 4,4,8,8-tetrabromopyrazabole in better than 70% yield. An increase in the molar ratio provides no further improvement in yield. On the other hand, lowering the ratio to the stoichiometry calculated for the utilization of all Br in BBr_3 results in a substantial decrease in yield of the desired product. This is in consonance with the noted formation of bromodiboranes(6) in this reaction.[3]

It is worth noting that the reaction of the pyrazabole $(CH_2)_2S_2B(\mu\text{-pz})_2BS_2(CH_2)_2$ with BBr_3 proceeds extremely readily to give a high yield of pure 4,4,8,8-tetrabromopyrazabole.

The mass spectrum of $Br_2B(\mu\text{-pz})_2BBr_2$ does not exhibit the molecular ion M, not even in the low-voltage spectrum. Rather, the highest observed ion cluster corresponds to M − Br, and the only other peak of substantial relative intensity is that of M − 3Br.

Reaction of Elemental Bromine with Pyrazabole. Analogous to the reaction of pyrazabole with BBr_3, the reaction with Br_2 also proceeds stepwise and the formation of specific products depends on the stoichiometry of the reactants. However, similar to the reaction with BBr_3, reaction according to eq 2 did not proceed cleanly. Rather, a mixture of pyrazabole and its mono- and

$$H_2B(\mu\text{-pz})_2BH_2 + Br_2 \rightarrow HBrB(\mu\text{-pz})_2BH_2 + HBr \quad (2)$$

$$HBrB(\mu\text{-pz})_2BH_2 + Br_2 \rightarrow HBrB(\mu\text{-pz})_2BBrH + HBr \quad (3)$$

dibromo derivatives was obtained. This suggests that the reaction rates of the processes according to eq 2 and 3, respectively, do not differ significantly. Also, no significant influence on the product distribution was observed with variations of concentration of reactants or temperature.

If 2 molar equiv of Br_2 is reacted with pyrazabole, 4,8-dibromopyrazabole was formed readily and could be isolated in reasonable yield. ^1H NMR data suggested the product to be a mixture of the cis and trans isomers in approximately 7:5 molar ratio.

Three molar equivalents of Br_2 reacted with pyrazabole to form a mixture of the di-, tri-, and tetrabromo derivatives, but no pure products could be isolated from such mixtures. On the other hand, 4,4,8,8-tetrabromopyrazabole was formed on reaction of pyrazabole with 4 molar equiv of Br_2, although refluxing of the mixture in CCl_4 is required in order to obtain a reasonable yield of product.

All of the brominated pyrazaboles are rather sensitive to moisture, including the tetrabromo derivative. It is noteworthy that some halogen exchange occurs when the reactions are performed in CCl_4 as solvent. In order to avoid contamination of the products with BCl groups, CH_2Br_2 seems to be the solvent of choice.

X-ray Crystal and Molecular Structures of Pyrazabole and 4,4,8,8-Tetrabromopyrazabole. The crystal structures of several pyrazaboles have previously been examined by X-ray diffraction, and it has been found that the central B_2N_4 ring of the tricyclic $B(\mu\text{-pz})_2B$ system can adopt a planar, boat, or chair conformation.[3,6,7] As yet, there seems to be no direct relation between a specific geometry and the nature of the boron substituents.

In the present work it was found that the parent pyrazabole crystallizes in the space group *Pbca*. The molecule has a butterfly

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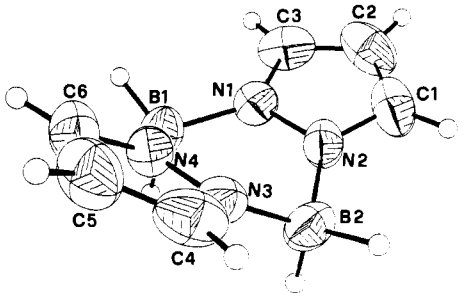

Figure 1. ORTEP plot of pyrazabole.

Table II. Atomic Coordinates for Pyrazabole and 4,4,8,8-Tetrabromopyrazabole

atom	*x/a*	*y/b*	*z/c*
	Pyrazabole		
B1	−0.0554 (3)	0.8217 (4)	0.4168 (1)
B2	0.1682 (3)	0.6886 (3)	0.3411 (1)
N1	−0.0824 (2)	0.8705 (2)	0.3626 (1)
N2	0.0205 (3)	0.8080 (2)	0.3273 (1)
N3	0.2490 (2)	0.7545 (2)	0.3889 (1)
N4	0.1461 (3)	0.8187 (2)	0.4238 (1)
C1	−0.0327 (4)	0.8672 (4)	0.2844 (1)
C2	−0.1702 (4)	0.9676 (4)	0.2918 (1)
C3	−0.1977 (4)	0.9672 (3)	0.3409 (1)
C4	0.4148 (3)	0.7639 (3)	0.4050 (1)
C5	0.4181 (4)	0.8333 (3)	0.4499 (1)
C6	0.2482 (4)	0.8672 (3)	0.4604 (1)
H11	−0.1074 (24)	0.6969 (21)	0.4235 (6)
H12	−0.1062 (27)	0.9161 (24)	0.4394 (7)
H21	0.2688 (29)	0.6879 (24)	0.3118 (7)
H22	0.1080 (26)	0.5701 (29)	0.3480 (7)
H1	0.0342 (31)	0.8344 (30)	0.2560 (9)
H2	−0.2284 (37)	1.0240 (37)	0.2685 (9)
H3	−0.2731 (32)	1.0147 (32)	0.3606 (8)
H4	0.4993 (29)	0.7268 (26)	0.3839 (8)
H5	0.5220 (33)	0.8580 (31)	0.4707 (8)
H6	0.1978 (29)	0.9173 (30)	0.4890 (8)
	4,4,8,8-Tetrabromopyrazabole		
Br	0.2241 (2)	0.3270 (1)	1.2397 (2)
B	0	0.3997 (9)	0
N	0.1173 (13)	0.4557 (4)	0.8931 (13)
C1	0.2316 (1)	0.4309 (7)	−0.2220 (22)
C2	0.3089 (26)	0.5	0.7024 (27)
H1	0.253 (21)	0.382 (8)	−0.214 (20)
H2	0.387 (28)	0.5	−0.394 (27)

arrangement of the three condensed rings with a boat-shaped central B_2N_4 moiety. The B–N distances are approximately equal, and the N–N bond lengths compare favorably with those found in other pyrazaboles.

In contrast, 4,4,8,8-tetrabromopyrazabole exhibits a planar ring system and is isostructural with the 4,4,8,8-tetrachloropyrazabole.[3] The shorter B–N bond distances in $Br_2B(\mu\text{-}pz)_2BBr_2$ as compared to those in $H_2B(\mu\text{-}pz)_2BH_2$ suggest that the $pzBBr_2$ group is a much stronger acid than the $pzBH_2$ group (even though the standard deviations are about 3–4 times larger in the tetrabromo derivative as compared to those in the parent compound). The B–Br distances are typical for a boron atom in a four-coordinate environment.

The molecular structures of pyrazabole and its tetra-*B*-bromo derivative are depicted in Figures 1 and 2, respectively. Atomic

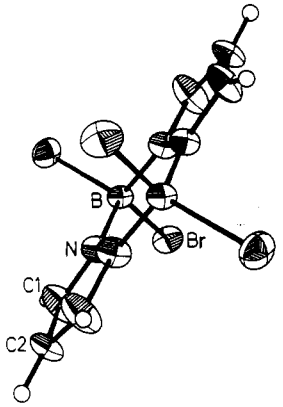

Figure 2. ORTEP plot of 4,4,8,8-tetrabromopyrazabole.

Table III. Selected Bond Distances (pm) for Pyrazabole (A) and 4,4,8,8-Tetrabromopyrazabole (B)

	A	B		A	B
B1–N1	155.4 (3)	152.1 (12)	N4–C6	133.3 (3)	
B1–N4	155.2 (3)		C3–C2	135.9 (5)	137.1 (19)
B2–N2	155.6 (3)		C4–C5	136.0 (4)	
B2–N3	154.9 (3)		C2–C1	136.2 (4)	
N1–N2	135.1 (3)	138.0 (14)	C5–C6	136.0 (4)	
N3–N4	135.0 (3)		B1–R1	113.5 (18)	200.9 (8)
N1–C3	133.7 (3)	133.3 (19)	B1–R3	107.7 (20)	
N3–C4	134.4 (3)		B2–R2	111.1 (20)	
N2–C1	133.9 (3)		B2–R4	111.2 (23)	

Table IV. Selected Bond Angles (deg) for Pyrazabole (A) and 4,4,8,8-Tetrabromopyrazabole (B)

	A	B		A
N1–B1–N4	104.7 (2)	110.2 (10)	B2–N3–N4	120.5 (2)
R1–B1–N1	110.5 (8)	108.7 (3)	N3–N4–B1	119.9 (2)
R1–B1–N4	108.2 (9)		N2–B2–N3	105.3 (2)
R3–B1–N1	107.9 (10)	108.9 (3)	R2–B2–N2	109.3 (11)
R3–B1–N4	107.4 (11)		R2–B2–N3	109.6 (11)
R1–B1–R3	117.4 (14)	111.4 (6)	R4–B2–N2	108.4 (11)
B1–N1–N2	120.2 (2)	124.9 (5)	R4–B2–N3	109.9 (10)
N1–N2–B2	120.0 (2)		R2–B2–R4	113.9 (15)

coordinates for the two compounds are given in Table II, selected bond distances are presented in Table III, and selected bond angle data are listed in Table IV.

Although large standard deviations are associated with the B–H bond distances in pyrazabole, the data suggest that the axial ones might be longer than the equatorial B–H bonds. A longer B–H bond would imply a more negative charge at such a hydrogen atom and, hence, preferential attack at this site by a nucleophile. The limited chemical evidence, e.g., observation of 4,8-dibromination rather than formation of a geminal dibromo derivative, seems to be in consonance with this interpretation.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.) and the Fonds der Chemischen Industrie (H.N.).

Supplementary Material Available: Anisotropic thermal parameter and structure factor tables for pyrazabole and 4,4,8,8-tetrabromopyrazabole (11 pages). Ordering information is given on any current masthead page.