values. Also, the pteridylaldehyde Mo—S and Mo═O bonds distances are longer by about 0.06 and 0.04 Å, respectively, from those in the violapterin complex.

All the Mo–ligand distances in the 6-pteridylaldehyde complex are slightly longer than in the free oxidized enzyme.[14] The effect is most pronounced for the Mo═S bond, which lengthens by some 0.05 Å on binding of 6-pteridylaldehyde. Such changes, which are on the threshold of significance for an EXAFS measurement, might occur through an increase in the molybdenum coordination number or through a weak association of pteridylaldehyde with the terminal Mo ligands.

The presence of a long-wavelength absorption band in the electronic spectra of the violapterin complex has been interpreted as involving a charge-transfer complex between the molybdenum center and heterocycle.[10] However, by X-ray absorption, the complex of violapterin with reduced enzyme is nearly indistinguishable from the free reduced enzyme. Also, a similar electronic absorption band is observed for the pteridylaldehyde complex.[11] An alternative explanation is that the absorption bands represent charge-transfer complexes between the pterin of the molybdenum cofactor[25] and the bound heterocycle. Such an assignment would be consistent with the EXAFS results, which show rather small changes in Mo site radial distances. However, the loss of this absorption band upon cyanolytic removal of the terminal sulfur remains unexplained.

Conclusions

Along with thiolate-like sulfurs presumably donated by the molybdenum cofactor, X-ray absorption spectroscopy clearly reveals a terminal Mo═O bond in the xanthine oxidase alloxanthine complex and, equally important, shows the absence of a short Mo═S bond in the Mo(IV) complex. The EPR spectrum of the corresponding Mo(V) complex exhibits an unusually large ^{33}S hyperfine coupling and a lack of proton hyperfine coupling, which have been taken to indicate the presence of Mo═S in the signal-giving species. These data can be reconciled by postulating deprotonation of Mo^{IV}—SH, upon oxidation, to Mo^{V}═S. Recent EPR spectroscopic evidence supports a Mo(O)(S) structure for the Mo(V) Very Rapid species.[26] Less plausible alternatives invoke an unusual geometry for a Mo^{V}—SH complex that would minimize proton hyperfine coupling or a covalent interaction for the Mo(IV) sulfido species to lengthen the terminal Mo═S bond.

The current results show that a Mo═O group is present at many points in the catalytic cycle of xanthine oxidase, being present in E$_{ox}$·S (the 6-pteridyaldehyde complex), at least one intermediate encountered in the course of hydroxylation (the Very Rapid species, by analogy with the alloxanthine complex), and finally E$_{red}$·P (the violapterin complex). This observation must be reconciled with recent evidence interpreted as indicating incorporation of oxygen from the Mo═O group into the product hydroxyl group in the course of catalysis.[27] We cannot exclude the involvement of a transient deoxy species in the catalytic cycle, on a time scale that is short compared to those of steady-state or rapid-freezing experiments. Detailed understanding of the catalytic mechanism of xanthine oxidase remains an elusive goal.

Acknowledgment. The spectra were recorded at the Stanford Synchrotron Radiation Laboratory, which is funded by the Department of Energy, Office of Basic Energy Sciences, and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. This work was supported in part by Grant DMB-8521645 from the National Science Foundation (R.H.).

Registry No. Mo, 7439-98-7; O_2, 7782-44-7; N_2, 7727-37-9; LMo^{V}O$(SC_6H_5)_2$, 105810-18-2; LMo^{IV}O$[S_2CN(n\text{-}Bu)_2]$, 107441-39-4; LMo^{IV}S$[S_2CN(n\text{-}Bu)_2]$, 107441-43-0.

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(25) Cramer, S. P.; Stiefel, E. I. *Molybdenum Enzymes*; Spiro, T. G., Ed.; John Wiley: New York, 1985; pp 411-441.

(26) George, G. N.; Bray, R. C. *Biochemistry* **1988**, *27*, 3603-3609.

(27) Hille, R.; Sprecher, H. *J. Biol. Chem.* **1987**, *262*, 10914-10917.

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Triazaboles and Related Triazole Derivatives of Boron[1]

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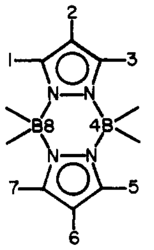
The reaction of trimethylamine–borane, $Me_3N\cdot BH_3$, with 1,2,4-triazole (=Hst) results in the formation of an oligomer mixture of the composition $[H_2B(st)]_n$; species with *n* up to 6 could be identified by mass spectrometry. Dimeric species = *sym*-triazaboles, $R_2B(\mu\text{-st})_2BR_2$ (**2**, R = hydrocarbon group), can be obtained in low yield from the condensation of R_3B with Hst, from the interaction of halodiorganylboranes, R_2BX (X = Cl, Br), with *N*-(trimethylsilyl)-1,2,4-triazole, $Me_3Si(st)$, and also by a transamination of a (dimethylamino)diorganylborane, Me_2NBR_2, with Hst. However, the major products are generally oligomeric materials $[R_2B(st)]_n$. The interaction of 3-amino-1,2,4-triazole (=Hat) with excess of R_3B ultimately gives a reasonable yield of a mixture of two isomeric triazaboles of type **2** with the amino groups in either the 1,5- or 1,7-positions, whereas transamination of Me_2NBR_2 with Hat preferentially gives the 1,5-diamino isomer but in low yield. Several boron derivatives of 1,2,3-triazoles have been isolated and characterized; these include tetrameric species (derived from 1,2,3-triazole = Hut or benzotriazole = Hbt) with a cyclic structure (**6**) resembling that of porphine, but also oligomeric materials $[R_2B(ut)]_n$ and $[R_2B(bt)]_n$.

Introduction

Although almost 100 different B- and/or C-substituted pyrazaboles (**1**), the neutral dimers of 1-pyrazolylboranes, are known, corresponding boron derivatives of triazoles, i.e., species where two four-coordinate boron atoms are linked by two triazolyl groups, have not yet been explored. Only one such compound, 4,4,8,8-tetraethyl-*sym*-triazabole (**2**, R = C_2H_5), has been described. This latter compound was obtained in moderate yield by the condensation reaction of Et_3B with 1,2,4-triazole.[3] While the present work was in progress, the interaction of 3-amino-1,2,4-triazole with an excess of trialkylboranes was reported to give reasonable yields of isomeric *sym*-triazaboles with NH_2 groups in either the 1,5- or 1,7-positions of **2** (R = C_3H_7, C_4H_9).[4]



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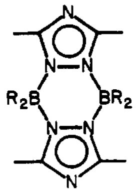

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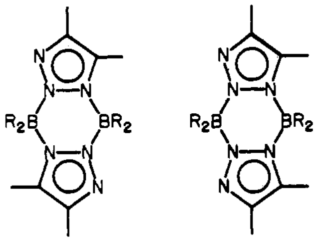
(1) Boron–Nitrogen Compounds. 121. Part 120: Mariategui, J. F.; Niedenzu, K. *J. Organomet. Chem.* **1989**, *369*, 137-145.

(2) Niedenzu, K.; Trofimenko, S. *Top. Curr. Chem.* **1986**, *131*, 1-37.

(3) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165-3170.

0020-1669/89/1328-4022$01.50/0

Triazaboles derived from 1,2,3-triazoles have not yet been described. Presumably such species could exist as the isomers **3a** and **3b**, respectively. However, the low-temperature reaction of benzotriazole (=Hbt) with Me_3B has been reported to give an unidentified complex. The latter decomposed on boiling in xylene to give an uncharacterized oligomer $[Me_2B(bt)]_n$.[5]



3a **3b**

The nitrogen atoms of the C_2N_3 rings of triazaboles (**2**, **3**) not involved in coordination to boron are potential donor sites. This feature should provide for interesting variations in the chemistry of the triazaboles as compared to that of the pyrazaboles (**1**). The present report describes some studies on the preparation and characterization of triazaboles and related triazole derivatives of boron.

Experimental Section

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

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (^{11}B, ^{15}N), XL-200 (^{11}B), or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H and ^{13}C NMR, external $Et_2O{\cdot}BF_3$ for ^{11}B NMR, external NH_3 for ^{15}N NMR); 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 hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. EI (electron impact) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer, data are listed to m/z 30 for 5% or more relative abundances (in parentheses) only. FD (field desorption) mass spectra were recorded on a Finnigan MAT 250 instrument, and FI (field ionization) mass spectra were recorded on a Varian MAT-CH5 instrument.

1,2,4-Triazole (=Hst; NMR data: $\delta(^1H)$ 8.60; $\delta(^{13}C)$ 147.6), 3-amino-1,2,4-triazole (=Hat; NMR data (solution in Me_2SO-d_6): $\delta(^1H)$ 12.2* (1 H, s), 7.55 (1 H, s), 5.95 (2 H, s); $\delta(^{13}C)$ 158.2, 148.1), and benzotriazole (=Hbt; NMR data: $\delta(^1H)$ 16.02 (1 H, s), 7.97 (2 H, m), 7.39 (2 H, m); $\delta(^{13}C)$ 139.0, 126.3, 115.1) were obtained from Aldrich Chemical Co., Milwaukee, WI. *N*-(Trimethylsilyl)-1,2,4-triazole (=Me_3Si(st); NMR data: $\delta(^1H)$ 8.26 (1 H, s), 8.14 (1 H, s), 0.54 (9 H, s); $\delta(^{13}C)$ 153.7, 145.9, −2.0) and *N*-(trimethylsilyl)-1,2,3-triazole (=Me_3Si(ut), where Hut = 1,2,3-triazole; NMR data (at room temperature): $\delta(^1H)$ 7.73 (2 H, s; the signal splits at 0 °C), 0.52 (9 H, s); $\delta(^{13}C)$ 135.9, 133.0, 126.8, −1.3, −1.5; $\delta(^{15}N)$ 336.3 (s) and 269.9 (s) for the (most abundant) 2-isomer, 372.2, 356.2, and 254.5 for the 1-isomer) were obtained from Petrarch Systems, Inc., Bristol, PA. Bromodimethylborane, Me_2BBr, was obtained from Morton Thiokol, Inc., Alfa Products, Danvers, MA; trimethylamine-borane, $Me_3N{\cdot}BH_3$, and triethylborane, Et_3B, were obtained from Callery Chemical Co., Callery, PA. Diethylchloroborane, Et_2BCl,[6] (dimethylamino)diethylborane, Me_2NBEt_2,[7] (dimethylamino)di-*n*-propylborane, $Me_2NB(n\text{-}C_3H_7)_2$,[8] diphenylbromoborane, Ph_2BBr,[9] and (dimethylamino)diphenylborane, Me_2NBPh_2,[10] were prepared by the indicated literature procedures.

***N*-(Trimethylsilyl)benzotriazole, $Me_3Si(bt)$ (Hbt = benzotriazole)**, was prepared by reacting equimolar (0.25 mmol) quantities of Hbt, Et_3N, and Me_3SiCl in 150 mL of benzene (reflux for 6 h). The precipitate of $Et_3N{\cdot}HCl$ was filtered off, and benzene was distilled off the clear filtrate (traces of unreacted benzotriazole sublimed out at this stage). The remaining product was distilled under reduced pressure to give 26.5 g (55%) of pure product, bp 125–126 °C/3 Torr.

NMR data: $\delta(^1H)$ 8.05 (1 H, d, J = 8.1), 7.57 (1 H, d, J = 8.3), 7.38 (1 H, t, J = 7.5, of d, J = 1.2), 7.27 (1 H, t, J = 6.6, of d, J = 1.5), 0.61 (9 H, s); $\delta(^{15}N)$ 387.1 (s), 347.0 (s), 235.0 (s). EI mass spectrum: m/z 191 (14), 148 (7), 74 (8), 73 (100), 64 (5), 63 (6), 45 (18), 43 (18), 39 (6).

$[H_2B(st)]_n$ (Hst = 1,2,4-Triazole). A mixture of 3.65 g (50 mmol) of $Me_3N{\cdot}BH_3$, 3.45 g (50 mmol) of Hst, and 75 mL of toluene was heated to reflux for 2–4 h until 1 molar equiv of hydrogen had evolved. A gummy precipitate was collected and recrystallized from 1,2-dichloroethane to give a powdery material beginning to melt near 235 °C and decomposing near 305 °C. Anal. Calcd for $[C_2H_4BN_3]_n$ (M_r = 80.89 for n = 1): C, 29.70; H, 4.98; N, 51.95. Found: C, 30.08; H, 5.07; N, 50.57.

NMR data (solution in Me_2SO-d_6): see text. Complete EI mass spectrum at 15 eV: m/z 485 (3), 405 (21), 404 (25), 403 (11), 324 (4), 323 (48), 322 (43), 312 (16), 320 (4), 242 (26), 241 (17), 240 (8), 174 (3), 162 (6), 161 (100), 160 (49), 159 (9), 133 (11), 132 (8), 106 (5), 105 (3), 69 (43), 42 (13), 32 (3), 31 (5). The FI mass spectrum exhibited three major peak groups in the regions m/z 404 and 323 (each ca. 70% of base peak) and 161 (base peak) and three peak groups of considerably less abundance (<10% of the base peak) in the regions m/z 484, 255, and 243. The FD mass spectrum exhibited four peak clusters centered at m/z 484, 403, 323, and 161.

$Me_2B(\mu\text{-}st)_2BMe_2$ and $[Me_2B(st)]_n$ (Hst = 1,2,4-Triazole). A solution of 20.1 g (166 mmol) of Me_2BBr in 100 mL of toluene was added dropwise with stirring to a solution of 23.63 g (167 mmol) of Me_3Si(st) in 100 mL of toluene. An exothermic reaction occurred, and the mixture was briefly refluxed. Toluene and Me_3SiBr were distilled off under reduced pressure. Part of the solid residue was sublimed off under vacuum (110 °C bath temperature at 10^{-3} Torr), and the sublimate was recrystallized from heptane to give 1.8 g of colorless product, mp 142–145 °C. Anal. Calcd for $(C_4H_8BN_3)_n$ (M_r = 217.88 for n = 2): C, 44.10; H, 7.40; N, 38.57. Found: C, 42.13; H, 7.18; N, 36.94.

NMR data: $\delta(^1H)$ 8.23 (1 H, s), 0.35 (3 H, s); $\delta(^{11}B)$ 0.6 (s, $h_{1/2}$ = 140 Hz); $\delta(^{13}C)$ 147.3, 10.4*; $\delta(^{15}N)$ 248.2, 236.5. EI mass spectrum: m/z 204 (10), 203 (100), 202 (48), 201 (6), 134 (8), 94 (11), 67 (8), 66 (6), 41 (19), 40 (6). The EI mass spectrum of the sublimation residue (decomposition occurred in the range of 240–260 °C) exhibited peaks up to the region m/z 420, indicating this material to be an oligomer $[Me_2B(st)]_n$ with n at least up to 4.

$Et_2B(\mu\text{-}st)_2BEt_2$ and $[Et_2B(st)]_n$ (Hst = 1,2,4-Triazole). When the original procedure[3] was repeated, variable amounts of the triazabole **2** (R = C_2H_5), mp 161–162 °C (lit.[3] 163–164 °C), were obtained but not more than about 30%.

NMR data: $\delta(^1H)$ 8.25 (1 H, s), 0.78 (2 H, q, J = 7), 0.56 (3 H, t, J = 7); $\delta(^{11}B)$ 2.9 (s, $h_{1/2}$ = 175 Hz); $\delta(^{13}C)$ 146.9, 16.1*, 8.4; $\delta(^{15}N)$ 248.0, 231.2. EI mass spectrum: m/z 246 (12), 245 (100), 244 (49), 243 (6), 187 (7), 133 (5), 53 (7), 41 (26), 40 (7).

Most of the material in each preparation of the preceding $Et_2B(\mu\text{-}st)_2BEt_2$ was a gummy residue. The FI mass spectrum of this product exhibited peaks indicating the presence of $[Et_2B(st)]_n$ with n up to 7, but those with n = 2–4 dominated the spectrum. On prolonged heating of the material (250 °C/3 Torr) additional dimer could be sublimed off but the total yield of the triazabole never exceeded 55%.

$Ph_2B(\mu\text{-}st)_2BPh_2$ and $[Ph_2B(st)]_n$ (Hst = 1,2,4-triazole) were prepared in a manner analogous to the preparation of the corresponding *B,B*-dimethyl derivatives via silazane cleavage (see above) using Ph_2BBr as the borane reagent. After solvent evaporation, a crude solid (melting with sintering over the range 150–250 °C) remained in essentially quantitative (97%) yield. The product was washed with water to remove unreacted triazole and then taken up in benzene, in which most of the material dissovled readily, leaving a gummy residue. After evaporation of the benzene from the clear solution, a colorless solid remained. It melted over a wide range to give a glassy material, which decomposed near 350 °C.

NMR data: $\delta(^1H)$ 7.47 (1 H, s), 7.24 (3 H, unresolved m), 6.93 (2 H, unresolved m); $\delta(^{11}B)$ 2.4 ($h_{1/2}$ = 1500 Hz). A molecular ion cluster at m/z 466 was observed in the EI mass spectrum of the material to suggest n = 2, i.e., a triazabole structure; the base peak was observed at m/z 313. The FD mass spectrum showed only the peak group for the monomer with n = 1 with the peaks m/z 234, 233, and 232 being observed in the correct calculated isotopic distribution for $C_{14}H_{12}BN_3$.

Thermal treatment of the above product (17 h at 250 °C/3 Torr) gave a 4.5% yield of a slightly tan sublimate, most of which dissolved in $CHCl_3$. After evaporation of the solvent, a colorless material of mp 252–255 °C remained. Anal. Calcd for $(C_{14}H_{12}BN_3)_n$ (M_r = 466.16 for n = 2): C, 72.14; H, 5.19; N, 18.03. Found: C, 71.62; H, 5.07; N, 17.67.

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(4) Dorokhov, V. A.; Amachyan, A. R.; Bochkareva, M. N.; Teslya, I. A.; Starikova, Z. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1987**, *36*, 147–151.

(5) Garnovskii, A. D.; Okhlobystin, O. Yu.; Osipov, O. A.; Yunusov, K. M.; Kolodyazhnyi, Yu, V.; Golubinskaya, L. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1972**, *42*, 910–914.

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

(7) Alam, F.; Niedenzu, K. *Inorg. Synth.* **1983**, *22*, 209–211.

(8) Emerick, D. P.; Komorowski, L.; Lipinski, J.; Nahm, F. C.; Niedenzu, K. *Z. Anorg. Allg. Chem.* **1980**, *468*, 44–54.

(9) Nöth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *11*, 399–405.

(10) Niedenzu, K.; Beyer, H.; Dawson, J. W. *Inorg. Chem.* **1962**, *1*, 738–742.

NMR data: $\delta(^1H)$ 8.12 (1 H, s), 7.08 (3 H, m), 6.77 (2 H, d, J = 8, of d, J = 2); $\delta(^{11}B)$ 2.0 (s, $h_{1/2}$ = 350 Hz); $\delta(^{13}C)$ 150.5, 133.4, 128.1, 128.0. The EI mass spectrum of this material showed a small cluster in the parent ion region of the dimer (=triazabole) near *m/z* 466; major peaks: *m/z* 390 (23), 389 (100), 388 (46), 387 (6), 321 (8), 320 (33), 319 (15), 311 (5), 269 (5), 166 (27), 164 (8), 163 (8), 77 (6), 51 (6).

$Et_2B(\mu\text{-at})_2BEt_2$ (Hat = 3-amino-1,2,4-triazole) was prepared in 66% yield as a mixture of 1,5- and 1,7-diamino isomers from excess of Et_3B and Hat following the previously reported procedure.[4] The crude material was recrystallized from dioxane to give a product of mp 284 °C dec. Anal. Calcd for $C_{12}H_{26}B_2N_8$ (M_r = 304.02): C, 47.41; H, 8.62; N, 36.86. Found: C, 46.38; H, 8.59; N, 33.45.

NMR data (solution in $Me_2SO\text{-}d_6$): $\delta(^1H)$ 8.09 (s) + 8.02 (s) (total 1 H, ratio ca. 2:1), 6.12 (2 H, s), 0.9–0.2 (10 H, unresolved m); $\delta(^{11}B)$ −2.6 ($h_{1/2}$ = 1500 Hz); $\delta(^{13}C)$ 159.2, 146.4, 13.7*, 8.9. The isomer with the ^1H NMR signal at 8.02 ppm is slightly better soluble in hot dioxane. The EI mass spectrum exhibited the base peak at *m/z* 275.

$(n\text{-}C_3H_7)_2B(\mu\text{-at})_2B(n\text{-}C_3H_7)_2$ (Hat = 3-Amino-1,2,4-triazole). A mixture of 5.0 g (59 mmol) of Hat, 25.2 g (179 mmol) of $Me_2NB(n\text{-}C_3H_7)_2$, and 100 mL of toluene was refluxed with stirring for 24 h. Toluene was distilled off under reduced pressure. The ^1H NMR spectrum of the remaining crude (liquid) product showed no (N)H signal. The material was covered with 10 mL of ethanol, 80 mL of hexane was added, and the mixture was refluxed for 1 h. The resultant precipitate was collected to give 1.7 g (16% yield) of crude material. It was recrystallized from dioxane to give a product mp 230–233 °C dec, corresponding to the previously described 1,5-diamino-4,4,8,8-tetra-*n*-propyltriazabole.

NMR data (solution in $Me_2SO\text{-}d_6$): $\delta(^1H)$ 8.07 (1 H, s), 5.09 (2 H, s), 0.9–0.4 (14 H, unresolved m); $\delta(^{11}B)$ 1.6 (s, $h_{1/2}$ = 1350 Hz). Lit.:[4] $\delta(^1H)$ (triazole region only) 8.04 (1 H, s), 6.06 (2 H, 2); $\delta(^{11}B)$ 1.3 (s).

$[Me_2B(ut)]_4$ (Hut = 1,2,3-Triazole).[11] A solution of 10.0 g (83 mmol) of Me_2BBr in 50 mL of hexane was added dropwise with stirring to a solution of 10.4 g (74 mmol) of $Me_3Si(ut)$ in 50 mL of hexane. The mixture was stirred at room temperature for 3 h, and the precipitate was collected, washed with pentane, and dried under vacuum to give 7.4 g (97% yield) of crude slightly tan material. The latter was recrystallized from cyclohexane to give colorless crystals, mp 183 °C, in 60–70% yield. Anal. Calcd for $C_{16}H_{32}B_4N_{12}$ (M_r = 435.76): C, 44.10; H, 7.40; N, 38.57. Found: C, 44.04; H, 7.37; N, 37.52.

NMR data: $\delta(^1H)$ 7.65 (1 H, s), 0.32 (3 H, s); $\delta(^{11}B)$ 0.4 (s, $h_{1/2}$ = 300 Hz); $\delta(^{13}C)$ 127.3, 7.5; $\delta(^{15}N)$ 359.8, 282.0. FD mass spectrum: *m/z* 422 (21), 421 (100), 420 (92), 419 (34), 418 (6). Calcd ratio for polyisotopic $C_{15}H_{29}B_4N_{12}$ (=$[Me_2B(ut)]_4$ minus CH_3): *m/z* 422 (21), 421 (100), 420 (92), 419 (32), 418 (5). The EI mass spectrum exhibited a weak ion cluster at *m/z* 421 and a base peak at *m/z* 312.

$[Et_2B(ut)]_4$ (Hut = 1,2,3-triazole) was prepared in analogous fashion as the preceding compound by employing Et_2BCl as the borane reagent. The compound was obtained in 50% yield as colorless crystals, mp 193–195 °C (after recrystallization from cyclohexane and then heptane). Anal. Calcd for $C_{24}H_{28}B_4N_{12}$ (M_r = 547.96): C, 52.61; H, 8.83; B, 7.89; N, 30.67. Found: C, 52.21; H, 9.05; B, 8.15; N, 30.06.

NMR data: $\delta(^1H)$ 7.62 (1 H, s), 0.87 (2 H, q, J = 8), 0.56 (3 H, t, J = 8); $\delta(^{11}B)$ 2.3 ($h_{1/2}$ = 800 Hz); $\delta(^{13}C)$ 128.0, 12.7, 8.7; $\delta(^{15}N)$ 361.4, 278.2. The EI mass spectrum (14 eV) exhibited an ion cluster at *m/z* 519 and a base peak at *m/z* 383.

$[H_2B(bt)]_n$ (Hbt = Benzotriazole). A mixture of 5.0 g (42 mmol) of Hbt, 3.1 g (42 mmol) of $Me_3N{\cdot}BH_3$, and 150 mL of toluene was heated under reflux for 4 h. A colorless precipitate formed on cooling to room temperature. It was collected, washed with petroleum ether, and dried under vacuum to give 5.1 g (93%) of crude product, mp 262–270 °C dec (after recrystallization from mesitylene). Anal. Calcd for $(C_6H_6BN_3)_n$ (M_r = 261.90 for n = 2); C, 55.03; H, 4.62; N, 32.09. Found: C, 55.07; H, 4.73; N, 31.34.

NMR data: $\delta(^1H)$ 7.94 (2 H, m), 7.48 (2 H, m), 4.2* (2 H); $\delta(^{11}B)$ −8.7 (s, $h_{1/2}$ = 300 Hz); $\delta(^{13}C)$ 138.7, 127.1, 114.6. The EI mass spectrum exhibited a parent ion cluster for n = 4 at *m/z* 524 and a base peak at *m/z* 261. In the FI mass spectrum, a base peak cluster was observed near *m/e* 523, a much smaller cluster (10% relative abundance) near *m/e* 260, and a very minor cluster (ca. 2% relative abundance) near *m/z* 131.

$[Me_2B(bt)]_4$ (Hbt = Benzotriazole). A solution of 5.0 g (40 mmol) of Me_2BBr in 25 mL of hexane was added dropwise and with stirring to a solution of 7.3 g (38 mmol) of $Me_3Si(bt)$ in 100 mL of hexane. A colorless gummy precipitate formed, and the mixture was allowed to stand overnight. The solution was decanted, and the residue was washed with hexane and dried under vacuum to give an essentially quantitative yield (6 g) of product. For purification it was dissolved in a minimal amount of benzene, and the solution was topped with the 6-fold amount of acetonitrile. When the solution was allowed to stand for several days, crystals of the compound formed, which were collected and dried, mp 190–195 °C. Anal. Calcd for $C_{32}H_{40}B_4N_{12}$ (M_r = 636.00): C, 60.43; H, 6.37; N, 26.43. Found: C, 60.09; H, 6.37; N, 26.17.

NMR data: $\delta(^1H)$ 7.61 (1 H, d, J = 7, of d, J = 3), 7.32 (1 H, d, J = 7, of d, J = 3), 0.55 (3 H, s); $\delta(^{11}B)$ 1.1 (s, $h_{1/2}$= 250 Hz). The highest ion peaks observed in the EI mass spectrum of the compound were at *m/z* 621, corresponding for the loss of one methyl group from the parent species.

$[Et_2B(bt)]_n$ (Hbt = Benzotriazole). A mixture of 6.0 g (50 mmol) of Hbt, 7 mL (50 mmol) of Et_3B, and 75 mL of xylene was refluxed for 2 h when gas evolution ceased. The colorless precipitate was collected, washed with water (to remove unreacted Hbt), and dried to give 8.2 g (88%) of crude (oligomeric) product, mp near 375 °C sintering and dec. Anal. Calcd for $(C_{10}H_{14}BN_3)_n$ (M_r = 374.10 for n = 2): C, 64.21; H, 7.54;, N, 22.46. Found: C, 64.40; H, 7.16; N, 22.09.

No solvent for recording NMR spectra was found. EI mass spectrum (15 eV): *m/z* 187 (7), 159 (9), 158 (79) 157 (18) 131 (11), 130 (79), 129 (21), 120 (13), 119 (100), 116 (10), 103 (5), 102 (11), 92 (6), 91 (74), 65 (5), 64 (26), 52 (6), 45 (35), 44 (32), 41 (10). The FD mass spectrum of the material exhibited an ion cluster in the region of the monomer only. No breakdown to yield a defined dimer or tetramer was found to occur on thermal treatment of the material.

Alternate Procedure. A mixture of 8.0 g (67 mmol) of Hbt, 5.0 g (44 mmol) of Me_2NBEt_2, and 200 mL of toluene was refluxed for 4 h. After cooling to room temperature, a colorless precipitate (2.0 g, 24%) of material, identical (mass spectrum) with that of the preceding experiment, was collected.

Alternate Procedure. A solution of 8 g (80 mmol) of Et_2BCl in 20 mL of hexane was added dropwise to a solution of 13 g (68 mmol) of $Me_3Si(bt)$ in 60 mL of hexane. The mixture was stirred at room temperature for 30 min, and the precipitate was collected, washed with hexane, and dried to give 13 g (essentially quantitative yield) of product, mp 385 °C sintering and dec. EI mass spectrum (15 eV): *m/z* 345 (2), 344 (2), 187 (14), 186 (5), 159 (12), 158 (98), 157 (26), 148 (5), 147 (21), 131 (13), 130 (100), 129 (29), 119 (29), 116 (14), 103 (11), 102 (11), 91 (30), 69 (6), 64 (9), 57 (6).

$[(n\text{-}C_3H_7)_2B(bt)]_n$ (Hbt = Benzotriazole). A mixture of 8.0 g (67 mmol) of Hbt, 5.0 g (35 mmol) of $Me_2NB(n\text{-}C_3H_7)_2$, and 200 mL of toluene was refluxed for 6 h. The clear solution was kept overnight, and the resultant precipitate was collected to give 2.4 g (32%) of crude product. It was recrystallized from toluene to give a material of mp 215–225 °C dec. Anal. Calcd for $(C_{12}H_{18}BN_3)_n$ (M_r = 430.22 for n = 2): C, 67.00; H, 8.43; N, 19.53. Found: C, 67.23; H, 8.61; N, 20.26.

NMR data: $\delta(^1H)$ 7.60 (1 H, unresolved), 7.33 (1 H, d, J = 6, of d, J = 3), 1.17 (2 H, t, J = 7), 0.75 (5 H, m); $\delta(^{11}B)$ −0.3 (s, $h_{1/2}$ = 1150 Hz); $\delta(^{13}C)$ 138.7, 126.1, 116.1, 36.0, 18.8, 18.0. EI mass spectrum (14 eV): *m/z* 215 (8), 173 (11), 172 (100), 171 (26), 144 (63), 143 (18), 142 (5), 119 (22), 116 (70), 102 (12), 91 (13), 71 (10), 32 (8). The highest ion cluster seen in the 70-eV EI mass spectrum of the compound was observed near *m/z* 817, indicating a loss of one alkyl group from the tetramer; the base peak was observed at *m/z* 172. The FD mass spectrum showed only peaks in the regions *m/z* 817, 387, and 215.

Solvent was stripped off the filtrate of the above experiment to give 1.5 g of a gummy residue. The FI mass spectrum of this material showed peaks in the regions *m/z* 387 and 239 only.

Results

Boron Derivatives of 1,2,4-Triazole (=Hst). The preparation of the parent compound of the *sym*-triazabole system, i.e., **2** with R = H, was attempted in analogy to the preparation of pyrazabole by condensation of $Me_3N{\cdot}BH_3$ with 1,2,4-triazole (=Hst). The reaction resulted in the formation of an oligomeric product, and no individual species could be separated. The highest ion cluster (of low abundance) in the (15 eV) EI mass spectrum of the product was observed in the region near *m/z* 485, indicating the presence of up to a hexameric material, i.e., $[H_2B(st)]_6$. The FI mass spectrum exhibited several peak groups (see experimental data) to support the assumption that an oligomer mixture was obtained. Such a mixture was also indicated by the ^{11}B NMR spectrum of the material, which exhibited a broad (approximately 2500 Hz) signal centered near −5 ppm, suggesting the formation of a number of species with different though similar ^{11}B chemical shifts. In addition, the ^1H NMR spectrum of the material exhibited five singlets at 9.25, 9.22, 8.59, 8.54, and 8.42 ppm in approximately 2:2:1:2:1 ratio, several additional but considerably

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(11) The crystal and molecular structure of this tetramer has been determined by single-crystal X-ray diffraction. The results will be published elsewhere in conjunction with other data.

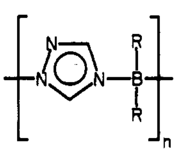
smaller signals for the triazolyl protons, and also a very broad (B)H resonance signal at 3–4 ppm.

The fragmentation pattern of the EI mass spectrum of the material was noticeably different from that observed for pyrazabole, $H_2B(\mu\text{-pz})_2BH_2$:[12] peak clusters corresponding to m/z values for $[H_2B(st)]_n + BH_2$, for example in the region m/z 175 corresponding to a species with $n = 2$ plus BH_2, were consistently observed. This suggests the possibility that all three nitrogen atoms of individual triazolyl groups may participate in the oligomer formation.

The reaction of Me_2BBr with (fluxional) *N*-(trimethylsilyl)-1,2,4-triazole, $Me_3Si(st)$, which was studied at various temperatures ranging 0–80 °C, gave only a small amount of the desired *sym*-triazabole **2** with $R = CH_3$; the bulk of the product was again what appears to be an oligomer mixture. Similarly, the transamination of Me_2NBPh_2 with Hst resulted primarily in a mixtureof oligomers.

On repeating of the original[3] condensation of Et_3B with Hst, only a small amount of the triazabole **2** ($R = C_2H_5$) was obtained. Even when the reactions were performed under seemingly identical conditions, the product yields varied considerably but never exceeded 30%; most of the product was a gummy mixture of oligomers as supported by the mass spectral data; however, the latter also seemed to indicate a slow conversion of oligomer to the corresponding triazabole (**2**) on heating of the material under vacuum. Indeed, when the cited gummy material was treated at temperatures near 250 °C/3 Torr, a substantial amount (up to 25%) of additional triazabole **2** ($R = C_2H_5$) sublimed off over a period of 24 h.

All of the data suggest that the primary coordination of individual *N*-triazolylborane units does not involve vicinal nitrogen atoms as in the triazabole structure **2** but that **4** is likely to be



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the better illustration for the oligomer and that, at least initially, the formation of the latter seems to predominate over that of a triazabole (**2**).

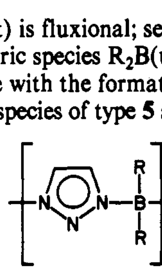
Similarly, although a small amount of the pure triazabole $Ph_2B(\mu\text{-st})_2BPh_2$ could be isolated and characterized, most of the material was oligomeric. The FD mass spectrum of the latter gave peaks only for the monomeric species $Ph_2B(st)$. This observation may suggest that the oligomer is a linear material.

Derivatives of 3-Amino-1,2,4-triazole (=Hat). The yield of an isolable *sym*-triazabole of type **2** is considerably increased by reaction of an excess of a trialkylborane with Hat. However, in this case isomeric species with the NH_2 groups in either the 1,5- or 1,7-positions were obtained. Usually, one of the isomers can be isolated in the pure state.

Replacement of the R_3B by Me_2NBR_2 in the reaction with Hat gave a considerably lower yield of **2** but led preferentially to the 1,5-diamino isomer.

It should be emphasized that in the reactions using Hat both the annular NH and the terminal NH_2 groups are borylated to form species of the type $R_2B[\mu\text{-}N_3C_2H(NHBR_2)]_2BR$ or even $R_2B[\mu\text{-}N_3C_2H\{N(BR_2)_2\}]_2BR_2$ as intermediates. (No effort was made to characterize these species; they are, however, readily recognized by the observation of three-coordinate boron at 33.3 ppm in the ^{11}B NMR spectra of such intermediates.) The NH_2 group is then restored during the workup via an alcoholysis to give the final product.

Derivatives of 1,2,3-Triazole (=Hut). N-Borylated 1,2,3-triazoles were prepared by reaction of *N*-(trimethylsilyl)-1,2,3-triazole, $Me_3Si(ut)$, with halodiorganylboranes, R_2BX (X = Br, Cl). (Note: $Me_3Si(ut)$ is fluxional; see Experimental Section.) The transient monomeric species $R_2B(ut)$ do not seem to exhibit a tendency to dimerize with the formation of triazaboles of type **3**. Rather, oligomeric species of type **5** appear to be the preferred



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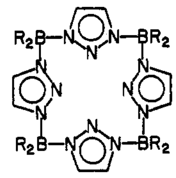
products. These may be linear and/or cyclic, but for $R = CH_3$ the cyclic species **5** with $n = 4$, i.e., **6** was found to be the exclusive



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product. Only one single resonance line was observed for the triazole rings in both the ^1H and ^{13}C NMR spectra of $[Me_2B(uz)]_4$, and the mass spectral data of the product clearly established the tetrameric nature of the species. The highest peak group observed in the EI spectrum (near m/z 421) was that for an ion where loss of a methyl group from the molecular ion M^+ of the tetramer had occurred, and the base peak of the spectrum (m/z 312) corresponded to a loss of a methyl group plus a $Me_2B(ut)$ unit from M. In addition, ions of relatively high abundances were observed for compositions corresponding to $Me_6B_3(ut)_2$ (m/z 259), $Me_3B_2(ut)_2$ (m/z 203), and $Me_4B_2(ut)$ (m/z 150). The FD mass spectrum of the species exhibited only a cluster in the m/z 421 region. These data clearly support the structure **6**, which resembles that of porphin and was confirmed by an X-ray crystal structure analysis.[11]

The *B,B*-diethyl derivative of N-borylated 1,2,3-triazole was also obtained as the tetramer (**6**); there were no indications for the formation of a triazabole of type **3** nor for that of other oligomeric materials.

Derivatives of Benzotriazole (=Hbt). The reaction of $Me_3N{\cdot}BH_3$ with Hbt gave what appeared to be primarily the tetramer $[H_2B(bt)]_4$ with a cyclic structure analogous to **6**. However, the FI mass spectral data suggest the additional presence of a small amount of a dimer and traces of a monomer. It may well be that under the reaction conditions the tetramer of type **6** is the dominant product but that some dimer and (linear?) oligomer are also formed. This conclusion is also borne out by the relative wide melting range of the product.

Reaction of Me_2BBr with $Me_3Si(bt)$ initially gave a gummy material, $[Me_2B(bt)]_n$, which was obviously oligomeric in nature. Slow crystallization gave a sharp melting product, the ^1H NMR spectrum of which exhibited only two sharp signals in the aromatic region. In conjunction with the mass spectral data, the crystalline material is identified as the tetramer corresponding to **6** (see also below).

Similarly, the reaction of Hbt with $Me_2NB(n\text{-}C_3H_7)_2$ proceeded to give what appeared to be the tetramer $[(C_3H_7)_2B(bt)]_4$, since the highest peak seen in the 70-eV EI mass spectrum of the resultant product was observed at m/z 817. In the 14 eV spectrum, the highest peak was observed at m/z 215 (M^+ for a dimer) with a base peak at m/z 170. This would indicate the ready loss of a propyl group from the parent ion M^+ of a triazabole of type **3**. (This fragmentation is analogous to that of *B,B,B′,B′*-tetraorganylpyrazaboles, $R_2B(\mu\text{-pz})_2BR_2$, which is generally dominated by a lack of a molecular ion and features the parent ion M^+ minus one organyl group as the highest ion that can be observed.[13]) On the other hand, the FD mass spectrum of the species showed a

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

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

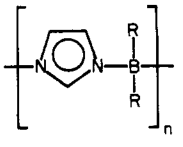
peak cluster in the region m/z 817, corresponding to a species $[R_2B(bt)]_4$ with n = 4 minus 43 (=C_3H_7), as well as peaks near m/z 387 and 215. Another interesting feature was the observation of only two ^1H NMR signals for the C_6H_4 group of the species and also the equivalence of the C(1) and C(2) as well as C(3)/C(6) and C(4)/C(5) atoms of the benzene ring in the ^{13}C NMR spectrum. This cannot be in consonance with a triazabole structure **3** but clearly suggests a symmetrical structure where N(1) and N(3) of the five-membered C_2N_3 ring are involved in bonding to boron. These data seem to be best interpreted by assuming that the tetramer is formed as the primary product but is contaminated by additional oligomers.

Surprisingly, the EI and FD mass spectral data of $[Et_2B(bt)]_n$ obtained from either Et_3B and Hbt or Me_2NBEt_2 and Hbt exhibited only one ion cluster near m/z 187, suggesting it to be a monomer. A small amount of the dimer was seen in the EI mass spectrum of the product obtained from the reaction of Et_2BCl with $Me_3Si(bt)$. Since the effect of a BEt_2 versus those of a $B(C_3H_7)_2$ group on the degree of oligomerization should be negligible, it may well be that the method of preparation affects the value of n.

Discussion

When pyrazole (=Hpz) or C-substituted derivatives thereof (=Hpz*) are condensed with a trigonal borane (or a Lewis base adduct thereof), pyrazaboles of **1** are readily obtained.[2] However, reactions involving 3-monosubstituted pyrazoles lead to the formation of isomers; i.e., mixtures of the 1,5- and 1,7-disubstituted pyrazaboles are obtained.[14-16] This illustrates the fluxionality of the assumed intermediate monomeric 1-pyrazolylborane, $R_2B(pz^*)$ (containing trigonal boron), a feature that has been well established.[15,17-19]

The reaction of 1,2,4-triazole (=Hst) with a trigonal borane to a yield a *sym*-triazabole (**2**) should pose no problem were it not for the fact that the third annular nitrogen can also serve as a binding site to boron. Thus, either an intermediate monomeric *N*-triazolylborane, $R_2B(st)$, may utilize vicinal nitrogen atoms of the triazole ring to dimerize and yield a triazabole (**2**) or coordinative saturation of the boron may occur by linking of the N(1) and N(4′) atoms of two triazole rings, rendering the formation of a dimer to be unlikely. Rather, this latter situation is similar to that of boron derivatives of imidazole (=Hiz), where the few known monomeric species, $R_2B(iz)$, have also been found to be fluxional, undergoing a 1,3-shift of the N-bonded boryl group.[18] However, if the boron substituents are not strongly electron-donating, association occurs to give oligomeric $[R_2B(iz)]_n$ species of type **7** containing four-coordinate boron.[20-23] Although the tetrameric species with n = 4 and presumably cyclic structure appears to predominate,[22,23] higher molecular weight chain-type oligomers with n = 40–80 have been reported.[20] On the other hand, if C(2) is substituted, e.g., by using 2-methylimidazole, reaction with a trigonal borane provides a (presumably cyclic) tetramer in essentially quantitative yield.[20]



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In the case of a N-borylated 1,2,4-triazole species there is no obvious reason why a pyrazabole-type dimerization should be favored over an oligomerization typical for imidazolylboranes. Presumably, both processes compete although the present results suggest that oligomerization (to yield **4**) is favored over dimerization (to yield **2**). This observation can be interpreted by assuming that after attachment of boron to N(1) of Hst, N(2) and N(4) are of about equal basicity and coordinative saturation of the boron could lead to the formation of both **2** and oligomers **4**. The fluxionality (=migration of the BR_2 group among the various nitrogen sites) of the assumed monomeric intermediate $R_2B(st)$ may also favor the formation of both types of species. Since proloned thermal treatment of the initial product gave increased yields of **2**, the latter generally appears to be the thermodynamically favored product.

This situation is different when 3-amino-1,2,4-triazole is employed. It is likely that in this case the fluxionality of the presumed monomeric intermediate is impaired by the substitution at C(3) of the triazole ring, thus forcing dimerization rather than oligomerization.

The oligomerization involving N(1) and N(3) as binding sites for boron is clearly preferred in the case of boron derivatives of 1,2,3-triazoles, and the formation of tetrameric species (**6**) seems to predominate. This observation supports the assumption that, as a rule, nonneighboring nitrogen atoms generally are the preferred binding sites for the coordinative saturation of boron of N-borylated 1,2,3-triazole monomers rather than formation of a N(1)–B–N(2′) arrangement. These results suggest that monomeric N-borylated triazoles behave more similar in their intermolecular coordinative behavior to the corresponding imidazole rather than pyrazole derivatives.

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(14) Petersen, L. K.; Thê, K. I. *Can. J. Chem.* **1979**, *57*, 2520–2522.

(15) Alam, F.; Niedenzu, K. *J. Organomet. Chem.* **1983**, *243*, 19–30.

(16) Niedenzu, K.; Niedenzu, P. M.; Warner, K. R. *Inorg. Chem.* **1985**, *24*, 1604–1606.

(17) Niedenzu, K.; Weber, W. *J. Organomet. Chem.* **1980**, *195*, 25–28.

(18) Weber, W.; Niedenzu, K. *J. Organomet. Chem.* **1981**, *205*, 147–146.

(19) Alam, F.; Niedenzu, K. *J. Organomet. Chem.* **1982**, *240*, 107–119.

(20) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3903–3904.

(21) Boenig, I. A.; Conway, W. R.; Niedenzu, K. *Synth. React. Inorg. Met.-Org. Chem.* **1975**, *5*, 1–5.

(22) Breakall, K. R.; Rendle, D. F.; Storr, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1584–1589.

(23) Müller, K.-D.; Komorowski, L.; Niedenzu, K. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 149–155.