Inorg. Chem. **1986**, *25*, 1771–1774 **1771**

Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506

Boron–Nitrogen Compounds. 110.[1] Reactions of Boroxins and Diboroxanes with Pyrazole

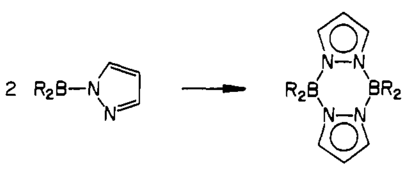
J. Bielawski and K. Niedenzu*

Received October 21, 1985

Tetraorganyldiboryl oxides (1,3-diboroxanes) $(R_2B)_2O$ ($R = C_2H_5$, C_6H_5), react at elevated temperatures with excess pyrazole, Hpz, to give an essentially quantitative yield of the corresponding pyrazabole, $R_2B(\mu\text{-pz})_2BR_2$. The 1,3-diboroxane $[(CH_3)_2NBR]_2O$ ($R = C_6H_5$) reacts with Hpz in refluxing toluene to form the triply bridged pyrazabole $RBB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ as the major product besides substantial quantities of the diboroxane derivative $[(pz)RB(\mu\text{-pz})_2BR]_2O$. In the latter, two pyrazabole moieties are linked by an oxygen bridge between boron atoms. The boroxin adduct $(\text{–BRO–})_3\cdot\text{Hpz}$ ($R = C_6H_5$) is obtained on direct interaction of triphenylboroxin with pyrazole at room temperature. As based on NMR data, two boron atoms of the boroxin ring are coordinated to pyrazole nitrogen atoms and the N-bonded proton is delocalized. In contrast, all three boron atoms are coordinated in 1:1 molar mixtures of the boroxin with either 3,5-dimethylpyrazole or imidazole. The adduct $(\text{–BRO–})_3\cdot 3\text{Hpz}$ was identified as a transient species. It undergoes a slow condensation on standing in solution at room temperature. At elevated temperatures the reaction progresses readily to yield the triply bridged pyrazabole $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$. When a neat mixture of the two reagents is refluxed, the pyrazabole $R_2B(\mu\text{-pz})_2BR_2$ is obtained. Triethylboroxin and pyrazole interact readily even at room temperature beyond mere complexation to form $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ with $R = C_2H_5$. Additional pyrazole and even minor increases in temperature promote the condensation process.

Introduction

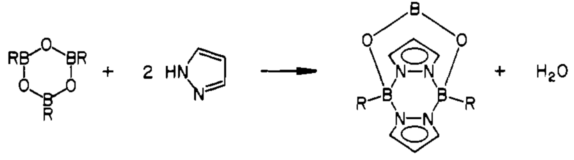
Although a few monomeric 1-pyrazolylboranes containing trigonal boron, $R_2B(pz)$ (**1**) (Hpz = pyrazole), are known,[2-6] most of such species rather dimerize to form pyrazaboles, $R_2B(\mu\text{-pz})_2BR_2$ (**2**), by intermolecular association as shown in eq 1.[7] As based on CNDO calculations, this dimer formation is energetically highly favored, leads to good electronic saturation of the boron, and is generally independent of the conformation of the resultant B_2N_4 ring system.[8]



(1)

1 **2**

In a surprising reaction, a novel type of pyrazaboles has recently been obtained by condensation of triorganylboroxins, $(\text{–BRO–})_3$, with pyrazole according to eq 2.[9] The resultant species of type **3**, $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$, represented the first examples of a neutral pyrazabole species where the two boron atoms are linked by three bridging units. They are intramolecular association products of compounds of the type $RB[OBR(pz)]_2$ and thus can also be viewed as diboroxane derivatives.



(2)

3

The present study reports a detailed investigation of the interaction of pyrazole with triorganylboroxins and 1,3-diboroxanes.

Experimental Section

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

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfied shifts from the reference (internal Me_4Si for ^1H and ^{13}C NMR, external $Et_2O\cdot BF_3$ for ^{11}B 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 Hz. Details for 2D NMR experiments have been given elsewhere.[10]

Infrared spectra (frequencies in cm^{-1}) were recorded on a Perkin-Elmer Model 621 or a Bomem DA3 spectrometer under standard operating conditions: s = strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad. Mass spectral data were obtained on a VG ZAB-2F spectrometer.

$(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$. A mixture of 7.7 g (50 mmol) of tetraethyldiboroxane, $[(C_2H_5)_2B]_2O$,[11] and 7.5 g (110 mmol) of pyrazole, Hpz, was heated to 120–130 °C for 6 h. When it was cooled to room temperature, the mixture solidified. It was crushed and washed with several portions of water (in order to remove unreacted pyrazole) to leave, after drying, 13.3 g (98%) of crude product, mp 101–102 °C. It was recrystallized from ethanol to give a pure material, mp 107–108 °C (lit.[12] mp 106–107 °C), identical (NMR and mass spectral data) with an authentic sample of the compound.

$[(C_6H_5)_2B]_2O$.[13] The melting point (after sublimation, free of $(\text{–B}C_6H_5\text{O–})_3$ as based on ^1H NMR data) was 126–128 °C (lit.[13] mp 116–118 °C). NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.89 (2 H, d, J = 8), 7.47 (3 H, m); $\delta(^{11}B)$ 45.6 ($h_{1/2}$ = 500 Hz).

$(\text{–B}C_6H_5\text{O–})_3$.[14] NMR data: $\delta(^1H)$ (solution in $CDCl_3$) 8.23 (2 H, d, J = 8), 7.35 (3 H, m); $\delta(^{11}B)$ (solution in $CDCl_3$) 29.2 ($h_{1/2}$ = 350 Hz); $\delta(^{11}B)$ (solution in CD_3CN) 29.4 ($h_{1/2}$ = 100 Hz); $\delta(^{11}B)$ (solution in CS_2[15]) 30.4.

$(C_6H_5)_2B(\mu\text{-pz})_2B(C_6H_5)_2$. This compound was obtained in essentially the same manner and in comparable yield as described above for the corresponding *B,B,B′,B′*-tetraethyl derivative when $[(C_6H_5)_2B]_2O$ was used as the boron reagent; mp (after recrystallization from toluene) 277–279 °C (lit.[12] mp 273–274 °C).

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.49 (2 H, d, J = 2.7), 7.0 (6 H, m), 6.8 (4 H, m), 6.41 (1 H, t, J = 2.1); $\delta(^{11}B)$ 1.8 ($h_{1/2}$ = 300 Hz); $\delta(^{13}C)$ (proton decoupled) 146*, 137.3, 133.2, 127.0, 126.4, 105.5. As based on selective decoupling and 2D NMR experiments, the signal pairs

---

(1) Part 109: Bielawski, J.; Hodgkins, T. G.; Layton, W. J.; Niedenzu, K.; Niedenzu, P. M.; Trofimenko, S. *Inorg. Chem.* **1986**, *25*, 87–90.

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

(3) Weber, W.; Niedenzu, K. *J. Organomet. Chem.* **1981**, *205*, 147–156.

(4) Hodgkins, T. G.; Niedenzu, K.; Niedenzu, K. S.; Seelig, S. S. *Inorg. Chem.* **1981**, *20*, 2097–3000.

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

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

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

(8) Companion, A. L.; Liu, F.; Niedenzu, K. *Inorg. Chem.* **1985**, *24*, 1738–1740.

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

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

(11) Fenzl, W.; Köster, R. *Inorg. Synth.* **1983**, *22*, 188–190.

(12) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165–3170.

(13) Neu, R. *Chem. Ber.* **1954**, *87*, 802–805.

(14) *Gmelin Handbuch der Anorganischen Chemie*; Springer-Verlag: West Berlin, 1977; Vol. 44, Supplement Boron Compounds 13, pp 196–198.

(15) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: West Berlin, Heidelberg, New York, 1978.

0020-1669/86/1325-1771$01.50/0 © 1986 American Chemical Society

$\delta(^1H)/\delta(^{13}C)$ 7.49/137.3 and 6.41/105.5 can be assigned to the pyrazole CH groups.

The same pyrazabole was also obtained in ca. 70% yield when a neat mixture of $(-BC_6H_5O-)_3$ and excess Hpz (1:5 molar ratio) was refluxed for 4 h.

$[(CH_3)_2NBC_6H_5]_2O$.[16] A mixture of 20.8 g (67 mmol) of *B,B′,B″*-triphenylboroxin, $(-BC_6H_5O-)_3$,[14] 35.2 g (200 mmol) of bis(dimethylamino)phenylborane, $C_6H_5B[N(CH_3)_2]_2$,[17] and 50 mL of toluene was refluxed for 90 min. The solvent was stripped off under vacuum, 40 mL of petroleum ether (bp 50–75 °C) was added, and the mixture was cooled to −25 °C. The desired product precipitated in large needles, which were collected, and the purification procedure was repeated. The colorless crystals were dried for 24 h under vacuum to give 17.2 g of product, mp 47–48 °C. An additional quantity, 13.2 g, was obtained on workup of the mother liquors to give a total yield of 54%. Anal. Calcd for $C_{16}H_{22}B_2N_2O$ (mol wt 280.0): C, 68.63; H, 7.92; N, 10.00. Found: C, 68.91; H, 7.57; N, 9.38.

NMR data: $\delta(^1H)$ (solution in CCl_4) 7.05 (s, 5 H), 2.80 (s, 3 H), 2.67 (s, 3 H), coalescence of the two Me signals at 66 °C; $\delta(^{11}B)$ (solution in CH_2Cl_2) 29.4 (s, $h_{1/2}$ = 300 Hz); $\delta(^{13}C)$ (solution in $CDCl_3$) 132.4, 127.6, 127.0, 38.7, 36.3, boron-bonded carbon atom not observed.

Reaction of $[(CH_3)_2NBC_6H_5]_2O$ with Hpz. A mixture of 20.8 g (67 mmol) of $(-BC_6H_5O-)_3$,[14] 35.2 g (200 mmol) of $C_6H_5B[N(CH_3)_2]_2$,[17] and 50 mL of toluene was refluxed for 90 min in order to give a solution of $[(CH_3)_2NBC_6H_5]_2O$ (see above). After this solution was cooled to room temperature, 27.2 g (400 mmol) of pyrazole and an additional 250 mL of toluene were added and the mixture was refluxed with stirring for 4 h. About 200 mL of the toluene was removed under reduced pressure, and the mixture was cooled to room temperature. A colorless crystalline material, 7.4 g, precipitated and was collected, washed with a small amount of toluene and then with petroleum ether and dried under vacuum. These crystals, A, had a melting point of 248–249 °C.

On standing of the filtrate for 48 h, an additional precipitate, B, had formed, which was collected, washed with a small amount of toluene, and dried. This second fraction, 8.9 g having a melting point near 200 °C, showed a ^1H NMR spectrum closely resembling that of the previously described[9] triply bridged pyrazabole $C_6H_5B(\mu\text{-}pz)_2(\mu\text{-}BC_6H_5O)BC_6H_5$; also the ^{11}B NMR spectrum showed the expected peaks at 26.8 and 1.9 ppm but in an area ratio of about 1:4, indicating that the compound was not pure.

The remainder of toluene was then removed from the filtrate and approximately 35 g of a slightly yellow sticky residue was obtained, which was similar (^1H NMR spectrum) to fraction B with which it was combined.

Purification and Characterization of Fraction A, $[(pz)(C_6H_5)B(\mu\text{-}pz)_2BC_6H_5]_2O$. Fraction A was washed with hot cyclohexane and then recrystallized from toluene to give a pure product, mp 251–253 °C. Anal. Calcd for $C_{42}H_{38}B_4N_{12}O$ (mol wt 770.09): C, 65.51; H, 4.97; B, 5.61; N, 21.83. Found: C, 65.67; H, 5.11; B, 5.26; N, 21.70.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ unresolved overlapping multiplets from 7.7 to 6.2; $\delta(^{11}B)$ 1.8 ($h_{1/2}$ = 600 Hz). Mass spectral data: see text. Infrared spectrum (KBr pellet): 3152 sh, 3130 sh, 3115 ms, 3072 w, 3042 wm, 3008 m, 1946 w, 1870 w, 1812 w, 1763 w, 1645 w, br, 1588 w, 1510 sh, 1495 ms, 1445 m, 1430 s, 1411 vs, 1381 s, 1331 sh, 1311 s, 1260 m, 1250 vs, 1221 vs, 1198 vs, 1181 sh, 1172 wm, 1145 ms, 1121 sh, 1077 vs, 1041 wm, 1027 sh, 1008 ms, 972 sh, 965 sh, 930 m, 914 sh, 890 sh, 868 sh, 856 s, 823 ms, 799 ms, 773 sh, 755 s, 730 s, 694 ms, 665 vw, 632 ms, 614 w.

Fraction B was recrystallized from cyclohexane to give about 30 g of colorless crystals, mp 207–211 °C, identical (NMR and mass spectral data) with the previously[9] described triply bridged pyrazabole $RB(\mu\text{-}pz)_2(\mu\text{-}OBRO)BR$ (**3**) ($R = C_6H_5$). The cyclohexane-insoluble residue was recrystallized from toluene to give an additional crop of A (5 g).

$(-BC_6H_5O-)_3\cdot$Hpz. To a solution of 3.1 g (10 mmol) of $(-BC_6H_5O-)_3$ in 85 mL of benzene was added a solution of 0.7 g (10 mmol) of pyrazole (=Hpz) in 15 mL of benzene. The mixture was stirred for 4 h at ambient temperature. The resultant precipitate was collected and dried to give 2.7 g of material, mp 164–166 °C. On evaporation of the solvent, an additional 0.8 g of less pure material (mp 156–161 °C) was obtained to provide for a total yield of 92%. Anal. Calcd for $C_{21}H_{19}B_3N_2O$ (mol wt 379.85): C, 66.40; H, 5.05; B, 8.54; N, 7.38. Found: C, 66.55; H, 5.24; B, 8.56; N, 7.26.

NMR data (solution in CD_3CN): $\delta(^1H)$ 7.98 (4 H, m), 7.79 (3 H, m, containing a doublet (2 H) that collapses to a singlet on selective decoupling of the triplet at δ 6.45), 7.40 (10 H, m), 6.45 (1 H, t, J = 2.5), uneven base line suggesting that an additional but extremely broad proton signal is camouflaged by the observed peaks; $\delta(^{11}B)$ 29.6 (1 B, s, $h_{1/2}$ = 140 Hz), 20.9 (2 B, s, $h_{1/2}$ = 400 Hz). Infrared spectrum (KBr pellet): 3322 s, 3165 w, 3140 w, 3070 wm, 3025 wm, 1955 w, 1900 w, 1840 w, 1770 w, 1598 s, 1574 w, 1528 w, 1490 wm, 1482 wm, 1442 sh, 1438 vs, 1410 s, 1390 sh, 1380 vs, 1342 sh, 1330 s, 1320 s, 1295 wm, 1275 ms, 1248 vs, 1205 wm, 1190 s, 1170 m, 1152 sh, 1118 s, 1085 ms, 1065 wm, 1050 m, 1024 sh, 1018 m, 998 w, 978 m, 968 sh, 915 sh, 910 w, 904 sh, 870 w, 830 wm, 810 s, 770 s, 758 sh, 742 m, 695 vs, 680 wm, 665 sh, 635 w, 615 sh, 570 s.

$(-BC_6H_5O-)_3\cdot Hpz(Me)_2$. This material was prepared in a manner analogous to that for the preceding compound from 3.1 g (10 mmol) of $(-BC_6H_5O-)_3$ and 0.95 g (10 mmol) of 3,5-dimethylpyrazole (=Hpz(Me)$_2$) using 100 mL of benzene. The resultant clear solution was reduced in volume to about 30 mL and cooled in an ice bath to yield 2.9 g of a colorless precipitate, mp 146–149 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.99 (5 H, m), 7.39–7.34 (10 H, m), 5.89 (1 H, s), 2.29 (6 H, s), integration suggesting one additional H as a very broad signal in the aromatic region ranging from 8.2 to 6.9 ppm; $\delta(^{11}B)$ 20.5 (s, $h_{1/2}$ = 750 Hz).

$(-BC_6H_5O-)_3\cdot$Hidz. This material was prepared in a fashion similar to that for the preceding compound by mixing 3.1 g (10 mmol) of $(-BC_6H_5O-)_3$ and 0.7 g (10 mmol) of imidazole (=Hidz) in 100 mL of benzene; mp 163–169 °C dec.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.84* (5 H, unresolved), 7.31 (10 H, m), 6.89* (1 H, s), 6.41* (2 H, s), integration suggesting one additional H as a very broad signal in the aromatic region ranging from 8.1 to 6.8 ppm; $\delta(^{11}B)$ 19.5*.

Reaction of $(-BC_2H_5O-)_3$ with Hpz. To a solution of 3.4 g (20 mmol) of triethylboroxin, $(-BC_2H_5O-)_3$,[18] in 15 mL of ether (or benzene) was added with stirring a solution of 1.4 g (20 mmol) of pyrazole (=Hpz) in 15 mL of ether (or benzene). A slightly exothermic reaction occurred, and the mixture was stirred overnight at ambient temperature. The solvent was removed under reduced pressure to yield 4.6 g (96% of the calculated yield for a 1:1 molar adduct) of a material, mp 64–72 °C (from ether) or 70–85 °C (from benzene), respectively. The ^{11}B NMR spectrum of a freshly prepared material exhibited $\delta(^{11}B)$ 26.0 (ca. 2 B, $h_{1/2}$ = 1100 Hz) and 1.8 (ca. 1 B, $h_{1/2}$ = 220 Hz). The spectrum changed on standing of the solution, indicating a continuous though slow reaction. Similarly, ^1H NMR spectra were not reproducible and their appearance depended on the storage time of the solution. With time, the spectra gave increasing evidence for the presence of the triply bridged pyrazabole **3** ($R = C_2H_5$), suggesting that even at room temperature a process beyond mere complexation occurred. Indeed, on refluxing of a 1:3 molar solution of the two reactants for only 2 h in diethyl ether a ca. 80% conversion (based on boroxin) to **3** was observed. Furthermore, even on standing of a 1:1 molar mixture of $(-BC_2H_5O-)_3$ and Hpz in ether at room temperature for 2 days, most of the material had converted to **3**.

$(-BC_2H_5O-)_3\cdot Hpz(Me)_2$ was prepared by mixing 1.30 g (7.8 mmol) of $(-BC_2H_5O-)_3$ and 0.74 g (7.8 mmol) of 3,5-dimethylpyrazole (=Hpz(Me)$_2$) in 5 mL of chloroform. On slow evaporation of the solvent, an oily residue remained, which solidified on standing to give a crystalline material, mp 67–71 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 10.32* (1 H, s), 5.94 (1 H, s), 2.37 (6 H, s), 0.86 (9 H, m), 0.65 (6 H, m); $\delta(^{11}B)$ 24.0 ($h_{1/2}$ = 670 Hz).

Results and Discussion

The amination of a boron–oxygen bond is a relatively rare event. It is, however, considerably promoted by chelate formation and by subsequent reactions that influence the amination equilibrium.[19] In view of the reaction according to eq 1 and the inherent stability of the pyrazabole ring system[8] it is, therefore, not surprising that *B*-organo-substituted 1,3-diboroxanes of the type $(R_2B)_2O$ ($R = C_2H_5, C_6H_5$) readily react with pyrazole, Hpz, to give essentially quantitative yields of the corresponding pyrazaboles, $R_2B(\mu\text{-}pz)_2BR_2$.

The reaction of the diboroxane $[(CH_3)_2NBC_6H_5]_2O$ with pyrazole was expected to proceed smoothly by displacement of dimethylamine to give $[(pz)RB]_2O$ ($R = C_6H_5$ = $RB(\mu\text{-}pz)_2(\mu\text{-}O)BR$ (**3**, but where the bridging O–BR–O group is replaced by a single oxygen) and, possibly, the pyrazabole $(pz)RB(\mu\text{-}pz)_2B(pz)R$. However, in refluxing toluene, the major product was the triply bridged pyrazabole **3**, besides which substantial quantitites

---

(16) Taken from: Weber, W. Ph.D. Dissertation, University of Mainz, Mainz, West Germany, 1979.

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

(18) Ashby, E. C. *J. Am. Chem. Soc.* **1959**, *81*, 4791–4795.

(19) *Houben-Weyl Methoden der Organischen Chemie*: Thieme Verlag: Stuttgart, New York, 1983; Vol. 13/3b, pp 40–41.

Table I

	m/z							
	696	695	694	693	692	691	690	689
fa(calcd)	0.004	0.031	0.144	0.388	0.304	0.103	0.016	0.001
fa(obsd)	0.006	0.029	0.134	0.395	0.301	0.113	0.021	0.003

Table II

$B_3C_{27}H_{24}N_6O$

	m/z						
	484	483	482	481	480	479	478
fa(calcd)	0.002	0.022	0.138	0.465	0.298	0.070	0.006
fa(obsd)	0.001	0.018	0.131	0.442	0.307	0.066	0.004

$B_3C_{24}H_{22}N_8O$

	m/z						
	474	473	472	471	470	469	468
fa(calcd)	0.002	0.019	0.129	0.469	0.304	0.071	0.006
fa(obsd)	0.001	0.018	0.123	0.462	0.310	0.082	0.006

of another species were obtained. The latter was identified as $(pz)RB(\mu\text{-}pz)_2BROBR(\mu\text{-}pz)_2RB(pz) = [(pz)RB(\mu\text{-}pz)_2BR]_2O$, i.e., a 1,3-diboroxane where two pyrazabole units are linked by an oxygen bridge between two boron atoms.

It is possible that $RB(\mu\text{-}pz)_2(\mu\text{-}O)BR$ is initially formed. Under the reaction conditions, a B–O bond of this species may then be attacked by additional Hpz to yield the hydroxypyrazabole $(HO)RB(\mu\text{-}pz)_2BR(pz)$. This latter process may be promoted by the anticipated ring strain encountered in the B–O–B link of $RB(\mu\text{-}pz)_2(\mu\text{-}O)BR$. Subsequently, two molecules of the hydroxypyrazabole condense with the elimination of water to give the observed diboroxane $[(pz)RB(\mu\text{-}pz)_2BR]_2O$. The water generated in the pyrazolysis of B–O bonds could interact with $[(CH_3)_2NBR]_2O$, producing $(\text{-}BRO\text{-})_3$ in the process. The boroxin then can react with pyrazole in the fashion observed earlier[9] to give the cited triply bridged pyrazabole $RB(\mu\text{-}pz)_2(\mu\text{-}OBRO)BR$ (**3**).

The suggested structure of $[(pz)RB(\mu\text{-}pz)_2BR]_2O$ rests primarily on the results of the elemental analysis and mass spectroscopic data. The NMR spectra data are inconclusive, and due to solubility difficulties, no molecular weight determination could be performed. In the mass spectrum of the species, the parent ion P (calculated monoisotopic mass 770 amu) was not observed. (This latter event is frequently the case for B-organo-substituted pyrazaboles.[20]) Rather, an extremely weak fragmentation ion was seen for P − 67 = 703 (loss of a pz group) and a cluster of high abundance was seen for P − 77 = 693 (indicative of the loss of a phenyl group from the parent). The isotope pattern of the latter peak suggests that the species contains four boron atoms; moreover, calculated and observed fractional abundances (fa) strongly support the composition $B_4(C_6H_5)_3(pz)_6O = B_4C_{42}H_{38}N_{12}O$ (Table I).

The next major fragmentation peaks that were observed are centered at *m/z* 481 and 471, respectively. These two peaks suggest the fragments $B_3(C_6H_5)_3(pz)_3O = B_3C_{27}H_{24}N_6O$ and $B_3(c_6H_5)_2(pz)_4O = B_3C_{24}H_{22}N_8O$, as is supported by the calculated and observed isotopic patterns (Table II).

Between these major peaks several clusters of low abundances were observed, which are readily interpreted by reasonable fragmentations, e.g., *m/z* 693 − 67 = 626 and 626 − 77 = 549. The next major peak was found at *m/z* 377, corresponding to the fragment $B_2(C_6H_5)_2(pz)_3$, i.e., a pyrazabole moiety X of the parent diboroxane X_2O. Again, observed and calculated isotopic patterns for $B_2C_{21}H_{19}N_16$ agree very well (Table III). Additional major fragments in the high-molecular-weight range are found near *m/z* 326, 259, 249, and 221, all of which represent reasonable fragments of the formulated parent.

The preceding data support the suggested structure of the diboroxane $[R(pz)B(\mu\text{-}pz)_2BR]_2O$. This species represents a novel type of pyrazabole inasmuch as two pyrazabole moieties are boron-linked by an oxygen bridge. All previously described materials containing more than one pyrazabole structure in the molecule are C-bonded polymers of undetermined chain lengths.[21]

Table III

	m/z					
	380	379	378	377	376	375
fa(calcd)	0.001	0.017	0.132	0.558	0.253	0.030
fa(obsd)	0.002	0.014	0.126	0.544	0.260	0.024

It is of interest to note that brief heating of the diboroxane $[(pz)RB(\mu\text{-}pz)_2BR]_2O$ with methanol led to the formation of more of the triply bridged pyrazabole **3** ($R = C_6H_5$). The structure of such triply bridged pyrazaboles has recently been confirmed by an X-ray diffraction study on the species with $R = C_2H_5$.[22] As expected, the central B_2N_4 ring was found to exist in a boat conformation with B–N bond distances of about 1.58 Å. The B–O bonds of the bridging O–BR–O group are distinctly shorter (1.36 Å) than those of the pyrazabole boron atoms (1.45 Å).

When $(\text{-}BC_6H_5O\text{-})_3$ and Hpz were combined in 1:1 molar ratio in solution at room temperature, the adduct $(\text{-}BC_6H_5O\text{-})_3\cdot Hpz$ could be isolated and characterized.

Such 1:1 molar adducts of *B,B′,B″*-triorganylboroxins with amines, $(\text{-}BRO\text{-})_3\cdot L$ (L = amine), have been known for a long time.[23] However, the first X-ray crystal structure determination of such a species has been reported only recently.[24] It was found that in the solid state the amine is coordinated to a single boron atom of the boroxin ring, leaving the other two in an sp^2 environment. This was not seen in the room-temperature ^{11}B NMR spectra of a series of such adducts, which exhibited only a single boron resonance line (shifted upfield as compared to the signal for the pure boroxin), suggesting equal donation to all three boron atoms of the boroxin ring. However, at lower temperatures, a signal splitting was indeed observed with the low-field to high-field peak being in a ratio of 2:1, thus illustrating coordination of only one boron atom(in consonance with the crystal structure data).

However, the adduct $(\text{-}BC_6H_5O\text{-})_3\cdot Hpz$ was found to be distinctly different from the "normal" 1:1 molar boroxin adducts with amines as described above. At room temperature, the ^{11}B NMR spectrum of the species exhibited two signals, $\delta(^{11}B)$ 29.4 and 20.9, respectively, but in a ratio of 1:2 (low-field peak to high-field peak). This observation suggests that both nitrogen atoms of the pyrazole donate to boron, leaving only one boron atom of the boroxin ring in an sp^2 environment. This unusual coordination was further substantiated by the ^1H NMR spectrum of the adduct, where the two NCH protons of the pz ring were evidenced by only one signal, $\delta(^1H)$ 7.79, indicating their equivalence. The NH proton showed up as an extremely broad signal residing under the aromatic protons, suggesting extensive delocalization. The sharpness of the N–H stretching mode in the infrared spectrum of the compound corresponds to that observed for the adduct $R_2HN\cdot B(pz)_3$ ($R = CH_3$), where the N-bonded proton was found to be delocalized[25] but also readily displaced to give a saltlike species.[26]

When an additional 2 molar equiv of Hpz was added to a solution of $(\text{-}BRO\text{-})_3\cdot Hpz$ ($R = C_6H_5$) and a ^{11}B NMR spectrum was recorded immediately, the peak $\delta(^{11}B)$ 29.4 had almost disappeared and a shoulder $\delta(^{11}B)$ 20.9 remained and accompanied the new strong signal $\delta(^{11}B)$ 18.8 ($h_{1/2}$ = 40 Hz); in addition, a very small signal, $\delta(^{11}B)$ 2.5, could be seen (see Figure 1). These observations may be interpreted by coordination of all three boron atoms with a pyrazole moiety as the dominant feature, i.e., identification of the species $(\text{-}BC_6H_5O\text{-})_3\cdot 3Hpz$ with the signal $\delta(^{11}B)$ 18.8. However, ^1H and ^{11}B NMR spectra of a solution

---

(20) Seelig, S. S. Thesis, University of Kentucky, 1979.

(21) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118–5126.

(22) Niedenzu, K.; Shore, S. G., to be submitted for publication.

(23) Yabroff, D. L.; Branch, G. E. *J. Am. Chem. Soc.* **1932**, *54*, 2569; **1933**, *55*, 1663–1665.

(24) Yalpani, N.; Boese, R. *Chem. Ber.* **1983**, *116*, 3347–3358.

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

(26) Niedenzu, K.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 4222–4223.

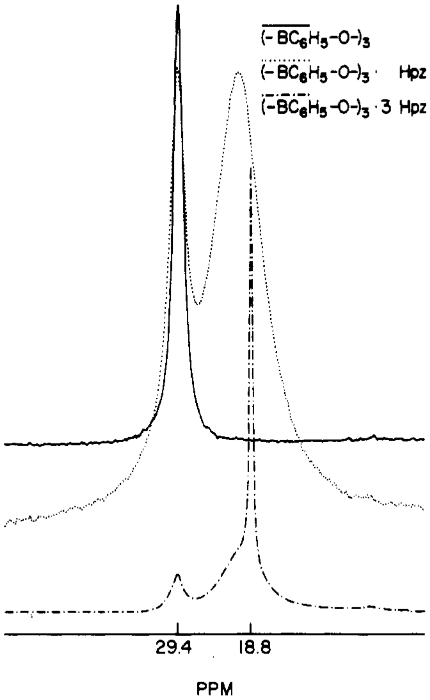


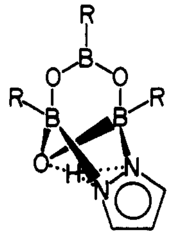
Figure 1. ^{11}B NMR spectra of (-BC$_6$H$_5$O-)$_3$, (-BC$_6$H$_5$O-)$_3$·Hpz, and (-BC$_6$H$_5$O-)$_3$·3Hpz.

of (-BC$_6$H$_5$O-)$_3$·3Hpz evidence considerable changes after only a few hours of standing at room temperature, indicating subsequent transformation. The reaction rate of the latter increases with temperature, and on heating of (-BC$_6$H$_5$O-)$_3$ with Hpz in bromoform[9] or mesitylene, condensation occurs very readily, yielding the triply bridged pyrazabole **3**. On the other hand, refluxing a neat mixture of (-BC$_6$H$_5$O-)$_3$ and Hpz yielded the pyrazabole R$_2$B(μ-pz)$_2$BR$_2$. Since no formation of the anticipated R(pz)B(μ-pz)$_2$BR(pz) was observed, the thermal stability of the latter must be less than that of **3**.

In contrast, 3,5-dimethylpyrazole was found to form a 1:1 molar complex with triphenylboroxin that, at room temperature, exhibits only one ^{11}B NMR signal in consonance with the case for the previously described[24] adducts. Hence, it is worth noting that under the conditions when triphenylboroxin and pyrazole were found to form the triply bridged pyrazabole **3**, no similar reaction occurred between the cited boroxin and 3,5-dimethylpyrazole. These observations suggest that the methyl groups exert a strong influence by directing the interaction with the boroxin to simple complexation rather than to the formation of a precursor for subsequent condensation. Similarly, (-BC$_6$H$_5$O-)$_3$ and imidazole formed a 1:1 molar complex of the "normal" type, i.e., where in solution all three boron atoms of the boroxin are coordinated to the base; only one ^{11}B NMR signal was observed.

Surprisingly, no adduct (-BC$_2$H$_5$O-)$_3$·Hpz could be isolated and identified. The room-temperature ^{11}B NMR spectrum of a freshly prepared equimolar mixture of the materials in benzene showed two signals in an approximate area ratio of 2:1 (low field to high field), thus suggestng the formation of a "normal" boroxin-amine complex. However, the low-field signal (δ(^{11}B) 26.0) was exceedingly broad ($h_{1/2}$ = ca. 1100 Hz!), and after brief standing of the solution, the latter signal separated into two recognizable peaks with δ(^{11}B) near 32.1 and 28.2 ppm, respectively, accompanied by an increase in the intensity of the signal at 1.8 ppm. These observations suggest that even at room temperature (-BC$_2$H$_5$O-)$_3$ and Hpz interact fairly readily beyond mere complexation. This was also confirmed by changes in the ^{1}H NMR spectrum on standing of the solution. In order to support the assumption of a low-temperature interaction beyond simple adduct formation, a mixture of the two compounds was heated to reflux in diethyl ether solution. After only 2 h reaction time, most of the boroxin had reacted to form the triply bridged pyrazabole **3** (R = C$_2$H$_5$) with δ(^{11}B) 31.5 (1 B) + 1.8 (2 B). Moreover, after standing of a mixture of (-BRO-)$_3$ and Hpz in ether at room temperature for several hours, most of the material had interacted to give **3** and essentially equantitative conversion was observed within a few days.

Although the rate of interaction of triorganylboroxins with pyrazole seems to be influenced by the nature of the substituents, there is no evidence to suggest principal differences. Rather, the present results imply that on interaction of triorganylboroxin with pyrazole the adduct (-BRO-)$_3$·Hpz is the initial product. This complex is, however, not analogous to the previously reported base adducts of triorganylboroxins[24] but seems to have a special structure that may be illustrated by **4**. Moreover, this complexation is but an intermediate stage and, even at room temperature (and promoted by the presence of additional Hpz), a condensation occurs that leads to the formation of a triply bridged pyrazabole of type **3**. The ready formation of this latter species may result from the fact that it is partially preformed in the initial product, as is suggested in **4**. Additional attack by pyrazole on **4** would proceed by elimination of water to give the observed product **3**.



4

On the other hand, (-BC$_2$H$_5$O-)$_3$ and 3,5-dimethylpyrazole form a 1:1 molar complex exhibiting only one ^{11}B NMR signal that did not change on prolonged standing of a solution of the material. This observation indicates the formation of a "normal" type complex in analogy to (-BC$_6$H$_5$O-)$_3$ (see above) and the previously described species,[24] thus illustrating the strong steric effect of the methyl groups.

The different reaction rates for the boroxins with R = C$_2$H$_5$ and C$_6$H$_5$, respectively, seem to reflect a steric effect. The flexible and smaller ethyl groups permit very ready formation of **4** and its subsequent reaction with additional pyrazole to yield **3**. This process is much slower in the case of triphenylboroxin, where the complex (-BRO-)$_3$·3Hpz seems to be a transient species. Steric factors also seem to determine the different complexation of 3,5-dimethylpyrazole with boroxins, where only the "normal" (fluxional) coordination (see above) to all three boron atoms in a 1:1 molar complex was observed and no condensation to species of type **3** could be realized.

Acknowledgment. The authors gratefully acknowledge a generous gift of triethylboroxin by Professor R. Köster, Max-Planck-Institut für Kohlenforschung, Mülheim, West Germany. This work was supported by the Office of Naval Research.

Registry No. **2** (R = C$_6$H$_5$), 6431-90-9; **2** (R = C$_2$H$_5$), 14695-69-3; **3** (R = C$_6$H$_5$), 99593-93-8; **3** (R = C$_2$H$_5$), 99604-53-2; **4** (R = C$_6$H$_5$), 101834-77-9; Hpz, 288-13-1; Hpz(Me)$_2$, 67-51-6; Hidz, 288-32-4; [(C$_2$H$_5$)$_2$B]$_2$O, 7318-84-5; [(C$_6$H$_5$)$_2$B]$_2$O, 4426-21-5; (-BC$_6$H$_5$O-)$_3$, 3262-89-3; [(CH$_3$)$_2$NBC$_6$H$_5$]$_2$O, 101834-81-5; C$_6$H$_5$B[N(CH$_3$)$_2$]$_2$, 1201-45-2; [(pz)(C$_6$H$_5$)β(μ-pz)$_2$BC$_6$H$_5$]$_2$O, 101834-76-8; (-BC$_6$H$_5$O-)$_3$·Hpz(Me)$_2$, 101834-78-0; (-BC$_6$H$_5$O-)$_3$·Hidz, 101834-79-1; (-BC$_2$H$_5$O-)$_3$·Hpz(Me)$_2$, 101834-80-4; (-BC$_2$H$_5$O-)$_3$, 3043-60-5.