On the Structures of the 1:1 Adducts of Triorganylboroxins and Pyrazole[1)]

Mohamed Yalpani* and Roland Köster

Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr

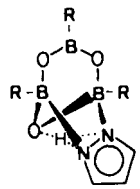
Received March 10, 1988

The structures of the 1:1 adducts **3**, **4** of triorganylboroxins and pyrazole have been reinvestigated. Detailed NMR analyses reveal that, contrary to recent reports, they form a normal 1:1 adduct in which only one nitrogen and one boron atom are involved in bonding as our earlier studies had shown.

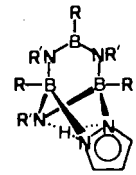
Über die Strukturen der 1:1-Additionsverbindungen aus Triorganoboroxinen und Pyrazol[1)]

Im Gegensatz zu Mitteilungen von anderer Seite ergeben detaillierte NMR-Untersuchungen über die Struktur der 1:1-Additionsverbindungen **3**, **4** aus Triorganylboroxinen und Pyrazol, daß wie üblich nur ein Bor-Atom an ein Stickstoff-Atom der Base gebunden ist.

In two recent publications by Bielawski and Niedenzu[2,3)] on the reactions of pyrazoles with triorganylboroxins and borazines, spectroscopic evidence is presented to support the formation of 1:1 adducts having the unusual structures **1** and **2**. In these both the nitrogen atoms of the pyrazole have become simultaneously bonded to two of the three boron atoms of the boroxin and borazine rings, respectively.



1: R = Et, Ph



2: R = Et
R' = Me

In an earlier report on the structure of several amine adducts of triorganylboroxins $(RBO)_3$ with R = Et, Ph we have shown[4)] that in solutions the amine nitrogen atom rapidly fluctuates between the boron atoms of the boroxin ring. This process is slowed down in solution at lower temperatures and in the solid state, as shown in the structures determined by X-ray method; the amine nitrogen atom is then bonded to only one of the three boron atoms. This arrangement even persists in the crystalline 2:3 adduct $[(PhBO)_3]_2 \cdot (4\text{-}H_2NC_6H_4NH_2)_3$ in which the stoichiometry of the two partners formally suggests participation of all the six boron atoms of the two boroxin rings in bonding with the six available nitrogen atoms of the three amine molecules present in the crystal. However, crystal structure data demonstrated that only one of the three *p*-phenylenediamine molecules is involved in bonding to the two boroxin rings. The remaining two diamine molecules occupy sites at non bonding distances serving only to contribute to the lattice stability[4)].

This discrepancy between our findings[4)] and those now reported[2,3)], specially since only pyrazole itself and none of its derivatives or the related hydrazines[5)] seem to interact with boroxins to form the unusual 1:1 adducts of the type **1**, prompted us to further scrutinize this reaction.

Results and Discussion

In the reported procedure for preparing the triphenyl- and triethylboroxin adducts of the type **1** reaction times of several to about 12 hours are given. In our experience adduct formation is at room temperature a very fast exothermic process[4)]. To avoid secondary reactions we therefore quenched the reaction mixture shortly after mixing the components by cooling to affect crystallization of the products. Initially the ^1H-, ^{13}C-, and ^{11}B-NMR spectra of these solid products were determined by insuring minimal exposure to room temperature between their dissolution in the appropriate solvents ($CDCl_3$, CD_2Cl_2, CD_3CN, or $[D_8]THF$) and the measurements.

The room temperature ^{11}B-NMR spectrum of the 1:1 adduct **3** of pyrazole and triphenylboroxin in $CDCl_3$ showed a single broad signal at $\delta = 22.8$. A similarly obtained spectrum of the 1:1 adduct **4** of pyrazole and triethylboroxin (in $CDCl_3$) showed also a single broad signal at $\delta = 27.0$. When these extreme precautions were not taken and the solutions where left at room temperature for about 1/2 h before the measurements, for **3** a strong broad signal at $\delta = 26.7$ and a small peak at $\delta = 2.0$ in a ratio of about 9:1 was observed. In CD_3CN we observe signals at $\delta = 29.0$, 23.7, and 1.8 in a ratio of about 2:19:1. Similarly, for **4** the ^{11}B-NMR spectrum in $CDCl_3$ showed signals at $\delta = 32$ (shoulder), 26.1 and 2.0 in a ratio of about 9:1. Leaving this latter sample solution a further 24 h at room temperature resulted in a slightly deshielded ($\Delta\delta = 0.8$) main broad signal at $\delta = 26.9$ and an increase of the relative intensity of the signal at $\delta = 2.0$ with a new ratio of about 5.5:1. However, in neither situation could the reported 1:2 ratio of the signals at $\delta \approx 30$ and at $\delta \approx 2.0$ be found as required by structure **1** and described by the authors[2)].

Even more informative are the ^1H- and ^{13}C-NMR spectra of **3** and **4**. The ^1H-NMR spectra of solutions which had been briefly exposed to room temperature are shown in Fig-

  0009–2940/88/0909–1553 $ 02.50/0

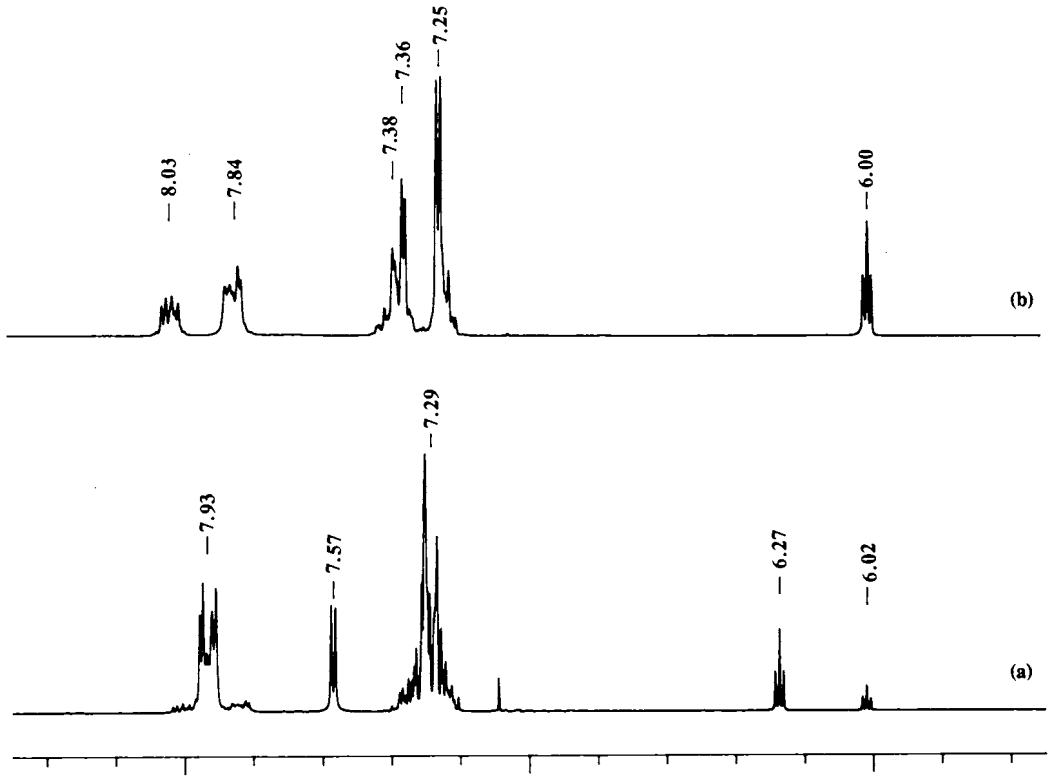


Figure 1. Room temperature ^{1}H-NMR spectra (a) of **3** plus in situ formed **5**, (b) of pure **5** formed in the dehydration process

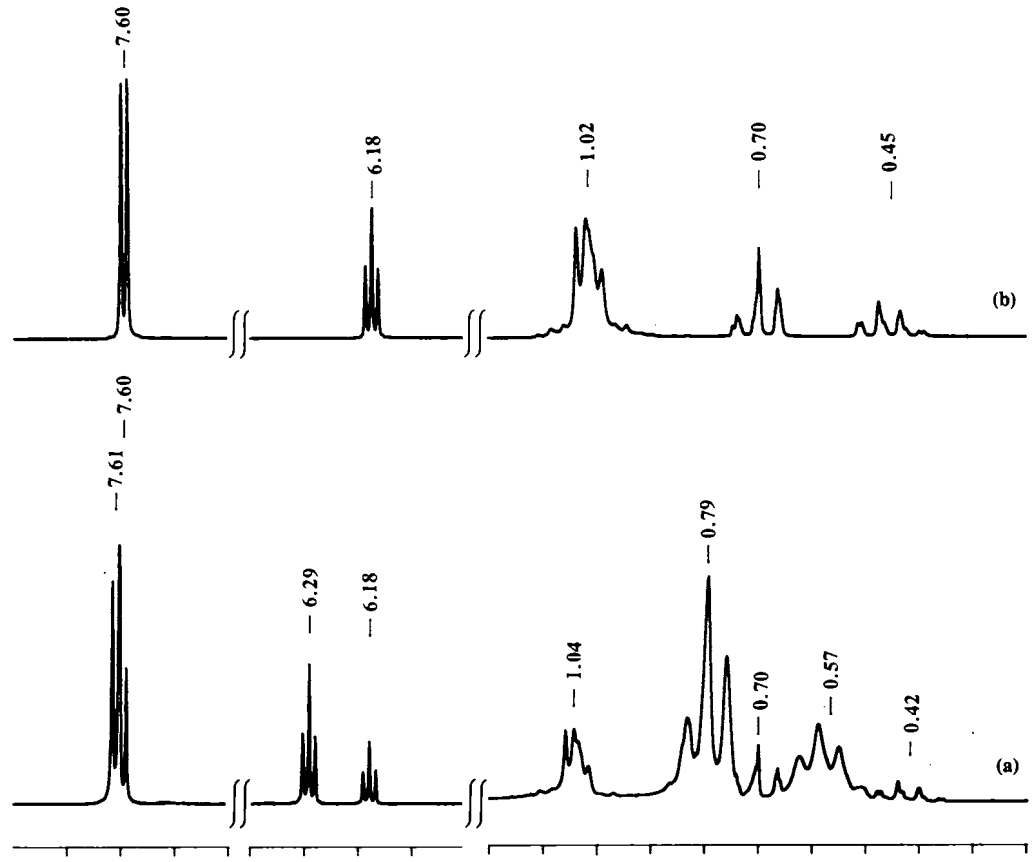
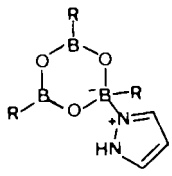


Figure 2. Room temperature ^{1}H-NMR spectra (a) of **4** plus in situ formed **6**, (b) of pure **6** formed in the dehydration process

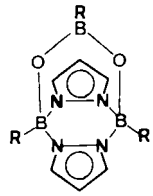
ures 1a and 2a, respectively. Both spectra are indicative of a two-component mixture, the minor component (cf below) being present to the extent of about 20%. In Figure 1a a single set of signals at δ = 7.93 (m), assignable to the *ortho* protons of the aromatic rings of the boroxin moiety of **3**, appear in about a 2:3 ratio to the *meta* and *para* aromatic protons at δ = 7.29 (m). Similarly for **4**, aside from the signals for the minor component there is only a single A_3B_2 set of ^{1}H-NMR signals at δ = 0.79 (t) and 0.57 (q) as depicted in Fig. 2a in accordance with the equivalence of all the three ethyl groups of the triethylboroxin moiety. A similar equivalence of the three substituents on the boroxin rings of **3** and **4** is also evident in their ^{13}C-NMR spectra (cf experimental section).

In the ^{1}H-NMR spectra of both **3** and **4** the protons at the α-carbon atoms of the pyrazole moiety appear to be equivalent and form a doublet at δ = 7.57 and 7.61, respectively. When the prior room-temperature exposure of solutions of **3** and **4** had been avoided the minor components were nearly absent in the ^{1}H-NMR spectra. In the low-temperature ^{1}H-NMR spectrum of **4** (CD_2Cl_2, −80°C) the equivalence of the two protons on the α-carbons of the pyrazole moiety was abolished, resulting in two separate signals at δ = 8.0 (br, 1H) and 7.8 (br, 1H), besides the signal at 6.35 (dd, 1H) for the β-H proton of the pyrazole ring. Since in this low-temperature spectrum the ethyl substituents appeared as a broad signal, we also obtained a low temperature ^{13}C-NMR spectrum of **4** (CD_2Cl_2, −80°C) which similarly showed three signals for the three carbon atoms of the pyrazole ring [δ = 135.0 (d), 132.7 (d), 106.8 (d)] as well as one single broad signal at δ = 16.9 (t) and one single narrow signal at δ = 9.1 (q) for the two carbon atoms of all the three ethyl substituents.

We therefore conclude, that the initially formed product is a normal 1:1 adduct of the known type[4] as depicted by **3** and **4**.



3: R = Ph
4: R = Et



5: R = Ph
6: R = Et

At ambient temperatures in solution beside the fluctuation of the nitrogen atom among the three boron atoms of the boroxin ring an additional rapid exchange of the boron atom coordination of the two nitrogen atoms of the pyrazole moiety also takes place. While the rate of the $B^1/B^2/B^3$-exchange process is still fast relative to the NMR time scale even at −80°C, the nitrogen N^1/N^2-exchange process is slowed down or has stopped as evident by the nonequivalence of the carbons as well as the protons of the pyrazole ring.

Bielawski and Niedenzu also describe a 1:3 adduct, formed from triphenylboroxin with three equivalents of pyrazole, and present a ^{11}B-NMR spectrum with mainly a single very sharp signal at δ = 18.8. They assign this to a complex in which all three boron atoms have become coordinated by the nitrogen atoms of the three pyrazole molecules. This complex is reported to be unstable reverting slowly over days to the OBO-bridged pyrazabole **5**[2]. We repeated this work but crystallized the adduct formed, immediately after mixing the components, by cooling the reaction solution to −80°C. The ^{11}B NMR of the solid obtained immediately after its redissolution in $CDCl_3$, showed signals at δ = 21.2 and 2.0 in the ratio of about 20:1.

A similarly obtained ^{1}H-NMR spectrum showed essentially the same peak pattern as shown in Figure 1a albeit with signal intensities compatible with a 1:3 ratio of boroxin to pyrazole. These spectra were also unstable in time. The similarity of the spectra of the 1:1 and "1:3" adducts of triphenylboroxin and pyrazole suggests that in both cases a "normal" coordination of only one nitrogen atom per boroxin molecule takes place. The identities of the initially formed minor components in the reactions of triphenyl- and triethylboroxin with pyrazole were established to be the OBO-bridged pyrazaboles **5** and **6** by comparison with authentic materials[6], prepared by an improved method (cf below).

The ^{1}H-NMR spectra of **5** and **6** are depicted in Figures 1b and 2b and collated with the spectra shown in Figures 1a and 1b. It was furthermore noticed that, nearly independent of the boroxin pyrazole ratios used, the room-temperature conversions of **3** or **4** to **5** or **6** came to an abrupt halt after several days at about 50–60% conversion. Heating of the solutions did not result in further changes of the spectra, however addition of a drying agent such as molecular sieves or anhydrous Na_2SO_4 brought about a complete transformation to **5** or **6**. We therefore conclude that initially formed adducts **3** or **4** are in a multistep equilibrium with the respective OBO-bridged pyrazaboles **5** or **6**. The dehydration can be driven to completion by adding a drying agent or, more efficiently, by azeotropic distillation. The relatively long reaction times of 6–7 h and the heating process at about 145°C for **5**, or at about 120°C for **6**, used by the authors[6], can be avoided and complete conversion to pure **5** and **6** achieved.

Experimental

All reactions were carried out under dry oxygen-free argon. All solvents were freshly distilled under argon from appropriate drying agents. – ^{1}H-, ^{13}C-, and ^{11}B-NMR spectra: Bruker (AC 200) spectrometer, chemical shifts in ppm relative to internal Me_4Si for ^{1}H and ^{13}C shifts and from external Et_2O-BF_3 for ^{11}B shifts. – DSC measurements: DuPont 1090 instrument.

Preparation of **3**: To 1.56 g (5.0 mmol) of triphenylboroxin, dissolved in 5 ml of CH_2Cl_2, was added a solution of 0.34 g (5.0 mmol) of pyrazole in 3 ml of CH_2Cl_2. The mixture was stirred for about 5 min at room temperature, then cooled to −80°C, and the colourless solid that separated was collected by filtration (1.80 g, 94%) [m.p. (DSC) 150–165°C dec.]. – δ(^{1}H) ($CDCl_3$) = 10.94 (br, 1H),

7.93 (m, 6H), 7.57 (d, 3.0 Hz, 2H), 7.29 (m, 9H), 6.27 (t, 3.0 Hz, 1H). – $\delta(^{13}C)$ ($CDCl_3$) = 134.1 (d), 133.5 (d), 133.7 (br, s), 130.5 (d), 127.4 (d), 106.4 (d). – $\delta(^{11}B)$ ($CDCl_3$) = 23.7 ($h_{1/2} \approx 800$ Hz).

Preparation of **4**: To 1.58 g (9.4 mmol) of triethylboroxin in 3 ml of CH_2Cl_2 was added a solution of 0.64 g (9.4 mmol) of pyrazole in 5 ml of CH_2Cl_2. The mixture was briefly stirred, then cooled to −80°C and worked up as above to give a colourless solid product (1.8 g, 81%) [m.p. (DSC) 60–70°C dec.]. – $\delta(^1H)$ ($CDCl_3$) = 11.11 (br, 1H), 7.61 (d, 3.0 Hz, 2H), 6.29 (t, 3.0 Hz, 1H), 0.79 (t, 7.4 Hz, 9H), 0.57 (q, 7.4 Hz, 6H). – $\delta(^{13}C)$ ($CDCl_3$) = 132.3 (br, d), 105.7 (d), 9.2 (br, t), 7.3 (q). – $\delta(^{11}B)$ ($CDCl_3$) = 26.1 ($h_{1/2} \approx 670$ Hz).

Preparation of **5**: From a solution of 1.53 g (12.5 mmol) of phenylboronic acid and 0.67 g (9.8 mmol) of pyrazole in about 40 ml of benzene about 25 ml of the solvent and the water formed were removed by azeotropic distillation. The remaining solvent was evaporated in vacuo. The solid residue was recrystallized from hexane (1.69 g, 94%). – $\delta(^1H)$ ($CDCl_3$) = 8.03 (m, 2H), 7.84 (m, 4H), 7.36 (m, 6H), 7.25 (d, 3.0 Hz, 4H), 7.23 (m, 3H), 6.00 (t, 3.0 Hz, 2H). – $\delta(^{13}C)$ ($CDCl_3$) = 139.0 (br, s), 135.9 (d), 134.5 (d), 133.6 (d), 129.8 (d), 128.3 (d), 127.5 (d), 127.0 (d), 104.5 (d). – $\delta(^{11}B)$ ($CDCl_3$) = 27.7 (1B, $h_{1/2} \approx 780$ Hz), 1.5 (2B, $h_{1/2} \approx 240$ Hz).

Preparation of **6**: From a solution of 2.0 g (11.9 mmol) of triethylboroxin and 1.65 g (24.3 mmol) of pyrazole in 40 ml of benzene about 2/3 of the solvent was removed by azeotropic distillation. After evaporation of the rest solvent and drying in vacuo, the solid product was recrystallized from hexane (3.1 g, 91%). – $\delta(^1H)$ ($CDCl_3$) = 7.60 (d, 3.0 Hz, 4H), 6.18 (t, 3.0 Hz, 2H), 1.02 (m, 10H), 0.70 (t, 7.5 Hz, 3H), 0.45 (q, 7.5 Hz, 2H). – $\delta(^{13}C)$ ($CDCl_3$) = 133.6 (d), 104.5 (d), 9.0 (br, t), 8.3 (q), 8.15 (q). – $\delta(^{11}B)$ ($CDCl_3$) = 32.18 (1B, $h_{1/2} \approx 450$ Hz), 1.98 (2B, $h_{1/2} \approx 140$ Hz).

CAS Registry Numbers

1 (R = Et): 114959-03-4 / **1** (R = Ph): 101834-77-9 / **2**: 114959-04-5 / **3**: 114959-01-2 / **4**: 114959-02-3 / **5**: 99593-93-8 / **6**: 99604-53-2 / triphenylboroxin: 3262-89-3 / pyrazole: 288-13-1 / triethylboroxin: 3043-60-5 / phenylboronic acid: 98-80-6

---

[1] The identical text of this paper, conceived mainly to be corrective of the structures I and II of our reference 2), was first sent for publication to Inorganic Chemistry (on Dec. 21, 1987). There it was rejected without any objective scientific reasoning. Herein we like to express our bewilderment at such a deplorably subjective treatment of purely scientific matters.

[2] J. Bielawski, K. Niedenzu, *Inorg. Chem.* **25** (1986) 1771.
[3] J. Bielawski, M. K. Das, E. Hanecker, K. Niedenzu, H. Nöth, *Inorg. Chem.* **25** (1986) 4623.
[4] M. Yalpani, R. Boese, *Chem. Ber.* **116** (1983) 3347.
[5] M. K. Das, J. F. Mariategui, K. Niedenzu, *Inorg. Chem.* **26** (1987) 3114.
[6] J. Bielawski, K. Niedenzu, *Inorg. Chem.* **25** (1986) 85.

[61/88]