Journal of Organometallic Chemistry, 369 (1989) 137–145
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09906

Boron–nitrogen compounds

CXX *. Complexes of *B*-triethylboroxin with ethylenediamine and derivatives thereof

J. Francisco Mariategui and Kurt Niedenzu
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506 (U.S.A.)

(Received January 12th, 1989)

Abstract

B-Triethylboroxin forms colorless 1/1 molar complexes of the type $(C_2H_5BO)_3 \cdot L$ with L = ethylenediamine (**1**) and various derivatives of the latter, i.e., *N,N*-dimethylethylenediamine (2), *N,N,N′,N′*-tetramethylethylenediamine (**3**), piperazine (**4**), 1,4-diazabicyclo[2.2.2]octane (**5**), diethylenetriamine (**6**), and tris(2-aminoethyl)amine (**7**). The cited boroxin also forms 2/1 molar complexes, $2(C_2H_5BO)_3 \cdot L$, with L = ethylenediamine (**8**) and those derivatives of the latter which may be considered as symmetrical species, i.e., *N,N,N′,N′*-tetramethylethylenediamine (**9**), piperazine (**10**), 1,4-diazabicyclo[2.2.2]octane (**11**), and diethylenetriamine (**12**). NMR spectroscopic data suggest that the complexes are fluxional in solution at room temperature with a single nitrogen coordinating to the three boron atoms of a given boroxin ring and where, in solution, the 1/1 molar complexes of symmetrical amines appear to exchange their donor sites. There seem to be no principal differences in the complexing of $(RBO)_3$ with $R = C_2H_5$ or C_6H_5. Two species of the unusual composition $3(RBO)_3 \cdot 2H_2NCH_2NH_2$ were also identified.

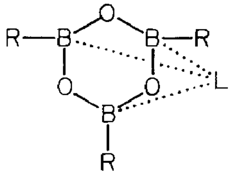
Introduction

The Lewis acidity of boron in *B*-triorganylboroxins, $(RBO)_3$, is relatively low; nevertheless, a number of 1/1 molar complexes with various bases, especially nitrogen donor molecules, have been described [2]. Recently, it has been established that complexes of the type $(RBO)_3 \cdot L$ (L = amine) are fluxional at room temperature and in solution with all three boron atoms of the boroxin ring participating in

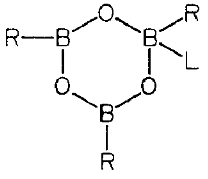
---

* For part CXIX see ref. 1.

the bonding (**A**); only at low temperatures or in the solid state is the N-to-B bonding arrested and localized at one individual boron atom (**B**) [3]. The same



(A)



(B)

general feature was found to hold true for the corresponding complexes with L = hydrazines, where the latter were also found to interact with boroxins in strictly monodentate fashion [4].

A few complexes of diamines with boroxins have also been described. Firstly, *p*-phenylenediamine has been reported to form a 3/2 molar adduct with *B*-triphenylboroxin [5]. However, in the solid state only one of the amine molecules was found to be directly involved in the bonding, donating each of its two nitrogen atoms to a boron atom of a different boroxin ring. The remaining two amine molecules merely fill empty space in the lattice structure [3]. Similarly, 1,4-diazabicyclo[2.2.2]octane has been found to form a 1/2 molar complex with *B*-triphenylboroxin, where in the solid state each nitrogen atom of the base interacts with a boron atom of a different boroxin ring, but in which the crystal lattice is stabilized by three solvated benzene molecules [3]. A 2/3 molar complex of *B*-triphenylboroxin with 1,4-diazabicyclo[2.2.2]octane has also been reported, and various additional complexes of polyamines with boroxins were identified by selected elemental analysis data, but limited supporting data (primarily infrared spectra) have been presented [6]. No chemically stable species have yet been identified in which two nitrogen atoms of a diamine coordinate with two boron atoms of the same boroxin ring.

In an extension of previous studies on the reactions of boroxins with molecules containing two nitrogen donor sites [4,7], the interaction of *B*-triethylboroxin with ethylenediamine and some derivatives thereof has been investigated in order to elucidate the coordination behavior in the boroxin/diamine system in more detail. Some data on corresponding complexes of *B*-triphenylboroxin are also reported.

Complexes of *B*-triethylboroxin with ethylenediamine and *N*-methylated derivatives thereof

The complex $(C_2H_5BO)_3 \cdot H_2NCH_2CH_2NH_2$ (**1**) was obtained from equimolar quantities of the *B*-triethylboroxin and ethylenediamine. The complex is thermally quite stable and can be sublimed under vacuum without noticeable decomposition. The ^1H NMR spectrum of $(C_2H_5BO)_3$ consists of a single broad and unresolved signal near 1 ppm. In consonance with similar previous observations [3], this signal is resolved in the spectrum of **1** into a triplet at 0.88 ppm and a quartet at 0.60 ppm. The room temperature ^{11}B NMR spectrum of the adduct consists of a broad signal at 22.8 ppm. On lowering of the temperature, this signal broadens further ($h_{1/2}$ 1000 Hz at 0 °C and 2500 Hz at -20 °C) and becomes slightly unsymmetrical but no separation of signals was observed. The NMR data suggest that, in accord with the previous findings [3], the molecule is fluxional as indicated in **A** with a nitrogen interacting with all three boron atoms of the boroxin ring. Addition of some excess of ethylenediamine to a solution of **1** does not cause any changes in either the ^{1}H or the ^{11}B NMR spectrum of the material. This observation suggests that the free amine is also rapidly exchanging with the bonded amine, and that the bonding site of the diamine is not localized at a given nitrogen atom.

B-Triethylboroxin also forms a 2/1 molar complex with ethylenediamine, $2(C_2H_5BO)_3 \cdot H_2NCH_2CH_2NH_2$ (**8**). The complex is also thermally quite stable and can be purified by sublimation. The signals of the ethyl group are again well resolved in the ^{1}H NMR spectrum of the complex. The ^{11}B NMR spectrum of **8** exhibits a signal at 25.8 ppm, indicating that each N atom of the diamine coordinate fluxionally to the boron atoms of a different boroxin ring.

In the system $(C_2H_5BO)_3/(CH_3)_2NCH_2CH_2NH_2$, only a 1/1 molar complex (**2**) could be isolated in the solid state. Although in solution a 2/1 as well as a 3/2 molar species seem to exist (as is based on ^{1}H NMR data) and solid materials of that composition remain after mixing of the reagents and subsequent solvent evaporation, attempts to purify the materials by sublimation resulted in ready loss of boroxin and only the 1/1 molar complex **2** was obtained as the ultimate pure product. The ^{11}B NMR spectrum of **2** exhibited a single peak at 23.5 ppm ($h_{1/2}$ 350 Hz) at 50 °C. At 25 °C there was a slight shift to 22.4 ppm and a broadening of the signal ($h_{1/2}$ 700 Hz). The signal rapidly broadened on further lowering of the temperature, the maximum shifted to higher field, and a new peak began to emerge near 32 ppm. At -20 °C there were two clear maxima near 30 and 5 ppm, respectively, and the peaks were in approximately 2/1 ratio; but even at -50°C no complete peak separation could be achieved.

For the system $(C_2H_5BO)_3/(CH_3)_2NCH_2CH_2N(CH_3)_2$ both a 1/1 (**3**) and 2/1 (**9**) molar complex could be isolated; **3** is a distillable liquid, **9** a low melting solid. It is of interest to note that if an equimolar amount of $(C_2H_5BO)_3$ was added to a solution of the diamine in cyclohexane and rigorous removal of adhering solvent from the isolated product was attempted under vacuum at room temperature, only **9** was obtained; on the other hand, interaction of the neat reagents (amine being added to the boroxin) yielded only **3**. If the latter was kept under vacuum at room temperature for prolonged periods of time (24 h or more), it slowly lost amine and, ultimately, **9** was formed. If the two reagents were combined in 3/2 molar ratio in hydrocarbon solution, both **3** and **9** were formed simultaneously. After evaporation of the solvent, the solid complex **9** could be filtered off and **3** was obtained as filtrate.

At 40 °C, the ^{11}B NMR spectrum of **3** consisted of a single resonance time at 25.5 ppm ($h_{1/2}$ 225 Hz). On further lowering of the temperature extensive broadening of the signal occurred with loss of features. The ^{11}B NMR spectrum of **9** at 50 °C consisted of a single peak at 29.6 ppm ($h_{1/2}$ 250 Hz), and at -50 °C at extremely broad peak with maxima at 31.9 and 22.4 ppm and a small spike at 0.5 ppm were observed.

Complexes of *B*-triethylboroxin with additional ethylenediamine derivatives

As expected, *B*-triethylboroxin forms both a 1/1 (**4**) and 2/1 (**10**) molar complex with piperazine, $HN(CH_2CH_2)_2NH$. No other species could be identified in this system. Both **4** and **10** are only sparingly soluble in chloroform and addition of boroxin to a solution of either complex caused precipitation. Remarkably, no separate ^1H NMR signals were observed for the (N)H in **10** but the signals overlapped with those for the C-bonded protons of the piperazine. In contrast, the (N)H protons were clearly seen in the spectrum of **4**, suggesting an accidental signal overlap in the spectrum of **10**.

Similarly, *B*-triethylboroxin and 1,4-diazabicyclo[2.2.2]octane, $N(CH_2CH_2)_3N$, formed 1/1 (**5**) and 2/1 (**11**) molar complexes. Of these, **11** has been reported earlier and also has a known analog in the *B*-triphenylboroxin/amine system (**16**, see below) [13]. The ^{11}B NMR data for both **5** and **11** again showed the fluxionality of the N-to-B coordination in such complexes, though on lowering of the temperature the signals merely broadened and turned featureless and no peak separation could be observed.

Furthermore, *B*-triethylboroxin forms both a 1/1 (**6**) and a 2/1 (**12**) complex with diethylenetriamine, $HN(CH_2CH_2NH_2)_2$, as isolable species. Reaction of a larger than 2/1 molar excess of the boroxin did not produce any other product. Reaction of excess amine with the boroxin yielded what appeared to be a 1/3 molar species, but which lost amine under reduced pressure and at elevated temperatures and no additional defined species was isolated.

B-Triethylboroxin and tris(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$, formed only a 1/1 molar complex, **7**, as an isolable species. The ^{11}B NMR signal of **7** was not affected by addition of excess of the amine. However, addition of one molar equivalent of $(C_2H_5BO)_3$ caused a shift of the signal from 22.9 to 25.1 ppm in addition to the appearance of a new signal at 32.4 ppm.

Complexes of *B*-triphenylboroxin with ethylenediamine and selected derivatives thereof

In the system $(C_6H_5BO)_3/H_2NCH_2CH_2NH_2$, the 1/1 molar complex (**13**) has been reported previously [6,8]; NMR data of the species have now been recorded. In addition, the 2/1 molar complex (**14**) has been prepared. Both feature only a single ^{11}B NMR resonance signal at room temperature, reflecting the fluxionality of the species.

In the system $(C_6H_5BO)_3/N(CH_2CH_2)_3N$, a material analyzing as a 2/3 molar complex (decomposing at 165–166 °C) has been obtained previously but was not further characterized [6]. The material could be reproduced, although a purified product has a noticeably higher decomposition temperature than previously reported. NMR data support the cited formulation of this 2/3 molar complex (**17**). As noted above, a 2/1 molar adduct (**16**) has been described earlier [3]. Although only one ^{11}B NMR signal was observed indicating complexation of all boron atoms (= fluxional model), an X-ray study has shown that in the solid state each nitrogen atom of the diamine is bonding to a single boron atom of a different boroxin ring. Moreover, the lattice of a crystalline material obtained by recrystallization from benzene was found to be stabilized by three benzene molecules [3]. The observations suggest that the 2/3 molar complex **17** may be viewed as the 2/1 molar species in which the crystal structure is stabilized by two additional amine molecules, as was found to be the case for the complex $2(C_6H_5BO)_3 \cdot 3H_2NC_6H_4\text{-}4\text{-}NH_2$ [3]. In addition to the cited 2/3 and 2/1 molar species derived from 1,4-diazabicyclo-

[2.2.2]octane, the 1/1 complex (**15**) also exists and was characterized in the present study.

Species of the type $3(RBO)_3 \cdot 2H_2NCH_2CH_2NH_2$

In addition to the 1/1 and 2/1 molar complexes of *B*-triorganylboroxins with ethylenediamine and derivatives thereof as described in the preceding sections, two unusual species of the composition $3(RBO)_3 \cdot 2H_2NCH_2CH_2NH_2$ (**18**: $R = C_2H_5$; **19**: $R = C_6H_5$) have been isolated in the present study. The structure of these species is not well understood. Both exhibit ^{11}B NMR signals in the general areas observed for the other complexes of *B*-triorganylboroxins with amines, but the signals are accompanied by a shoulder on the low-frequency side close to the area of the signals of uncomplexed boroxin. It is possible that these species of unusual composition are in reality 2/1 molar complexes of the boroxins with the diamine, but which are stabilized by both an additional boroxin and an additional amine molecule. Since both materials survive purification procedures without changes, it is unlikely that the two additional molecules merely adhere to the species ("solvate"), or that they are equimolar mixtures of the 2/1 and 1/1 molar complexes. This is also suggested by the ^1H NMR data which show only one set of signals for both the amine and the boroxin protons illustrating their spectroscopic identity.

Conclusions

B-Triethylboroxin consistently forms 1/1 molar complexes of the type $(C_2H_5BO)_3 \cdot L$ with L = ethylenediamine and all derivatives thereof which were employed in the present study. Complexation of the boroxin causes resolution of the ^1H NMR signals of the boron-bonded ethyl groups into the expected pattern. The room-temperature ^{11}B NMR spectra of the complexes generally exhibit a single resonance signal ranging from about 22 to 24 ppm. This observation supports the existence of a fluxional molecule where, in solution, a nitrogen atom of the donor molecule coordinates to all of the boron atoms of a single boroxin ring [3]. At low temperatures, the ^{11}B NMR signals broaden but only for $L = (CH_3)_2NCH_2CH_2NH_2$ was a sufficient separation into a low-field (2 B) and high-field (1 B) signal observed to clearly document the arrest of the fluxionality.

In no case was a complex with a boroxin to amine ratio < 1 observed. Addition of amine to a solution of a 1/1 molar complex did not bring about the appearance of new ^1H NMR signals, nor was the ^{11}B NMR signal affected to any significance. These observations suggest that at room temperature and in solution not only is there intramolecular but also intermolecular exchange occurring. The available data suggests that for symmetrical molecules such as $H_2NCH_2CH_2NH_2$ either nitrogen can bind to the boroxin ring and the donor sites of a given donor molecule are exchanging. In addition, an exchange of free and complexed amine (or boroxin in selected cases) seems to occur and all of the processes are rapid on the NMR time scale.

No analogs to the previously reported species $2(C_6H_5BO)_3 \cdot 3L$ (L = *p*-phenylenediamine) were observed in the *B*-triethylboroxin/ethylenediamine system. However, *B*-triethylboroxin forms 2/1 molar adducts of the type $2(C_2H_5BO)_3 \cdot L$ with ethylenediamines with $\delta(^{11}B)$ ranging from about 25 to 27 ppm. Similar

Table 1

Complexes of the type $(C_2H_5BO)_3 \cdot L$

No.	L	M.p. in °C (b.p. in °C/torr)	$\delta(^{11}B)$ (ppm) ($h_{1/2}$ in Hz)	$\delta(^{1}H)$ (ppm)
1	$H_2NCH_2CH_2NH_2$ [a]	102–104 [b]	22.8 (500)	2.9(br) (4H, s), 2.81 (4H, s), 0.87 (9H, t), 0.54 (6H, q)
2	$(CH_3)_2NCH_2CH_2NH_2$ [a]	68–69 [b]	22.4 (700)	2.78(2H, t), 2.6(br) (2H, s), 2.24 (6H, s), 0.87 (9H, t), 0.53 (6H, q)
3	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	(67–68/5) [c]	23.6 (500)	2.74 (4H, s), 2.37 (6H, 2), 0.87 (9H, t), 0.60 (6H, q)
4	$HN(CH_2CH_2)_2NH$ [d]	144–147 [e]	23.0 (450)	2.97 (8H, s), 2.4(br) (2H, s), 0.87 (9H, t), 0.57 (6H, q)
5	$N(CH_2CH_2)_3N$ [f]	73–74 [b]	23.3 (425)	2.94 (12H, s), 0.86 (9H, t), 0.56 (6H, q)
6	$HN(CH_2CH_2NH_2)_2$	64–65 [b]	23.0 (900)	2.9(br) (5H, s), 2.78 (8H, s), 0.88 (9H, t), 0.53 (6H, q)
7	$N(CH_2CH_2NH_2)_3$ [g]	49–51 [b]	22.9(1000)	2.78 (6H, t), 2.7(br) (6H, s), 0.87 (9H, t), 0.55 (6H, q)

[a] Prepared in petroleum ether (b.p. 30–60 °C). [b] Purified by sublimation under vacuum. [c] Purified by distillation. [d] Prepared in hexane. [e] Recrystallized from benzene/hexane (1/3, v/v). [f] Prepared in benzene. [g] Prepared in pentane.

Table 2

Complexes of the type $2(C_2H_5BO)_3 \cdot L$

No.	L	M.p. in °C	$\delta(^{11}B)$ (ppm) ($h_{1/2}$ in Hz)	$\delta(^{1}H)$ (ppm)
8	$H_2NCH_2CH_2NH_2$ [a]	154–156 [b]	25.8(500)	3.9(br) (2H, s), 2.97 (2H, s), 0.88 (9H, t), 0.60 (6H, q)
9	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	44–47 [c]	27.1(400)	2.84 (4H, s), 2.41 (12H, s), 0.89 (9H, t), 0.74 (6H, q)
10	$HN(CH_2CH_2)_2NH$ [d]	186–188 [e]	26.1(500)	3.00 (5H, s), 0.91 (9H, t), 0.68 (6H, q)
11	$N(CH_2CH_2)_3N$ [d]	106–107	26.0(500) [f]	2.94 (6H, s), 0.87 (9H, t), 0.60 (6H, q)
12	$HN(CH_2CH_2NH_2)_2$	124–127 [c]	25.6(450)	3.7(br) (5H, s), 2.80 (8H, s), 0.91 (18H, t), 0.53 (12H, q)

[a] Prepared in petroleum ether (b.p. 30–60 °C). [b] Purified by sublimation or recrystallization from chloroform. [c] Purified by sublimation under vacuum. [d] Prepared in benzene. [e] Recrystallized from benzene/hexane (1/3, v/v). [f] Lit. [3]: $\delta(^{11}B)$ 26.2; $\delta(^{1}H)$ 3.1 (12H, s), 0.87 (9H, t), 0.66 (6H, q).

complexes have been observed previously and it has been established that in such complexes each donor site of L binds fluxionally to a different boroxin ring [3]. Hence, it may not be surprising that complexes of this type appear to be limited to those donor species L which can be viewed as symmetrical bifunctional donors, i.e., including diethylenetriamine. Apparently, the secondary nitrogen of this latter amine behaves as non-coordinating center of the molecule. This situation is altered when the (N)H is replaced by an additional $CH_2CH_2NH_2$ group, and $N(CH_2CH_2NH_2)_3$ forms only a 1/1 molar complex, probably engaging the tertiary nitrogen as the donor site. A crude species of the composition $2(C_2H_5BO)_3 \cdot (CH_3)_2NCH_2CH_2NH_2$ can be obtained in the solid state, but it readily loses boroxin to form the 1/1 molar complex. This observation suggests a preferential donor site and also that the second boroxin molecule in the initial product is merely "solvating", although (as is based on the NMR data) it exchanges with the coordinated boroxin.

An unusual composition is that of $3(RBO)_3 \cdot 2H_2NCH_2CH_2NH_2$. The 3/2 molar complex where $R = C_2H_5$ can be sublimed under vacuum and for $R = C_6H_5$ it can be recrystallized without any change of composition. These observations and in conjunction with the NMR data make it unlikely that the species are merely stoichiometric mixtures of the 2/1 and 1/1 molar complexes. The data may rather suggest that these materials may be viewed as the 2/1 molar complexes but which are solvated by both additional boroxin and amine. The two solvating molecules then may stabilize the structures, similar to the situation encountered in the cited 2/3 molar complexes (where two amine molecules stabilize the structure but are not directly involved in the bonding), but in solution the non-bonding moieties may be exchanging with the bonded moieties.

No principal differences seem to exist between complexes of $(RBO)_3$ with $R = C_2H_5$ or $R = C_6H_5$. Any seemingly abnormal behavior is likely due to the larger and more rigid phenyl groups. Thus, for $R = C_6H_5$ and $L = N(CH_2CH_2)_3N$ both a 2/1 as well as the 2/3 complex have been described previously [3,6], but the normal 1/1 complex also exists and was characterized in the present study. On the other hand, in the $(C_2H_5BO)_3/N(CH_2CH_2)_3N$ system only the 1/1 and the 2/1 complexes exist, since the latter does not seem to require stabilization of the solid state structure by additional species to form the 2/3 molar complex.

Experimental section

All solvents and reagents were rigorously dried. Many of the compounds are extremely hygroscopic and reactions and transfers were carried out under inert atmosphere (argon or nitrogen). Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded on solutions in $CDCl_3$ on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H NMR, external $(C_2H_5)_2O \cdot BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and (br) = broad signal. Unless otherwise noted all ^{11}B NMR signal are singlets. Coupling constants *J* are given in Hz.

Preparation of complexes of the type $(C_2H_5BO)_3 \cdot L$ *(general procedure)*

Equimolar quantities of the two reagents (10–20 mmol scale) were mixed with or without solvent (as indicated in Table 1). An exothermic reaction was observed in most cases and the mixtures were stirred at ambient temperature for 30 min. Precipitated products were collected (in the absence of solvent the material usually solidified on cooling to room temperature) and were purified by the indicated methods (see Table 1). Yields were essentially quantitative.

Preparation of complexes of the type $2(C_2H_5BO)_3 \cdot L$ *(general procedure)*

Complexes of the type $2(C_2H_5BO)_3 \cdot L$ were prepared in analogous fashion as described above by the reaction of two molar equivalents of the boroxin with one equivalent of the amine. Details are given in Table 2.

$(C_6H_5BO)_3 \cdot H_2NCH_2CH_2NH_2$ (**13**). This compound was prepared by the indicated literature procedure [6,8]. NMR data: $\delta(^1H)$ 8.01 (6H, m), 7.40 (9H, m), 2.84 (4H, s), 2.6(br) (4H, s); $\delta(^{11}B)$ 20.9 (s, $h_{1/2}$ 750 Hz).

$2(C_6H_5BO)_3 \cdot H_2NCH_2CH_2NH_2$ (**14**). The compound was prepared by combining the reagents in 2/1 molar ratio in benzene, from which it was recrystallized to give a pure product, m.p. 170–173° C. NMR data: $\delta(^1H)$ 7.98 (6H, m), 7.39 (9H, m), 2.93 (2H, s), 2.6(br) (2H, s); $\delta(^{11}B)$ 23.7 ($h_{1/2}$ 800 Hz).

$(C_6H_5BO)_3 \cdot N(CH_2CH_2)_3N$ (**15**). Equimolar quantities of the reagents were combined in methylene chloride. A yield of 80% of crystalline material was obtained, m.p. 187–190° C (after recrystallization from tetrahydrofuran). NMR data: $\delta(^1H)$ 8.02 (2H, m), 7.41 (3H, m), 2.96 (4H, s); $\delta(^{11}B)$ 20.2 ($h_{1/2}$ 875 Hz).

$2(C_6H_5BO)_3 \cdot N(CH_2CH_2)_3N$ (**16**). The compound was prepared by the literature method [3]; m.p. 196–198° C decomp. (after purification by dissolution in methylene chloride and precipitation with pentane). NMR data: $\delta(^1H)$ 7.97 (2H, m), 7.39 (3H, m), 3.13 (2H, s); $\delta(^{11}B)$ 22.2 ($h_{1/2}$ 1500 Hz) (lit. [3]: $\delta(^{11}B)$ 22.2).

$2(C_6H_5BO)_3 \cdot 3N(CH_2CH_2)_2N$ (**17**). The compound was prepared in tetrahydrofuran and was recrystallized from the same solvent to give a 94% yield of crystalline product, m.p. 177–179° C (lit. [6]: decomp. at 165–166° C). No sign of decomposition was observed when the purified material was heated under vacuum to 150° C for 24 h. NMR data: $\delta(^1H)$ 8.02 (2 H, m), 7.40 (3 H, m), 3.89 (6 H, s); $\delta(^{11}B)$ 21.2 ($h_{1/2}$ 860 Hz).

$3(C_2H_5BO)_3 \cdot 2H_2NCH_2CH_2NH_2$ (**18**). This compound was prepared by mixing the two reagents in 3/2 molar ratio in petroleum ether (b.p. 30–60° C). The resultant precipitate was purified by sublimation under vacuum to give a colorless product, m.p. 144–147° C, in essentially quantitative yield. NMR data: $\delta(^1H)$ 3.8(br) (8H, s), 2.95 (8H, s), 0.88 (27H, t, J 7 Hz), 0.59 (18H, q, J 7 Hz); $\delta(^{11}B)$ 24.5 ($h_{1/2}$ 600 Hz) + shoulder at 32.4.

$3(C_6H_5BO)_3 \cdot 2H_2NCH_2CH_2NH_2$ (**19**). The compound was prepared from 3/2 molar quantities of the reagents in benzene; m.p. 149–151° C (after recrystallization from chloroform). NMR data: $\delta(^1H)$ 8.00 (18H, m), 7.41 (27H, m), 2.94 (8H, s), 2.8(br) (8H, s); $\delta(^{11}B)$ 21.9 ($h_{1/2}$ 700 Hz) + shoulder at 29.2.

Acknowledgments

This work was supported by the Office of Naval Research (K.N.). The authors gratefully acknowledge a generous gift of *B*-triethylboroxin from Professor R.

Köster, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, West Germany.

References

1 C. Habben, L. Komorowski, W. Maringgele, A. Meller and K. Niedenzu, Inorg. Chem., in press.
2 Gmelin Handbuch der Anorganischen Chemie, Erg.-Werk (New Supplement Series) Vol. 44, Borverbindungen, Part 13, 1977, p. 120–140.
3 M. Yalpani and R. Boese, Chem. Ber., 116 (1983) 3347.
4 M.K. Das, J.F. Mariategui and K. Niedenzu, Inorg. Chem., 26 (1987) 3114.
5 W.L. Fielder, M.M. Chamberlain and C.A. Brown, J. Org. Chem., 26 (1961) 2154.
6 J.M. Ritchey, Ph.D. Dissertation, University of Colorado, 1968, p. 1–202.
7 J. Bielawski and K. Niedenzu, Inorg. Chem., 25 (1986) 1771.
8 L. Letsinger and S.B. Hamilton, J. Am. Chem. Soc., 80 (1958) 5411.