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Tris(ω-aminoalkoxy)boranes

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Abstract

Tris(ω-aminoalkoxy)boranes of the type $B[O(CH_2)_nNRR']_3$ ($n=2$: $R=R'=H$, $R=H$ and $R'=CH_3$, $R=R'=CH_3$, $R=R'=C_2H_5$; $n=3$: $R=R'=H$, $R=R'=CH_3$, $R=R'=C_2H_5$) have been prepared by the reaction of either $B(OCH_3)_3$ or $(CH_3)_3N \cdot BH_3$ with excess of ω-aminoalcohols, $HO(CH_2)_nNRR'$. ^{11}B NMR spectral data suggest the occurrence of both intra- and intermolecular N–B coordination in these species.

Introduction

On the basis of chemical studies [1–3] and spectroscopic data [4, 5] it has been shown that $B[O(CH_2)_2]_3N$ (**1**) is stabilized by intramolecular N–B coordination. This feature was subsequently confirmed by several single-crystal X-ray diffraction studies [6–9], and a crystal structure determination of $B[O(CH_2)_3]_3N$ (**2**, as the trihydrate) has demonstrated that intramolecular N–B coordination also exists in this latter compound [10]. However, the experimentally determined B–N bond distances are surprisingly long ranging from 1.65 to 1.69 Å for **1** and found with 1.65 Å° for **2**. (Usually, the B–N bond lengths in compounds containing four-coordinate boron bonded to nitrogen are shorter than 1.60 Å [11]. The longest known B–N bond involving an isolated four-coordinate boron seems to be that in $CH_3CH \cdot BF_3$ with 1.630 Å [12]). The reported ^{11}B chemical shift data for **1** range from 16.1 to 10.7 ppm [5, 13, 14], and $\delta(^{11}B)$ 1.0 ppm has been given for **2** [13]. The latter datum is in the range normally found for $\delta(^{11}B)$ of species containing isolated four-coordinate boron, whereas the former values seem to be in better agreement with those found for trigonal boron in triesters of the type $B(OR)_3$ (containing only non-functional hydrocarbon groups) with $\delta(^{11}B)$ 19–15 ppm [15].

Presumably, *sym*-tris(ω-aminoalkoxy)boranes of the type $B[O(CH_2)_nNRR']_3$ (**3**, $n=2$ or 3) may also be stabilized by intramolecular N–B coordination. Only a few such compounds are known and the reported data are somewhat contradictory. For example, $B[O(CH_2)_2N(CH_3)_2]_3$ has been described as a non-volatile material [16], but a boiling point of 152 °C (12 torr) is given elsewhere [17]. Studies of the chemical behavior of tris(ω-aminoalkoxy)boranes have been limited to the preparation of some adducts with borane(3) [16, 17], and the interaction of $B[O(CH_2)_2N(CH_3)_2]_3$ with BF_3 (in a sealed tube at 110 °C) was found to yield $F_2BO(CH_2)_2N(CH_3)_2$ [17].

Results and discussion

Preparative data

The reaction of diborane(6) with $HO(CH_2)_2NH_2$ has been reported to yield $B[O(CH_2)_2NH_2]_3$ (**3a**) and a polymeric material of the composition $[BO(CH_2)_2N]_n$ [15]. The former compound (**3a**) was also obtained by transesterification of $B(O\text{–}n\text{-}C_3H_7)_3$ [18], and analogous transesterifications employing $B(OR)_3$ with $R=C_2H_5$ [19], n-C_3H_7 [17] or n-C_4H_9 [16] have also been described. In the present work, the transesterification of $B(OCH_3)_3$ with $HO(CH_2)_nNRR'$ according to eqn. (1) was used as a general and facile method for the preparation of tris(ω-aminoalkoxy)boranes.

$$B(OCH_3)_3 + 3HO(CH_2)_nNRR' \longrightarrow 3CH_3OH + \underset{\mathbf{3}}{B[O(CH_2)_nNRR']_3} \qquad (1)$$

$n=2$
3a: $R=R'=H$
3b: $R=H$, $R'=CH_3$
3c: $R=R'=CH_3$
3d: $R=R'=C_2H_5$

$n=3$
3e: $R=R'=H$
3f: $R=R'=CH_3$
3g: $R=R'=C_2H_5$

The reactions proceeded readily on heating a mixture of the neat reagents to reflux for a few hours. It was

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found best to use an excess of the aminoalcohol, and yields of the resultant esters in the order of 85–95% were obtained.

Compounds of type **3** have also been prepared by the reaction of diborane(6) with aminoalcohols [16]. Heating of a mixture of trimethylamine–borane with an aminoalcohol to reflux (eqn. (2)) appears to be a more convenient procedure, although relative long reaction times (10–12 h) were generally required to ensure yields of about 90%.

$$(CH_3)_3N\cdot BH_3 + 3HO(CH_2)_nNRR' \longrightarrow (CH_3)_3N + 3H_2 + \mathbf{3} \quad (2)$$

When the latter reaction was performed with an excess of $(CH_3)_3N\cdot BH_3$, a mixture of both **3** and $HB[O(CH_2)_nNRR']_2$ was obtained (as based on ^{11}B NMR data), which could not be separated; the formation of a monoester of the type $H_2BO(CH_2)_nNRR'$ was never observed.

Compound **3a** is a solid and **3e** is a very viscous material; the other species of type **3** are all fairly high boiling liquids. The pure esters boil without foaming, and all are quite sensitive to moisture.

^{11}B NMR Spectra

The ^{11}B chemical shifts for boron esters of the type R_2BOR' (R and R' = non-functional organic substituents) range from 54 to 45 ppm, from 32 to 25 ppm for species of the type $RB(OR')_2$, and from 19 to 15 ppm for $B(OR)_3$ compounds. On the other hand, $\delta(^{11}B)$ is normally found in the 10 to −5 ppm range for compounds containing isolated four-coordinate boron atoms [15].

The chemical shift $\delta(^{11}B)$ 14.5 recorded for $B[O(CH_2)_2]_3N$ (**1**) in the present work is quite different from that reported for $B[O(CH_2)_3]_3N$ (**2**) with $\delta(^{11}B)$ 1.0 [13]. (The latter datum is in good agreement with the presence of four-coordinate boron.) In contrast, the intramolecular B–N distances of the two cited species in the solid state have been found to be essentially identical [6–10]. Although the $\delta(^{11}B)$ value of **1** is slightly solvent-dependent (see 'Experimental'), it was found to be independent of the concentration for 3.7 to 0.5 mol.% solutions (in $CDCl_3$).

A ^{11}B chemical shift of 13.8 ppm was recorded for the ester $B[(O(CH_2)_2N(CH_3)_2]_3$ (**3c**). This value was not affected by addition of either triethylamine, diethylamine or n-propylamine. On the other hand, $\delta(^{11}B)$ was found to be concentration dependent. For example, the cited signal of **3c** (13.8 ppm) was observed for a 14.2 mol.% solution. At a concentration of only 3.7 mol.%, a shoulder appeared at 10.4 ppm, which at a concentration of 1 mol.% accounted for about 10% of the total boron. At a concentration of 0.3 mol.%, the major signal was now observed at 11.7 ppm and a shoulder at 10.5 ppm accounted for about 15% of the total boron.

Similar observations were made for the ^{11}B NMR spectra of other species of type **3**. At a concentration of 26.6 mol.%, only one ^{11}B NMR signal was observed for $B[O(CH_2)_2NHCH_3]_3$ (**3b**) at 5.0 ppm ($h_{1/2}$ = 350 Hz). The signal sharpened and migrated on dilution and $\delta(^{11}B)$ 5.5 ($h_{1/2}$ = 160 Hz) was observed for a concentration of 13.8 mol.%, $\delta(^{11}B)$ 5.7 ($h_{1/2}$ = 120 Hz) for a 9.3 mol.% solution, and $\delta(^{11}B)$ 6.0 ($h_{1/2}$ = 100 Hz) for a 5.3 mol.% solution. On further dilution to a concentration of 2.2 mol.%, the main signal (75%) was observed at 6.3 ppm ($h_{1/2}$ = 90 Hz) and a second signal emerged as a shoulder at 9.4 ppm. For a 1 mol.% solution, the main signal was observed at 6.6 ppm ($h_{1/2}$ = 80 Hz; 75%) and a clearly separate second but broad signal at 9.7 ppm ($h_{1/2}$ = 1000 Hz) appeared. At a concentration of only 0.2 mol.%, the signal at 6.5 ppm now accounted for only 40% of the boron, and the major signal was observed at 9.8 ppm ($h_{1/2}$ = 300 Hz).

The effect of the concentration on the ^{11}B chemical shift was best seen for solutions of $B[O(CH_2)_2N(C_2H_5)_2]_3$ (**3d**); relevant data are summarized in Table 1. (Over the range from −38 to 40 °C, there was essentially no effect of temperature on the given chemical shift data.)

TABLE 1. ^{11}B NMR data for solutions (in $CDCl_3$) of variable concentrations (mol.%) of $B[O(CH_2)_2N(C_2H_5)_2]_3$ (**3d**)

Concentration	Signal #1		Signal #2	
	$\delta(^{11}B)^a$	Area (%)	$\delta(^{11}B)^a$	Area (%)
10.8	17.3 (425)	100	–	–
1.0	17.4 (285)	97	12.1 (350)	3
0.5	17.3 (310)	84	12.1 (325)	16
0.2	17.0 (410)	60	11.8 (475)	40
0.1	17 (shoulder)	25	11.7 (570)	75

[a] $h_{1/2}$ data in parentheses.

TABLE 2. ^{11}B NMR data for solutions (in $CDCl_3$) of variable concentrations (mol.%) of $B[O(CH_2)_3N(C_2H_5)_2]_3$ (**3g**)

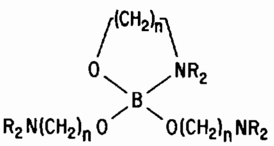
Concentration	Signal #1		Signal #2	
	$\delta(^{11}B)^a$	Area (%)	$\delta(^{11}B)^a$	Area (%)
5.3	17.5 (320)	100	–	–
1.8	17.6 (290)	95	12.4 (?)	5
0.7	17.6 (260)	90	12.3 (340)	8
0.3	17.6 (270)	80	12.2 (380)	20
0.15	17.5 (290)	66	12.2 (400)	34

[a] $h_{1/2}$ data in parentheses.

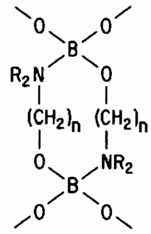
Similar observations were made for the ^{11}B NMR spectra of the esters derived from 3-aminopropanols. For example, the ^{11}B NMR spectrum of $B[O(CH_2)_3NH_2]_3$ (**3e**) exhibited a small peak near 20 ppm (5% of the total boron at 19.7 mol.% concentration) and a strong signal at 1.04 ppm ($h_{1/2}=235$ Hz). The latter signal sharpened on dilution (9.6 mol.%: 1.7 ppm, $h_{1/2}=125$ Hz) and a slight intensity increase (to 10%) of the low-field signal (now at 20.2 ppm) was observed. At 5.3 mol.% concentration, the signal at 20.4 ppm ($h_{1/2}=210$ Hz) accounted for 15% of the total boron, and the high-field signal was observed at 2.4 ppm ($h_{1/2}=100$ Hz). On further dilution, a third peak, $\delta(^{11}B)$ 1.5, appeared, which at 1 mol.% concentration was extremely broad ($h_{1/2}$ *c.* 1500 Hz) and accounted for 90% of the total boron, whereas the two previously observed signals (now at 20.5 ppm, $h_{1/2}=240$ Hz; and at 3.8 ppm, $h_{1/2}=90$ Hz) were of about equal abundance. A 9 mol.% solution of $B[O(CH_2)_3N(CH_3)_2]_3$ (**3f**) showed only one sharp signal at $\delta(^{11}B)$ 7.5 ($h_{1/2}=180$ Hz). At a concentration of 1.8 mol.%, the signal had shifted slightly to 7.8 ppm and a shoulder appeared near 10.3 ppm; and at 0.2 mol.%, the signal consisted of a considerably broader peak ($h_{1/2}=300$ Hz) with two distinct maxima at 7.3 and 6.9 ppm, respectively. The ^{11}B NMR spectrum of $B[O(CH_2)_3N(C_2H_5)_2]_3$ (**3g**) exhibited a single peak at relatively high concentrations. The intensity of this signal decreased on dilution and was accompanied by the emergence of another resonance signal. These data are summarized in Table 2.

Conclusions

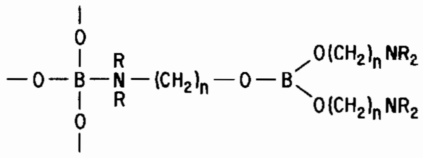
The outlined ^{11}B NMR data suggest the occurrence of different types of concentration-dependent N–B interaction for the tris(ω-aminoalkoxy)boranes. It seems reasonable to assume that at low concentrations intramolecular coordination as shown in **I** is most likely. However, with increasingly higher concentrations, intermolecular coordination may become more feasible and could result in cyclic structures such as **II**. Alternatively, linear coordination may also be possible. For example, the low-field peak observed in the ^{11}B NMR spectrum of **3e** near 20 ppm would suggest the presence of three-coordinate boron, which may well reflect a terminating moiety of a chain-type structure as is shown in **III**.



I



II



III

It is worth noting that in all cases the tris(ω-aminoalkoxy)boranes exhibited only one ^{15}N NMR signal (at room temperature). As compared to those of the ω-aminoalcohols, this signal is observed at about 7 ppm lower field for the corresponding boron compounds derived from the ethanol derivatives with primary or secondary nitrogen, whereas no clear trends are apparent in the other cases.

Experimental

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block. All reagents were obtained from Aldrich Chemical Co., Milwaukee, WI.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (^{11}B, ^{15}N) or 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 $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O \cdot BF_3$ for ^{11}B NMR, external NH_3 for ^{15}N NMR). Abbreviations are: 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. All ^{13}C NMR spectra were recorded in the proton-decoupled mode; ^{15}N chemical shifts for the ω-aminoalcohols are summarized in Table 3.

$B[O(CH_2)_2]_3N$ (1)

NMR data: $\delta(^1H)$ 3.95 (1H, t, $J=6$), 3.15 (1H, t, $J=6$); $\delta(^{11}B)$ 14.5 (s, $h_{1/2}=60$ Hz); $\delta(^{13}C)$ 61.8, 59.0. Lit.: $\delta(^{11}B)$ 10.7 (in H_2O) [14], 11.2 (in $CDCl_3$) [14], 14.2 (unspecified solvent) [13], 16.1 (in CCl_4) [5].

TABLE 3. ^{15}N NMR data for ω-aminoalcohols

ω-Aminoalcohol	δ(^{15}N)
$H_2N(CH_2)_2OH$	14.60
$CH_3HN(CH_2)_2OH$	17.85
$(CH_3)_2N(CH_2)_2OH$	19.73
$(C_2H_5)_2N(CH_2)_2OH$	37.36
$H_2N(CH_2)_3OH$	20.67
$(CH_3)_2N(CH_2)_3OH$	25.08
$(C_2H_5)_2N(CH_2)_3OH$	45.31

Preparation of $B[O(CH_2)_nNRR']_3$ (3)

General Procedure A. A mixture of 3 molar equivalents of aminoalcohol and 0.8 molar equivalent of $B(OCH_3)_3$ was heated to reflux for 3 h. Subsequently, methanol was distilled off under atmospheric pressure and the residue was distilled under vacuum. Excess of aminoalcohol distilled off first and the desired ester was obtained in 85–95% yield.

General Procedure B. Approximately 0.75 molar equivalent of $(CH_3)_3N \cdot BH_3$ was added to 3 molar equivalents of aminoalcohol. The mixture was slowly heated (oil-bath) and a clear solution resulted which was heated to reflux for 12–15 h. Excess of aminoalcohol was distilled off under vacuum and the desired ester was purified by distillation; yields ranged from 80–95%.

$B[O(CH_2)_2NH_2]_3$ (3a)

Melting point (m.p.) 96–98 °C. Lit.: m.p. 74 °C (after sublimation) [17]; m.p. 95–98 °C, b.p. 126–127 °C (8 torr) [18]. NMR data: δ(^{1}H) 3.70 (1H, t, $J=5$), 2.95 (1H, t, $J=5$), 2.70 (1H, s); δ(^{11}B) 6.8 (s, $h_{1/2}=225$ Hz); δ(^{13}C) 63.4, 42.8; δ(^{15}N) 21.54.

$B[O(CH_2)_2NHCH_3]_3$ (3b)

Boiling point (b.p.) 78 °C (1.5 Torr). Lit.: b.p. 109 °C (11 torr) [17]; 65 °C (0.5 torr) [18]. NMR data: δ(^{1}H) 3.73 (2H, t, $J=6$), 3.6*(1H, s), 2.76 (2H, t, $J=6$), 2.43 (3H, s); δ(^{11}B) 6.1 (s, $h_{1/2}=90$ Hz) (see also text); δ(^{13}C) 59.3, 52.1, 34.4; δ(^{15}N) 24.93. Lit. [19]: δ(^{1}H) 3.97 (2H, t), 3.23 (1H, s), 2.90 (2H, t), 2.60 (3H, s).

$B[O(CH_2)_2N(CH_3)_2]_3$ (3c)

Boiling point 110–111 °C (2 torr). Lit. [17]: b.p. 152 °C (12 torr). NMR data: δ(^{1}H) 3.84 (1H, t, $J=6$), 2.51 (1H, t, $J=6$), 2.30 (3H, s); δ(^{11}B) 13.8 ($h_{1/2}=200$ Hz) (see also text); δ(^{13}C) 60.6, 60.1, 45.4; δ(^{15}N) 23.63. At −25 °C: δ(^{11}B) 9.9.

$B[O(CH_2)_2N(C_2H_5)_2]_3$ (3d)

Boiling point 169 °C (2 torr). Lit. [19]: b.p. 152 °C (0.8 torr). NMR data: δ(^{1}H) 3.84 (2H, t, $J=6.5$), 2.59 (4H, unresolved m), 1.03 (3H, t, $J=7$); δ(^{11}B) 17.5 (s, $h_{1/2}=300$ Hz) (see also text); δ(^{13}C) 61.4, 53.4, 47.4, 11.5; δ(^{15}N) 40.76.

$B[O(CH_3)_3NH_2]_3$ (3e)

Boiling point 70–74 °C (8 torr). NMR data: δ(^{1}H) 3.62 (1H, t, $J=5$), 2.87 (1H, t, $J=5$), 2.87 (1H, t, $J=5.5$), 2.6* (1H, s), 1.65 (1H, p, $J=5.5$); δ(^{11}B) see text; δ(^{13}C) 59.0, 39.5, 32.5; δ(^{15}N) 21.18.

$B[O(CH_2)_3N(CH_3)_2]_3$ (3f)

Boiling point 158 °C (3 torr). Lit. [19]: b.p. 205 °C (0.6 torr). NMR data: δ(^{1}H) 3.68 (1H, t, $J=6$), 2.48 (1H, t, $J=7$), 2.28(3H, s), 1.69(1H, p, $J=6$); δ(^{11}B) 7.5 ($h_{1/2}=180$ Hz) (see also text); δ(^{13}C) 59.6, 56.5, 44.6, 29.2; δ(^{15}N) 27.61. Lit. [17]: δ(^{1}H) 4.09 (1 H, t), 2.70 (1 H, t), 2.50 (3 H, s), 1.86 (1 H, p).

$B[O(CH_2)_3N(C_2H_5)_2]_3$ (3g)

Boiling point 190–192 °C (2 torr). NMR data: δ(^{1}H) 3.80 (1H, t, $J=7$), 2.55–2.45 (3H, m) 1.66 (1H, p, $J=6$), 1.0 (3H, m = two overlapping t ($J=7$) at 1.01 and 1.00); δ(^{11}B) see text; δ(^{13}C) 60.8, 48.6, 46.2, 28.2, 10.9; δ(^{15}N) 43.15.

References

1 H. C. Brown and E. A. Fletcher, *J. Am. Chem. Soc., 73* (1951) 2802–2813.
2 H. Steinberg and D. L. Hunter, *Ind. Eng. Chem., 49* (1957) 174–181.
3 H. K. Zimmerman and H. Weidmann, *Liebigs Ann. Chem., 619* (1958) 28–35; *628* (1959) 37–45.
4 E. Funck, *Ber. Bunsenges. Phys. Chem., 71* (1967) 170–181.
5 D. Fenske and H. J. Becher, *Chem. Ber., 105* (1972) 2085–2088.
6 Z. Taira and K. Osaki, *Inorg. Nucl. Chem. Lett., 7* (1971) 509–512.
7 R. Mattes, D. Fenske and K.-F. Tebbe, *Chem. Ber., 105* (1972) 2089–2094.
8 H. Follner, *Monatsh. Chem., 104* (1973) 477–484.
9 M. Bonzcek and H. Follner, *Monatsh. Chem., 107* (1976) 283–288.
10 Z. Taira and K. Osaki, *Inorg. Nucl. Chem. Lett., 9* (1973) 207–208.
11 H. Hess, *Habilitationsschrift*, University of Stuttgart, Stuttgart, FRG, 1968.
12 D. F. Shriver and J. A. Ivers, *Inorg. Chem., 8* (1969) 2182–2189.
13 T. P. Onak, R. E. Williams and R. Swidler, *J. Chem. Phys., 67* (1963) 1741.
14 T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem., 63* (1959) 1533–1535.
15 H. Nöth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer, Berlin, 1978.
16 H. C. Miller, *U. S. Patent 2 990 423* (1961).
17 R. Kratzer, *Ph. D. Dissertation*, University of München, Munich, FRG, 1960.
18 L. H. Thomas, *J. Chem. Soc.,* (1946) 820–822.
19 R. Duggal and C. Mehrota, *Inorg. Chim. Acta, 43* (1980) 179–183.