Pergamon

Polyhedron Vol. 14, No. 19, pp. 2623–2630, 1995
Elsevier Science Ltd
Printed in Great Britain
0277–5387/95 $9.50+0.00

0277–5387(95)00130–1

SYNTHESIS AND CHARACTERIZATION OF AMINE ADDUCTS OF TRI(4-TOLYL)BOROXINE AND TRI(3,5-XYLYL)BOROXINE: MOLECULAR STRUCTURE OF $(4\text{-}MeC_6H_4)_3B_3O_3 \cdot$ CYCLOHEXYLAMINE

MICHAEL A. BECKETT,*† GARY C. STRICKLAND and K. SUKUMAR VARMA‡

Chemistry Department, University of Wales, Bangor LL57 2UW, U.K.

and

DAVID E. HIBBS, MICHAEL B. HURSTHOUSE* and K. M. ABDUL MALIK

Chemistry Department, University of Wales, Cardiff, PO Box 912, Cardiff CF1 3TB, U.K.

Abstract—19 1 : 1 adducts of the triarylboroxines $(4\text{-}MeC_6H_4)_3B_3O_3$ (PTB) and $(3,5\text{-}Me_2C_6H_3)_3B_3O_3$ (MXB) with *N*-donor ligands (cyclohexylamine, 4-picoline, 3-picoline, piperidine, morpholine, isobutylamine, methylamine, dimethylamine, isoquinoline and benzylamine) have been prepared by reaction of stoichiometric quantities of ligand and triarylboroxine in Et_2O at room temperature. All 19 adducts have been characterized by elemental analysis, M pt, IR and ^1H and ^{13}C NMR. $C_6H_{11}NH_2 \cdot$ PTB has been characterized in the solid state by a single-crystal X-ray diffraction study. Solid-state ^{11}B MAS NMR results for PTB and its adducts with cyclohexylamine and isoquinoline are reported. In solution-variable temperature ^1H NMR of the morpholine, cyclohexylamine, isoquinoline and benzylamine adducts of PTB and MXB indicate that a ligand dissociation–recombination process is occurring with $\Delta G^{\ddagger}$ of *ca* 43–49 kJ mol^{-1}.

In 1958 Synder and co-workers[1] reported the preparation of the 1 : 1 pyridine adduct of triphenylboroxine and proposed that the structure involved coordination of the pyridine nitrogen atom to one of the boron atoms of the boroxine ring analogous to that invoked by Burg[2] in 1940 for the 1 : 1 NH_3 and Me_3N adducts of $Me_3B_3O_3$. In 1968 Ritchey[3] prepared a series of 1 : 1 adducts of $Ph_3B_3O_3$ and studied their structures by ^1H NMR spectroscopy; this work indicated that at room temperature the three boron centres were equivalent. Low-temperature ^1H NMR and ^{11}B studies on quinuclidine $\cdot Ph_3B_3O_3$ and quinuclidine $\cdot Et_3B_3O_3$, respectively, by Yalpani and Boese[4] in 1983 indicated that in solution there is a temperature dependent fluctuation of the amine between the three borons of the boroxine ring. Boroxine/amine adducts of stoichiometry other than 1 : 1 have been prepared, e.g. $2NH_3 \cdot Me_3B_3O_3$,[2] $3p\text{-}NH_2C_6H_4NH_2 \cdot 2Ph_3B_3O_3$[5] and their structures have been discussed.[2,4]

This paper reports on the synthesis and characterization of series of hitherto unreported *N*-donor adducts of the triarylboroxines $(4\text{-}MeC_6H_4)_3B_3O_3$ (PTB) and $(3,5\text{-}Me_2C_6H_3)_3B_3O_3$ (MXB). We also report the first crystal and molecular structure of a

* Authors to whom correspondence should be addressed.

† MAB warmly remembers time spent in the Chemistry Department at Exeter University under the guidance of EWA, an excellent mentor.

‡ Current address: Pilkington Group Research, Pilkington Technology, Lathom, Lancashire L40 5UF, U.K.

"simple" 1 : 1 adduct, $C_6H_{11}NH_2 \cdot PTB$, and further investigate its structure in the solid state by MAS ^{11}B NMR. In solution, the dynamic ^1H NMR behaviour of $C_6H_{11}NH_2 \cdot PTB$ is compared with a selected range of other adducts.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of 1 : 1 amine adducts (**1–19**) of the triarylboroxines $(4\text{-}MeC_6H_4)_3B_3O_3$ (PTB) and $(3,5\text{-}Me_2C_6H_3)_3B_3O_3$ (MXB) were relatively straightforward[3] and proceeded well in high yield in Et_2O at room temperature according to eq. (1). The amines (L) used were cyclohexylamine, 4-picoline, 3-picoline, piperidine, morpholine, isobutylamine, methylamine, dimethylamine, isoquinoline and benzylamine.

$$L + Ar_3B_3O_3 \rightarrow L \cdot Ar_3B_3O_3$$

$$(Ar = 4\text{-}MeC_6H_4 3,5\text{-}Me_2C_6H_3) \quad (1)$$

Yields were generally near quantitative. All compounds gave satisfactory elemental analysis, were air-stable white crystalline solids with clearly defined melting points (Table 1), and were readily soluble in chlorinated and aromatic solvents but less soluble in Et_2O and petroleum ether. Compounds **1–19** were characterized by ^1H and ^{13}C NMR spectroscopy and IR spectroscopy. NMR results for the all adducts and solid-state studies on **1** are described below. IR spectra of compounds **1–19** (Table 2) all show very strong bands associated with B—O stretches in the region 1450–1250 cm^{-1}, but are not otherwise noteworthy.[1,6]

Solution NMR studies

The ^1H and ^{13}C spectra recorded at room temperature for adducts **1–19** at reported in Table 2. The data clearly show the equivalence of the methyl substituents on the aryl rings of PTB·L and MXB·L, demonstrating that at room temperature the three boron centres of the boroxine·ligand adduct are equivalent. These results are in accordance with those obtained by Ritchey[3] for various $Ph_3B_3O_3 \cdot L$ adducts. The ^1H signals of the aryl rings [δ 8.20(d,2H) and 7.30(d,2H) for PTB and δ 7.85(s,2H) and 7.25(s,1H) for MXB] are generally shifted slightly upfield upon adduct formation. This is in agreement with increased electron density on the boroxine ring causing increased shielding of protons on the adjacent aryl rings. Attempts to obtain ^{11}B spectra of compounds **1–19** at room temperature were unsuccessful.

The ^1H spectra of all compounds were tem-

Table 1. Analytical[a] and physical data for 1 : 1 amine : $Ar_3B_3O_3$ adducts

Complex[b]	Yield (%)	M pt (°C)	Analysis (%) C	H	N
1 Cyclohexylamine·PTB	98	237–239	71.9(71.6)	7.5(7.6)	3.4(3.1)
2 4-Picoline·PTB	97	251–252	72.8(72.6)	6.6(6.3)	3.3(3.1)
3 3-Picoline·PTB	97	251–253	72.7(72.6)	6.3(6.3)	2.9(3.1)
4 Piperidine·PTB	98	194	71.4(71.4)	7.5(7.3)	3.3(3.2)
5 Morpholine·PTB	96	175–178	68.1(68.1)	7.3(6.9)	3.2(3.2)
6 Isobutylamine·PTB	98	253–258	70.4(70.3)	7.7(7.6)	3.3(3.3)
7 Methylamine·PTB	97	261–263	68.9(68.7)	7.0(6.8)	3.4(3.6)
8 Dimethylamine·PTB	99	187	69.3(69.3)	7.4(7.1)	3.4(3.5)
9 Isoquinoline·PTB	94	205–207	75.5(74.9)	6.5(5.9)	2.6(2.9)
10 Benzylamine·PTB	98	232–235	72.8(73.0)	6.9(6.6)	2.9(3.0)
11 4-Picoline·MXB	97	244–246	73.6(73.7)	7.7(7.5)	2.8(2.9)
12 Isoquinoline·MXB	95	234–236	75.9(75.5)	6.4(6.5)	2.6(2.7)
13 Cyclohexylamine·MXB	96	253–255	72.5(72.8)	8.2(8.1)	2.9(2.8)
14 Piperidine·MXB	95	229–230	72.3(72.4)	8.2(7.9)	2.9(2.9)
15 Morpholine·MXB	94	238	69.5(69.7)	7.7(7.5)	2.8(2.9)
16 Isobutylamine·MXB	95	243	71.4(71.7)	8.1(8.1)	2.8(3.0)
17 3-Picoline·MXB	96	254–255	73.4(73.7)	6.9(6.8)	2.8(2.9)
18 Benzylamine·MXB	97	228–229	73.9(74.0)	7.5(7.2)	2.7(2.8)
19 Methylamine·MXB	94	258–260	70.3(70.4)	7.4(7.5)	2.8(3.3)

[a] Required amounts given in parentheses.

[b] PTB refers to $(4\text{-}MeC_6H_4)_3B_3O_3$, MXB $(3,5\text{-}Me_2C_6H_3)_3B_3O_3$.

Table 2. Spectroscopic (^1H, ^{13}C NMR[a] and IR[b]) data for 1 : 1 amine : $Ar_3B_3O_3$ adducts

Complex	Data
1	$\delta(^1H)$: 7.95 (d, 6H) ; 7.3 (d, 6H) ; 3.6 (s, 2H) ; 3.0 (m, 1H) ; 2.4 (s, 9H) ; 2.0 (d, 2H) ; 1.6 (m, 3H) ; 1.15 (m, 5H). $\delta(^{13}C)$: 156.52, 139.69, 133.89, 128.38, 50.63, 34.06, 25.05, 24.36, 21.63. IR : 3,500(br), 3281, 3180, 2940, 1610(s), 1574, 1416(br, vs), 1285(br, vs), 1179, 1122, 1053, 1020, 987, 898, 859, 822, 789, 766, 734, 703, 674, 554, 526.
2	$\delta(^1H)$: 8.9 (d, 2H) ; 8.05 (d, 6H) ; 7.3 (m, 8H) ; 2.5 (s, 9H) ; 2.25 (s, 3H). $\delta(^{13}C)$: 153.24, 143.30, 139.27, 135.92, 133.78, 128.31, 126.11, 21.63, 21.43. IR : 3415(br, s), 3128, 2987, 1614(s), 1514, 1434(br, vs), 1287(br, vs), 1177, 1126, 1078, 1046, 1018, 984, 844, 819, 753, 706, 675, 548, 526.
3	$\delta(^1H)$: 8.9 (m, 1H) ; 8.0 (d, 6H) ; 7.75 (d, 1H) ; 7.45 (t, 1H) ; 7.25 (d, 7H) ; 2.25 (s, 12H). $\delta(^{13}C)$: 143.82, 141.24, 141.16, 139.36, 135.95, 133.82, 128.35, 124.95, 21.67, 18.82. IR : 3500(br,w), 3014, 1612(s), 1560, 1514, 1385(br, vs), 1246(br, vs), 1179, 1122, 1081, 1049, 1020, 987, 853, 813, 762, 731, 700, 677, 633, 558, 528.
4	$\delta(^1H)$: 8.0 (d, 6H) ; 7.3 (d, 6H) ; 3.05 (s, 5H) ; 2.25 (s, 9H) ; 1.55 (s, 6H). $\delta(^{13}C)$: 156.34, 139.33, 134.06, 45.22, 25.27, 23.02, 21.63. IR : 3500(br), 2915, 1614(s), 1435(br, vs), 1286(br, vs), 1179, 1120, 1020, 983, 879, 847, 817, 762, 732, 674, 624, 525.
5	$\delta(^1H)$: 8.1 (d, 6H) ; 7.35 (d, 6H) ; 3.6 (t, 4H) ; 3.2 (br s, 1H) ; 3.0 (t, 4H) ; 2.5 (s, 9H). $\delta(^{13}C)$: 156.32, 139.64, 134.06, 128.37, 66.04, 44.15, 21.63. IR : 3425(br), 2922, 1610(s), 1560, 1465(br, vs), 1285(br, vs), 1179, 1127, 1107, 1087, 1049, 986, 886, 821, 762, 731, 699, 673, 638, 526.
6	$\delta(^1H)$: 7.8 (d, 6H) ; 7.15 (d, 6H) ; 3.45 (s, 2H) ; 2.5 (d, 2H) ; 2.3 (s, 9H) ; 1.5 (m, 1H) ; 0.7 (d, 6H). $\delta(^{13}C)$: 139.51, 133.82, 128.43, 47.62, 28.08, 21.64, 19.77. IR : 3244, 2962, 2360, 1923, 1827, 1615(s), 1435(br, vs), 1216 (br, vs), 1121, 734.
7	$\delta(^1H)$: 8.0 (d, 6H) ; 7.25 (d, 6H) ; 3.3 (br s, 2H) ; 2.4 (s, 9H) ; 2.3 (s, 3H). $\delta(^{13}C)$: 139.87, 133.94, 128.49, 26.02, 21.67. IR : 3500(br), 3279, 3234, 3030, 1924, 1611(s), 1577, 1514, 1413(br, vs), 1265(br, vs), 1180, 1110, 1048, 1020, 977, 855, 818, 790, 765, 734, 674.
8	$\delta(^1H)$: 8.0 (d, 6H) ; 7.35 (d, 6H) ; 3.0 (br s, 1H) ; 2.5 (s 9H) ; 2.4 (s, 6H). $\delta(^{13}C)$: 156.34, 139.45, 134.08, 128.30, 36.51, 21.65. IR : 3450(br), 3221, 3002, 1920, 1818, 1609(s), 1560, 1512, 1436(br, vs), 1289(br, vs), 1172, 1120, 1105, 1046, 1021, 969, 915, 878, 859, 816, 782, 761, 728, 675, 660, 552, 525.
9	$\delta(^1H)$: 9.7 (s, 1H) ; 8.9 (d, 1H) ; 8.2 (d, 1H) ; 8.05 (d, 6H) ; 7.9 (m, 3H) ; 7.75 (m, 1H) ; 7.2 (d, 6H) ; 2.45 (s, 9H). $\delta(^{13}C)$: 156.37, 147.58, 139.50, 137.06, 136.12, 134.81, 133.93, 129.45, 129.12, 128.34, 126.63, 123.17, 21.64. IR : 3128, 2967, 1641, 1609(s), 1453(br, vs), 1284(br, vs), 1210, 1177, 1122, 1047, 1021, 986, 941, 860, 823, 778, 749, 709, 676, 528.
10	$\delta(^1H)$: 8.0 (d, 6H) ; 7.25 (m, 11H) ; 4.0 (s, 2H) ; 3.6 (br s, 2H) 2.4 (s, 9H). $\delta(^{13}C)$: 156.35, 139.86, 135.63, 133.99, 129.34, 128.77, 128.49, 128.10, 44.66, 21.69. IR : 3500(br, w), 3341, 3250, 2987, 1614(s), 1538, 1450(br, vs), 1273 (br, vs), 1178, 1123, 991, 817, 759, 734, 689, 629, 521.
11	$\delta(^1H)$: 8.9 (d, 2H) ; 7.7 (s, 6H) ; 7.4 (d, 2H) ; 7.1 (s, 3H) ; 2.5 (s, 3H) ; 2.4 (s, 18H). $\delta(^{13}C)$: 152.61, 143.95, 136.60, 131.44, 125.93, 21.40, 20.28. IR : 3020, 2916, 2859, 1632(s), 1599(s), 1508, 1432 (br, s), 1387(br, s), 1337(br, s), 1280(br, s), 1241 (br, s), 1162, 1075, 1051, 994, 936, 887, 857, 827, 804, 771, 747, 719, 672, 621, 535, 487.
12	$\delta(^1H)$: 9.6 (s, 1H) ; 8.9 (d, 1H) ; 8.2 (d, 2H) ; 7.95 (m, 3H) ; 7.8 (m, 1H) ; 7.75 (s, 6H) ; 7.05 (s, 3H) ; 2.4 (s, 18H). $\delta(^{13}C)$: 147.44, 136.69, 135.97, 133.82, 131.60, 129.57, 129.16, 126.64, 123.26, 21.44. IR : 3423, 3019, 2915, 2858, 1641(s), 1599(s), 1391(br, s), 1281 (br, s), 1240, 1161, 1050, 974, 937, 887, 843, 806, 773, 744, 716, 674, 651, 620, 536.
13	$\delta(^1H)$: 7.65 (s, 6H) ; 7.05 (s, 3H) ; 3.1 (s br, 2H) ; 2.4 (s, 18H) ; 2.05 (d, 2H) ; 1.6 (m, 3H) ; 1.2 (m, 6H). $\delta(^{13}C)$: 136.73, 131.42, 50.58, 33.76, 25.01, 24.29, 21.42. IR : 3224, 2938, 2858, 1702, 1598 (s), 1568, 1468 (br, s), 1321 (br, s), 1238 (br, s), 1174, 1097, 1034, 856, 761, 728, 618, 535.

Table 2—*continued.*

Complex	Data
14	$\delta(^1H)$: 7.6 (s, 6H); 7.05 (s, 3H); 3.0 (s br, 5H); 2.4 (s, 18H); 1.6 (s br, 6H). $\delta(^{13}C)$: 155.05, 136.38, 131.46, 44.95, 25.00, 22.81, 21.23. IR: 3241, 2934, 2859, 1814, 1770, 1598(s), 1452 (br, s), 1167, 1131, 1058, 936, 874, 858, 816, 754, 683, 619, 565, 536.
15	$\delta(^1H)$: 7.65 (s, 6H); 7.1 (s, 3H); 3.6 (s br, 4H); 3.1 (t br, 5H); 2.4 (s 18H). $\delta(^{13}C)$: 136.79, 131.84, 65.93, 44.10, 21.47. IR: 3422, 3189, 3022, 2916, 2859, 1599(s), 1434(br, s), 1339(br, s), 1280(br, s), 1239(br, s), 1167, 1125, 1093, 1051, 935, 910, 880, 858, 814, 752, 730, 619, 535, 486.
16	$\delta(^1H)$: 7.7 (s, 6H); 7.15 (s, 3H); 3.75 (br s, 2H); 2.7 (d, 2H); 2.45 (s, 18H); 1.8 (m, 1H); 0.9 (d, 6H). $\delta(^{13}C)$: 136.78, 131.52, 47.43, 28.10, 21.44, 19.84. IR: 3275, 3235, 2960, 1599 (s), 1575 (s), 1350 (br, vs), 1174, 1038, 912, 857, 839, 785, 763, 722, 621, 593, 535.
17	$\delta(^1H)$: 9.0 (d, 1H); 8.9 (s, 1H); 7.8 (d, 1H); 7.75 (s, 6H); 7.6 (d, 1H); 7.15 (s, 3H); 2.5 (s, 3H); 2.45 (s, 18H). $\delta(^{13}C)$: 143.75, 141.40, 141.17, 136.73, 135.98, 131.57, 124.97, 21.48, 18.85. IR: 3096, 2914, 1760, 1598(s), 1453 (br, s), 1230 (br, s), 1053, 889, 852, 802, 770, 746, 619, 535, 510.
18	$\delta(^1H)$: 7.7 (s, 6H); 7.4 (m, 3H); 7.25 (m, 2H); 7.15 (s, 3H); 4.05 (s, 2H); 3.8 (br s, 2H); 2.5 (s, 18H). $\delta(^{13}C)$: 136.89, 135.79, 131.59, 129.38, 128.80, 128.08, 44.62, 21.47. IR: 3262, 3225, 3021, 2914, 2858, 1804, 1599(s), 1574(s), 1431 (br, s), 1335 (br, s), 1288(br, s), 1239 (br, s), 1181, 1098, 1051, 950, 905, 855, 835, 815, 784, 763, 747, 720, 694, 620, 586, 534.
19	$\delta(^1H)$: 7.7 (s, 6H); 7.15 (s, 3H); 3.55 (br s, 2H); 2.25 (s, 18H); 2.4 (s, 3H). $\delta(^{13}C)$: 136.83, 131.64, 131.51, 25.90, 21.40. IR: 3277, 3228, 2915, 1598(s), 1429 (br, s), 1338 (br, s), 1170, 1103, 1023, 916, 890, 857, 819, 790, 764, 731, 620, 578, 534.

[a] In $CDCl_3$ solution at room temperature.

[b] KBr pellets (cm^{-1}); medium intensity unless otherwise stated.

perature dependent and **1**, **5**, **9**, **10**, **12**, **13**, **15** and **18** were studied in detail with spectra recorded over the range −90–+20°C in CD_2Cl_2 solution. The behaviour of **1** is described here. At −90°C the methyl protons of the 4-tolyl rings appear as 2 signals [δ 2.40(6H), δ2.23(3H)] and the aromatic protons appear as four signals [δ 8.10(4H), 7.55(2H), 7.35(4H), 7.15(2H)]. Upon warming the sample, the methyl signals broaden, coalesce at −63°C, and then sharpen to a singlet. Similarly, the two downfield aromatic signals broaden and coalesce at −55°C, and the two upfield aromatic signals broaden and coalesce at −63°C. At +17°C the methyl protons appear as a sharp singlet (δ 2.43, 9H) and the aromatic protons appear as a pair of doublets (δ 7.95 and 7.30, 6H each, $J = 8.5$ Hz). These spectral changes indicate that the adduct is undergoing a ligand dissociation–recombination process or that it is involved in an intramolecular ligand scrambling process. Room-temperature ^1H spectra were recorded on **1** with an additional equivalent of free ligand added and attention was turned to the amino protons; in agreement with the ligand dissociation–recombination mechanism a single signal was observed at a weighted average of the free and complexed values. The ^{11}B spectrum of **1** over the temperature range (−90–+20°C) was not very informative with the signal being broad and essentially "lost" amongst the base line noise. The free energy of activation ($\Delta G^{\ddagger}$) for the ligand exchange process in **1** can be calculated from the Eyring equation using the exchange rate at coalescence temperature derived from peak separations at slow exchange.[7,8] Calculated data are recorded in Table 3 and the three sets of coalescing signals for **1** gave $\Delta G^{\ddagger}$ of *ca* 43 kJ mol^{-1}. The availability for **1** of exchange rates at two temperatures should enable Arrhenius parameters to be calculated. However, the calculations are much more sensitive to errors in temperature measurements than $\Delta G^{\ddagger}$ and therefore only rough approximations can be obtained. Nevertheless, by averaging the two exchange rates at −63°C an Arrhenius activation energy (*Ea*) of 46 kJ mol^{-1} was obtained.

Free energies of activation for selected PTB complexes (**1**, **5**, **9** and **10**) and the corresponding MXB

Table 3. Variable-temperature NMR data

Complex	T_c (K)	$\delta\nu$ (Hz)	k (s^{-1})[a]	$\Delta G^{\ddagger}$ (kJ mol^{-1})[b]
1[c]	210	36.8	81.7	43.1
1[d]	210	42.9	95.4	42.9
1[e]	218	104.3	231.6	43.0
5[c]	211	23.5	52.2	44.1
9[c]	215	46.3	102.8	43.8
10[c]	224	34.6	76.9	46.2
12[c]	223	47.5	105.5	45.4
13[c]	223	17.3	38.4	47.3
15[c]	233	19.0	42.2	49.3
18[c]	223	19.1	42.5	47.1

[a] $k = 2^{-1/2}\pi\delta\nu$.
[b] $\Delta G^{\ddagger} = -RT\ln(khk_B^{-1}T^{-1})$.
[c] From methyl resonances.
[d] From upfield aromatic protons.
[e] From downfield aromatic protons.

complexes (**13**, **15**, **12** and **18**), based upon coalescence of the methyl substituents of the aryl rings, are given in Table 3. The free energies of activation lie in the range 43.0–49.3 kJ mol^{-1} with MXB derivatives being higher than the corresponding PTB derivative by 0.9–5.0 kJ mol^{-1}. The relative order of $\Delta G^{\ddagger}$ of the more sterically hindered MXB derivatives correlates with steric bulk of the ligand, i.e. isoquinoline < benzylamine ~ cyclohexylamine < morpholine, rather than with ligand basicity (isoquinoline < morpholine < benzylamine < cyclohexylamine). The situation is less clear-cut for the less sterically congested PTB complexes where other factors must dominate. However, morpholine is in the higher half and isoquinoline is in the lower half of the range 43.0–46.2 kJ mol^{-1} for the PTB complexes.

Solid-state studies

The molecular structure of **1**, as determined by a single-crystal X-ray diffraction study, is shown in Fig. 1. This structure is in agreement with low-temperature ^1H NMR experiments. Selected bond lengths and angles are given in Table 4. The compound has a six-membered alternating B_3O_3 ring, similar to the starting boroxine ring system, but with an additional coordinate link from the nitrogen donor atom of the cyclohexylamine to one of three boron atoms (B1); bond angles about B(1) are in the range 102.9(3)–113.1(3)°. The remaining two boron atoms are three-coordinate and the three oxygen atoms are two-coordinate with bond angles about these annular atoms within the range 118.1(3)–123.4(2)°. The cyclohexylamine ligand adopts a chair conformation [CCC angles, 108.5(4)–112.4(3)°] with the amino group equatorial and the CNB angle at 119.2(2)°. BO distances within the B_3O_3 ring system can be constructively compared with those obtained from a crystallographic study[9] of $Ph_3B_3O_3$, namely 1.378(10)–1.390(9) Å. The BO distances to B(1) at 1.457(4) Å (av.) are considerably longer than the other BO distances indicative of a bond order of one. BO distances to O(3) [opposite B(1)] at 1.385(4) Å (av.)

Table 4. Selected bond lengths (Å) and angles (°) for $C_{27}H_{34}B_3NO_3$ (**1**)

B(1)—O(1)	1.451(4)	B(1)—O(2)	1.463(4)
B(2)—O(2)	1.355(4)	B(2)—O(3)	1.373(4)
B(3)—O(1)	1.342(4)	B(3)—O(3)	1.396(4)
B(1)—C(13)	1.600(5)	B(1)—N(1)	1.630(5)
B(2)—C(7)	1.564(5)	B(3)—C(1)	1.552(5)
N(1)—C(22)	1.492(4)		

O(1)—B(1)—O(2)	113.1(3)	O(1)—B(1)—C(13)	113.0(3)
O(2)—B(1)—C(13)	111.4(3)	O(1)—B(1)—N(1)	102.9(3)
O(2)—B(1)—N(1)	104.2(3)	C(13)—B(1)—N(1)	111.7(3)
O(2)—B(2)—O(3)	121.4(3)	O(2)—B(2)—C(7)	118.1(3)
O(3)—B(2)—C(7)	120.5(4)	O(1)—B(3)—O(3)	120.1(3)
O(1)—B(3)—C(1)	119.3(3)	O(3)—B(3)—C(1)	120.6(3)
B(3)—O(1)—B(1)	123.4(3)	B(2)—O(2)—B(1)	121.7(3)
B(2)—O(3)—B(3)	119.9(3)	C(22)—N(1)—B(1)	119.2(2)
C(23)—C(22)—N(1)	111.1(3)	C(23)—C(22)—C(27)	112.4(3)
N(1)—C(22)—C(27)	110.7(3)	C(22)—C(23)—C(24)	111.0(4)
C(23)—C(24)—C(25)	111.6(5)	C(24)—C(25)—C(26)	109.7(5)
C(25)—C(26)—C(27)	111.3(5)	C(22)—C(27)—C(26)	108.5(4)

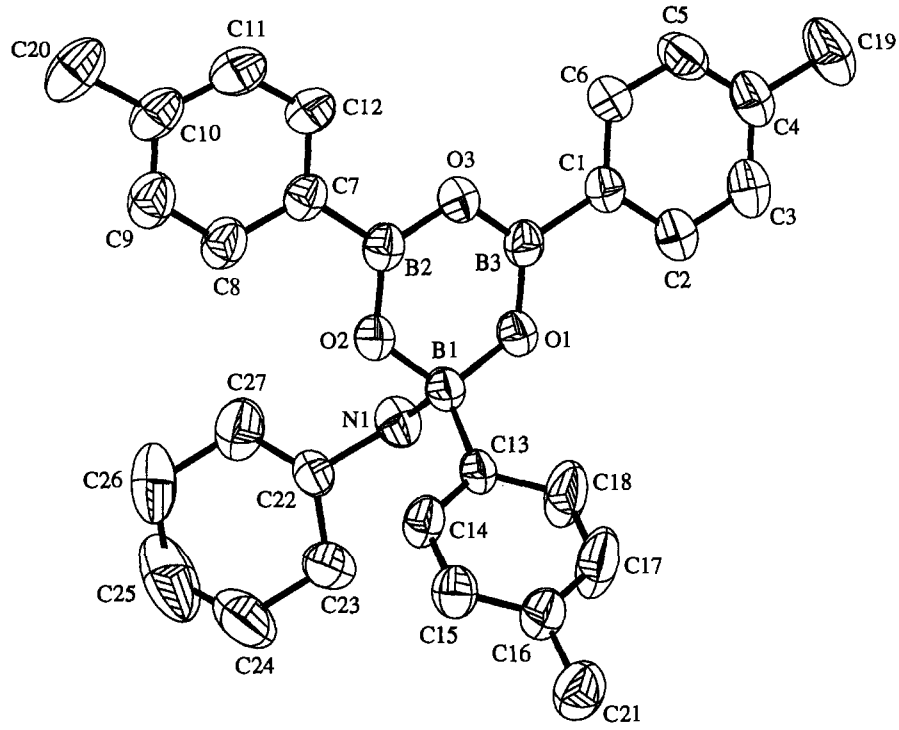

Fig. 1. Molecular structure of $(4\text{-}MeC_6H_4)_3B_3O_3 \cdot NH_2C_6H_{11}$ (**1**) showing the atom numbering scheme used.

Table 5. Crystal data and details of data collection and structure refinement for $C_{27}H_{34}B_3NO_3$ (**1**)

Empirical formula	$C_{27}H_{34}B_3NO_3$
Formula weight	452.98
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	$a = 13.381(2)$ Å
	$b = 11.091(1)$ Å
	$c = 18.084(1)$ Å
	$\beta = 93.662(9)°$
Volume (Å^3)	2678.3(5)
Z	4
Density (calculated) (Mg m^{-3})	1.123
Absorption coefficient (mm^{-1})	0.070
$F(000)$	968
Crystal size (mm)	$0.14 \times 0.08 \times 0.05$
Theta range for data collection (°)	1.95–25.08
Index ranges	$-13 \leftarrow h \leftarrow 15$, $-10 \leftarrow k \leftarrow 12$, $-21 \leftarrow l \leftarrow 18$
Reflections collected	10,087
Independent reflections	4023 [$R_{int} = 0.0698$]
Refinement method	Full-matrix least-squares on F^2
Data/parameters	4023/310
Goodness-of-fit on F^2	0.759
Final R^g indices (all data)	$R_1 = 0.1324$, $wR_2 = 0.1688$
R indices [for 1586 data with $I > 2\sigma(I)$]	$R_1 = 0.0613$, $wR_2 = 0.1505$
Largest diff. peak and hole (e Å^{-3})	0.274 and −0.228

[g] $R_1 = \Sigma(\Delta F)/\Sigma F_o$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; $w = 1/[\sigma(F_o^2) + (0.09P)^2]$, where $P = [\max(F_o^2) + 2F_c^2]/3$.

are significantly longer than the two remaining BO distances [B(2)—O(2) and B(3)—O(1)] at 1.349(4) Å (av.), which presumably have a stronger B—O π-interaction. A similar range and disposition of B—O bond lengths was observed in the structure of $2Ph_3B_3O_3 \cdot 3p\text{-}NH_2C_6H_4NH_2$.[4] The six-membered B_3O_3 ring is non-planar, as shown by the deviations of B(1) and O(3) atoms (−0.081 and −0.048 Å, respectively) from the plane of the other four atoms.

The solid-state $^{11}B\text{-}\{^1H\}$ MAS NMR spectrum of **1** has been recorded and can be interpreted, with the aid of computer simulation and "correction" of chemical shift values, in terms of superposition of two signals at $\delta + 32$ ppm (Cq 2.4 MHz) and $\delta + 15$ ppm (Cq 1.5 MHz), corresponding to three- and four-coordinate boron atoms, respectively. Similarly, the solid-state $^{11}B\text{-}\{^1H\}$ MAS NMR spectrum of PTB can be interpreted as a single three-coordinate signal ($\delta + 25$ ppm, Cq 3.0 MHz) whilst the spectrum of **9** again shows two diagnostic signals for three- and four-coordinate boron atoms at +33 (Cq 2.5 MHz) and +21 (Cq 3.0 MHz) ppm, respectively. Solid-state $^{11}B\text{-}\{^1H\}$ MAS NMR has been previously used to differentiate between three- and four-coordinate boron atoms in crystalline borates and peroxyborates.[10] These spectra illustrate the usefulness of $^{11}B\text{-}\{^1H\}$ MAS NMR with respect to molecular solids.

EXPERIMENTAL

General

Reactions were carried out by standard Schlenk techniques under N_2 and all solvents were dried before use. IR spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer as KBr discs. Multi-element NMR spectra were recorded on a Bruker AC CP/MAS NMR spectrometer operating at 250 MHz for ^1H and 62.9 MHz for $^{13}C\text{-}\{^1H\}$. Chemical shifts (δ) are given in ppm with positive values towards high frequency (downfield) from $SiMe_4$. $(4\text{-}MeC_6H_4)_3B_3O_3$ and $(3,5\text{-}Me_2C_6H_3)_3B_3O_3$ were prepared from $1,4\text{-}MeC_6H_4Br$ and $1,3,5\text{-}Me_2C_6H_3Br$, respectively, by adaptation of published methods.[11] The amines were obtained commercially and cyclohexylamine, 4-picoline, 3-picoline, piperidine, morpholine, isobutylamine, isoquinoline and benzylamine were distilled immediately before use. The complexes **1**–**19** were all prepared by the same method as detailed below for **1**. Analytical data and yields can be found in Table 1. ^1H and ^{13}C NMR data and IR data are given in Table 2.

Preparation of $C_6H_{11}NH_2 \cdot (4\text{-}MeC_6H_4)_3B_3O_3$ (**1**)

Cyclohexylamine (0.27 g, 2.8 mmol) in Et_2O (10 cm^3) was added to a stirred suspension of $(4\text{-}MeC_6H_4)_3B_3O_3$ (1.0 g, 2.8 mmol) in Et_2O (10 cm^3) at room temperature. The suspension of the triaryboroxine dissolved after a few minutes stirring and the resulting solution was filtered. The solution was reduced in volume to dryness and the product (1.24 g, 98%) was obtained, after oven drying (100°C, 4 h) as a white air-stable analytically pure solid (M pt, 237–239°C). Crystals suitable for X-ray diffraction study were grown by diffusion of 40–60°C petroleum ether into a layered solution of the complex in $CHCl_3$.

X-ray structure determination of $C_6H_{11}NH_2 \cdot (4\text{-}MeC_6H_4)_3B_3O_3$ (**1**)

The intensity data were recorded at 20°C using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using Mo-K_α radiation ($\lambda = 0.71069$ Å) by following previously described procedures.[12] The structure was solved by direct methods (SHELXS)[13] and refined on F_0^2 by full-matrix least-squares (SHELXL93)[14] using all unique data corrected for Lorentz and polarization factors. Absorption effects were ignored. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealised positions with the U_{iso}s tied to the U_{eq}s of the parent carbons. Sources of scattering factors are as in ref. 14. The calculations were performed on a 486DX2/66 personal computer. The crystal data and details of data collection and structure refinement are presented in Table 5. Supplementary materials deposited with the Editor include the atomic coordinates, anisotropic displacement coefficients, hydrogen-atom parameters, full list of bond lengths and angles and stucture factor tables.

Acknowledgement—We thank the EPSRC solid-state MAS NMR service (Durham University) for the spectra.

REFERENCES

1. H. R. Snyder, M. S. Konecky and W. J. Lennarz, *J. Am. Chem. Soc.* 1958, **80**, 3611.
2. A. Burg, *J. Am. Chem. Soc.* 1940, **62**, 2228.
3. J. M. Ritchey, Synthesis and properties of addition complexes of boroxines and other selected boron-containing systems, PhD thesis, University of Colorado (1968).
4. M. Yalpani and R. Boese, *Chem. Ber.* 1983, **116**, 3347.

5. W. L. Fielder, M. M. Chamberlain and C. H. Brown, *J. Org. Chem.* 1961, **26**, 2154.
6. L. Santucci and H. Gilman, *J. Am. Chem. Soc.* 1958, **80**, 193.
7. H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* 1956, **25**, 1228.
8. C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, *J. Chem. Soc.* (*A*) 1969, 53.
9. C. B. Brock, R. P. Minton and K. Niedenzu, *Acta Cryst.* 1987, **C43**, 1775.
10. D Muller, A. R. Grimmer, U. Timper, G. Heller and M. Shakibaie-Moghadam, *Z. Anorg. Allg. Chem.* 1993, **619**, 1262.
11. R. M. Washburn, E. Levens, C. Albright and F. Billig, *Org. Synth.* 1959, **39**, 3.
12. J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.* 1993, **32**, 5704.
13. G. M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467.
14. G. M. Sheldrick, SHELXL93 Program for Crystal Structure Refinement. University of Gottingen, Germany (1993).