



SYNTHESIS AND CHARACTERIZATION OF AMINE ADDUCTS OF TRI(4-TOLYL)BOROXINE AND TRI(3,5-XYLYL)BOROXINE: MOLECULAR STRUCTURE OF (4-MeC₆H₄)₃B₃O₃ · CYCLOHEXYLAMINE

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Abstract—19 1:1 adducts of the triarylboroxines (4-MeC₆H₄)₃B₃O₃ (PTB) and (3,5-Me₂C₆H₃)₃B₃O₃ (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 Et₂O at room temperature. All 19 adducts have been characterized by elemental analysis, M pt, IR and ¹H and ¹³C NMR. C₆H₁₁NH₂ · PTB has been characterized in the solid state by a single-crystal X-ray diffraction study. Solid-state ¹¹B 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 Δ*G*[‡] of *ca* 43–49 kJ mol^{−1}.

In 1958 Synder and co-workers¹ 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 Burg² in 1940 for the 1:1 NH₃ and Me₃N adducts of Me₃B₃O₃. In 1968 Ritchey³ prepared a series of 1:1 adducts of Ph₃B₃O₃ 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 ¹¹B studies on quinuclidine · Ph₃B₃O₃ and quinuclidine · Et₃B₃O₃, respectively, by Yalpani and Boese⁴ 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. 2NH₃ · Me₃B₃O₃,² 3*p*-NH₂C₆H₄NH₂ · 2Ph₃B₃O₃⁵ 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-MeC₆H₄)₃B₃O₃ (PTB) and (3,5-Me₂C₆H₃)₃B₃O₃ (MXB). We also report the first crystal and molecular structure of a

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

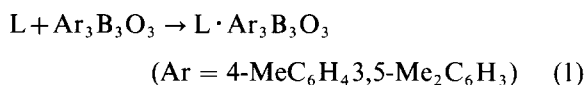
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“simple” 1 : 1 adduct, $C_6H_{11}NH_2 \cdot PTB$, and further investigate its structure in the solid state by MAS ^{11}B NMR. In solution, the dynamic 1H NMR behaviour of $C_6H_{11}NH_2 \cdot PTB$ is compared with a selected range of other adducts.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of 1 : 1 amine adducts (**1–19**) of the triarylboroxines $(4-MeC_6H_4)_3B_3O_3$ (PTB) and $(3,5-Me_2C_6H_3)_3B_3O_3$ (MXB) were relatively straightforward³ 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.



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. Com-

pounds **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 $1450–1250\text{ cm}^{-1}$, 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 $PTB \cdot L$ and $MXB \cdot L$, 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 Ritchey³ 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)	C	Analysis (%)	
				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 $(4-MeC_6H_4)_3B_3O_3$, MXB $(3,5-Me_2C_6H_3)_3B_3O_3$.

Table 2. Spectroscopic (¹H, ¹³C NMR^a and IR^b) data for 1 : 1 amine : Ar₃B₃O₃ adducts

Complex	Data
1	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.9 (d, 2H); 8.05 (d, 6H); 7.3 (m, 8H); 2.5 (s, 9H); 2.25 (s, 3H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.9 (m, 1H); 8.0 (d, 6H); 7.75 (d, 1H); 7.45 (t, 1H); 7.25 (d, 7H); 2.25 (s, 12H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.0 (d, 6H); 7.3 (d, 6H); 3.05 (s, 5H); 2.25 (s, 9H); 1.55 (s, 6H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.0 (d, 6H); 7.25 (d, 6H); 3.3 (br s, 2H); 2.4 (s, 9H); 2.3 (s, 3H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.0 (d, 6H); 7.35 (d, 6H); 3.0 (br s, 1H); 2.5 (s, 9H); 2.4 (s, 6H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.0 (d, 6H); 7.25 (m, 11H); 4.0 (s, 2H); 3.6 (br s, 2H) 2.4 (s, 9H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 8.9 (d, 2H); 7.7 (s, 6H); 7.4 (d, 2H); 7.1 (s, 3H); 2.5 (s, 3H); 2.4 (s, 18H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 7.6 (s, 6H); 7.05 (s, 3H); 3.0 (s br, 5H); 2.4 (s, 18H); 1.6 (s br, 6H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 7.65 (s, 6H); 7.1 (s, 3H); 3.6 (s br, 4H); 3.1 (t br, 5H); 2.4 (s 18H). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 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). $\delta(^{13}\text{C})$: 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	$\delta(^1\text{H})$: 7.7 (s, 6H); 7.15 (s, 3H); 3.55 (br s, 2H); 2.25 (s, 18H); 2.4 (s, 3H). $\delta(^{13}\text{C})$: 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 CDCl₃ 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 – $+20^\circ\text{C}$ in CD₂Cl₂ 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), δ 2.23(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 $+17^\circ\text{C}$ 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 ¹¹B spectrum of **1** over the temperature range (-90 – $+20^\circ\text{C}$) 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 (E_a) 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	<i>T_c</i> (K)	δ <i>v</i> (Hz)	<i>k</i> (s ⁻¹) ^a	Δ <i>G</i> [‡] (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 $k = 2^{-1/2}\pi\delta v$.^b $\Delta G^\ddagger = -RT \ln(kh/k_B T^{-1})$.^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 Δ*G*[‡] 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 B₃O₃ 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 B₃O₃ ring system can be constructively compared with those obtained from a crystallographic study⁹ of Ph₃B₃O₃, 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 C₂₇H₃₄B₃NO₃ (**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)

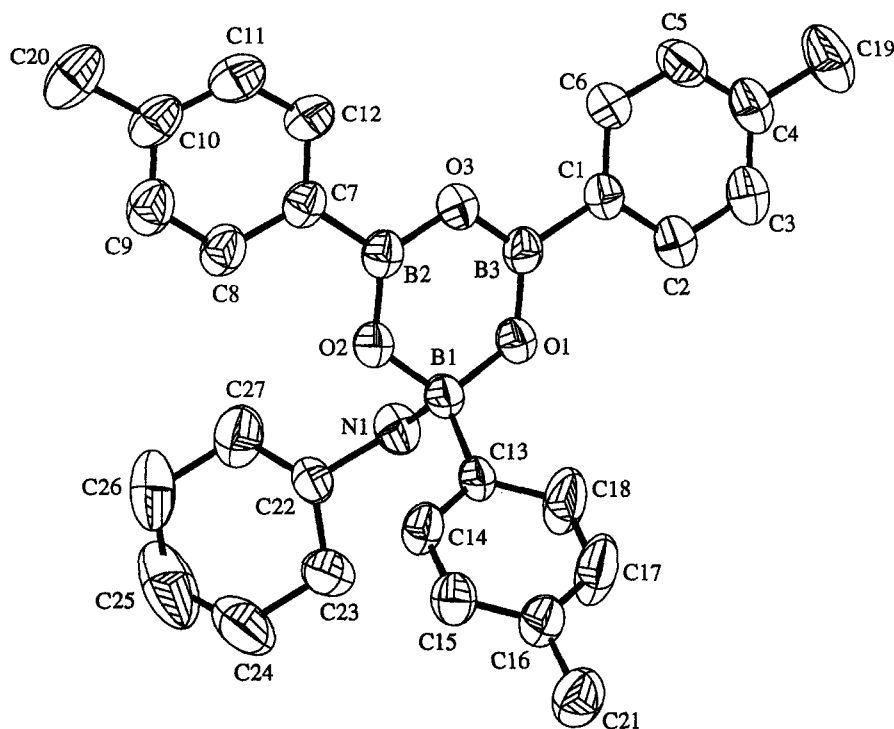


Fig. 1. Molecular structure of $(4\text{-MeC}_6\text{H}_4)_3\text{B}_3\text{O}_3 \cdot \text{NH}_2\text{C}_6\text{H}_{11}$ (**1**) showing the atom numbering scheme used.

Table 5. Crystal data and details of data collection and structure refinement for $\text{C}_{27}\text{H}_{34}\text{B}_3\text{NO}_3$ (**1**)

Empirical formula	$\text{C}_{27}\text{H}_{34}\text{B}_3\text{NO}_3$
Formula weight	452.98
Temperature (K)	293(2)
Wavelength ($\text{\AA}$)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	$a = 13.381(2) \text{ \AA}$ $b = 11.091(1) \text{ \AA}$ $c = 18.084(1) \text{ \AA}$ $\beta = 93.662(9)^\circ$
Volume ($\text{\AA}^3$)	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 ($^\circ$)	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 [$R_{\text{int}} = 0.0698$]
Refinement method	Full-matrix least-squares on F^2
Data/parameters	4023/310
Goodness-of-fit on F^2	0.759
Final R^s 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 ($\text{e \AA}^{-3}$)	0.274 and -0.228

$^s R_1 = \Sigma(\Delta F)/\Sigma F_o$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; $w = 1/[\sigma(F_o^2) + (0.09P)^2]$, 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 2Ph₃B₃O₃·3*p*-NH₂C₆H₄NH₂.⁴ The six-membered B₃O₃ 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 ¹¹B-{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 ¹¹B-{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 ¹¹B-{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 ¹¹B-{¹H} MAS NMR with respect to molecular solids.

EXPERIMENTAL

General

Reactions were carried out by standard Schlenk techniques under N₂ 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 ¹³C-{¹H}. Chemical shifts (δ) are given in ppm with positive values towards high frequency (downfield) from SiMe₄. (4-MeC₆H₄)₃B₃O₃ and (3,5-Me₂C₆H₃)₃B₃O₃ were prepared from 1,4-MeC₆H₄Br and 1,3,5-Me₂C₆H₃Br, 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 ¹³C NMR data and IR data are given in Table 2.

Preparation of C₆H₁₁NH₂·(4-MeC₆H₄)₃B₃O₃ (**1**)

Cyclohexylamine (0.27 g, 2.8 mmol) in Et₂O (10 cm³) was added to a stirred suspension of (4-MeC₆H₄)₃B₃O₃ (1.0 g, 2.8 mmol) in Et₂O (10 cm³) 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 CHCl₃.

X-ray structure determination of C₆H₁₁NH₂·(4-MeC₆H₄)₃B₃O₃ (**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_o^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 structure factor tables.

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