Synthesis of Boron Macrocycles from 1,2-Aminoalcohols and 2-Formylphenylboronic Acid

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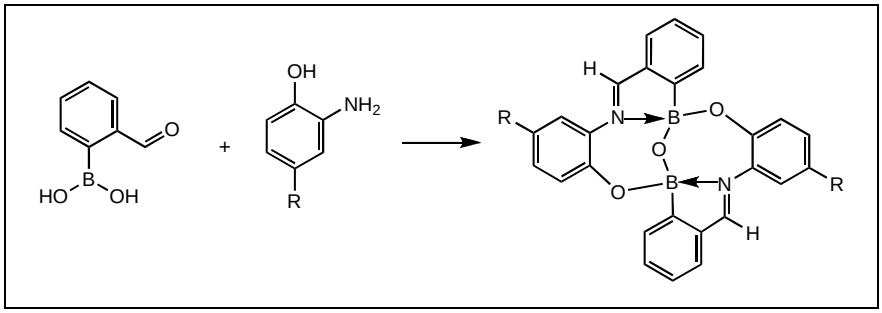

Condensation of aminoalcohols with 2-$HC(O)C_6H_4B(OH)_2$ afforded the macrocyclic compounds **1 - 7** with an OBOBO structural unit. Crystals of **1** were triclinic, space group P-1, a = 9.9818(12) Å, b = 12.8302(15) Å, c = 13.1663(15) Å, α = 105.503(2)°, β = 94.860(2)°, γ = 92.585(2)°, Z = 2.

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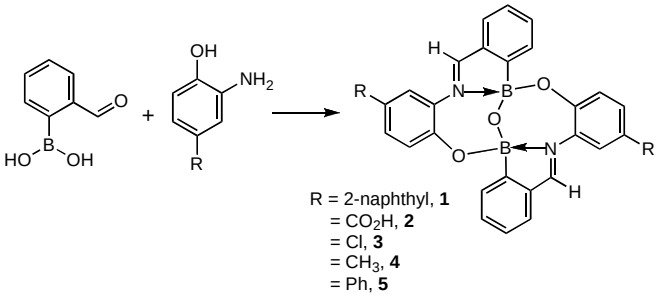
INTRODUCTION

Boronic acids [$RB(OH)_2$] and boronate esters [$RB(OR')_2$] are remarkably versatile functional groups. Their usefulness extends from synthetic applications such as Suzuki-Miyaura cross-coupling reactions [1] to their potent biological activities [2]. For example, an antifungal agent, 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxarole, was recently developed where the boron group is a key element in the compound's toxicity [2a]. As well, serine proteases, a diverse group of proteolytic enzymes responsible for the generation of most disease processes, are inhibited by certain aminoboronic acids [2c]. Simple aminoboronic acid derivatives are also being examined for application in boron neutron capture therapy, a binary form of cancer treatment that relies on delivering a compound containing boron-10 selectively to tumour tissues prior to irradiation by neutrons [2d]. Due to their synthetic utility and the wealth of biological activities demonstrated with boron-containing compounds we decided to examine the reactivity of 1,2-amino-alcohols and 2-formylphenylboronic acid [2-$HC(O)C_6H_4B(OH)_2$]. Results of our study are presented herein.

RESULTS AND DISCUSSION

Salicylaldimines are versatile intermediates in organic synthesis and have been used to prepare numerous pharmacologically important compounds [3]. For instance, Whiting and co-workers have used imines containing boronate esters to make enantio-enriched γ-phenyl-γ-amino alcohols [3a] and Höpfl has prepared air-stable cyclophane-type macrocycles from salicylidene-aminoaryl alcohols and arylboronic acids [3c]. In this study, we found that 2-formylphenylboronic acid adds to 1-amino-2-naphthol in ethanol to give the Schiff base macrocycle **1** (Scheme 1). Similar boron macrocycles containing a N→B-O fragment have shown significant antimicrobial properties [4]. While the imine proton is observed in the ^{1}H NMR spectra at δ 8.61 ppm, the boronic acid hydroxyl groups are absent. The diagnostic C=N stretching band is observed in the FT-IR spectra at *ca*. 1633 cm^{-1} and a peak at δ 7 ppm in the ^{11}B NMR spectra indicates that the boron atom is four coordinate [5].

Scheme 1



The molecular structure of **1** is shown in Figure 1 and crystallographic data given in Table 1. The two fragments form seven-membered rings and are connected *via* a B-O-B bridge [B(1)-O(1)-B(2) = 116.1(2)°] with B-O

bond distances of 1.405(3) Å. The B-O-B angle is somewhat smaller in **1** than that observed in a related heterocycle prepared through the reaction of 2-salicylideneamino hydroxyethane and *tris*-dimethylamine-borane, 124.4(2)° [6]. The two phenolic B-O distances in **1** are slightly longer (1.494(3) and 1.501(3) Å) than the bridged B-O-B bonds (avg. 1.405(3) Å). Similar distances and angles have been reported for other O-B-O ring systems [3b,7]. For instance, a related partial ester of trimetaboric acid derived from salen-type compounds and boric acid has distances of 1.414(6) Å (avg.) for the heterocyclic B-O bonds and 1.466(6) and 1.454(6) Å for the terminal B-O bonds [3b]. The aldimine functionality in **1** is stabilized by N→B interactions with average B-N bonds of 1.647(3) Å, which are characteristic of strong coordination [3c]. Similar bond distances have been reported in related oxime, salen, and salicylaldehyde derivatives [8].

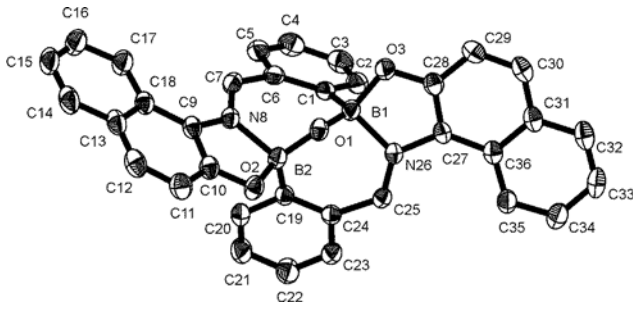


Figure 1. Molecular structure of **1** showing 30% probability ellipsoids with hydrogen atoms omitted for clarity. Selected bond angles (°) and distances (Å): B(1)-O(1) 1.405(3), B(1)-O(3) 1.494(3), B(1)-N(26) 1.644(3), B(2)-O(1) 1.405(3), B(2)-O(2) 1.501(3), B(2)-N(8) 1.649(3); O(1)-B(1)-O(3) 111.5(2), O(1)-B(1)-N(26) 107.9(2), O(3)-B(1)-N(26) 99.41(18), O(1)-B(2)-O(2) 111.1(2), O(1)-B(2)-N(8) 107.3(2), O(2)-B(2)-N(8) 98.77(18), B(2)-O(1)-B(1) 116.1(2).

It is possible that the formation of **1** proceeds *via* initial formation of a Schiff base followed by dehydration of the hydroxyl groups of the boronic acid group to form the anhydride dimer **1**. Anhydride formation is also observed with other 2-aminophenol derivatives to give the corresponding heterocycles **2-5**. Similar reactivity has been reported previously for analogous Schiff bases derived from 2-aminophenol and 2-(4,4,5,5,-tetramethyl-[1,3,2]-dioxaborolan-2-yl)benzaldehyde [5a]. Heterocyclic formation was also observed when 2-$HC(O)C_6H_4B(OH)_2$ was added to aliphatic 1,2-amino-alcohols; ethanolamine and 2-amino-1-phenylethanol (**6** & **7**, respectively, Figure 2).

CONCLUSION

Reactions of 2-$HC(O)C_6H_4B(OH)_2$ with 1,2-amino-alcohols gave novel boron macrocycles containing seven-membered rings with a B-O-B bridge. The aldimine functionality in these dimers is stabilized by intramolecular N→B interactions. All new boron-containing macrocycles will be tested for their potential antifungal and antibacterial activities, the results of which will be reported in due course.

Table 1.

Crystallographic data collection parameters for **1**·$2CH_2Cl_2$

Complex	**1**
Chemical formula	$C_{34}H_{22}B_2Cl_4N_2O_3$
fw	698.01
Crystal system	triclinic
Space group	P-1
a, Å	9.9818(12)
b, Å	12.8302(15)
c, Å	13.1663(15)
α, °	105.503(2)
β, °	94.860(2)
γ, °	92.585(2)
V, Å^3	1615.0(3)
Z	2
ρ_{calcd}, mg m^{-3}	1.435
Crystal size, mm^3	0.60 x 0.30 x 0.15
Temperature, K	183(1)
Radiation	MoKα (λ = 0.71073)
μ, mm^{-1}	0.408
Total reflections	8190
Total unique relections	5271
No. of variables	453
R_{int}	0.0208
Theta range, deg	1.61-24.99
Largest difference peak/hole, e Å^{-3}	0.995/-0.780
GoF on F^2	1.090
R1[a] (I>2σ(I))	0.0528
wR2[b] (all data)	0.1394

[a] $R1 = \sum ||F_o|-|F_c||/\sum|F_o|$. [b] $wR2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[F_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0564*P)^2 + (1.6623*P)]$, where $P = (\max(F_o^2, 0) + 2*F_c^2)/3$.

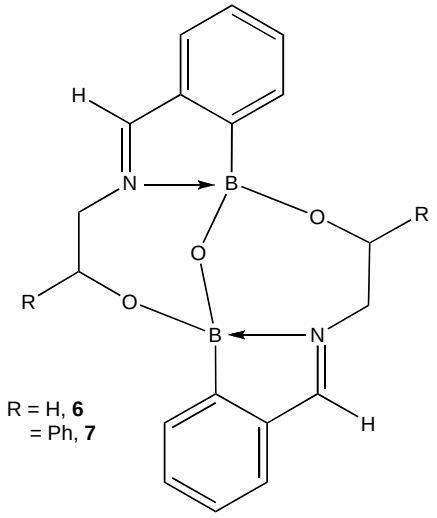


Figure 2. Boron macrocycles derived from aliphatic 1,2-aminoalcohols.

EXPERIMENTAL

Reagents and solvents were purchased from Aldrich Chemicals and used as received. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (^{1}H 270 MHz; ^{11}B 87 MHz; ^{13}C 68 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B)] and coupling constants (*J*) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), broad (br), and overlapping (ov). The infrared spectra were obtained using a Mattson Genesis II FT-IR spectrometer and are reported in cm^{-1}. Melting points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses were obtained on a Vario EL III.

Compound 1. An EtOH (5 mL) solution of 2-formylphenylboronic acid (303 mg, 2.02 mmol) was added to an EtOH (45 mL) solution of 1-amino-2-napthol (320 mg, 2.01 mmol). The reaction mixture was heated at reflux for 3 h at which point the reaction volume was decreased under vacuum to 20 mL and the solution allowed to stand at RT. A reddish-brown precipitate was collected by suction filtration and washed with cold EtOH (2 x 2 mL) to afford **1**. Yield: 218 mg (41 %). Mp = 252 - 254 °C. ^{1}H NMR (DMSO-d_6) δ: 9.72 (s, 2H, Ar), 8.61 (s, 2H, C(H)N), 7.91 (d, *J* = 8.2 Hz, 2H, Ar), 7.82 (d, *J* = 7.7 Hz, 2H, Ar), 7.76 (d, *J* = 8.2 Hz, 2H, Ar), 7.47 (dd, *J* = 7.7 Hz, 2H, Ar), 7.39 - 7.33 (ov m, 4H, Ar), 7.28 (dd, *J* = 7.7 Hz, 2H, Ar), 7.18 (s, 2H, Ar), 7.13 (d, *J* = 7.7 Hz, 2H, Ar); ^{11}B NMR ($CDCl_3$) δ: 7 (br); ^{13}C{^{1}H} NMR (DMSO-d_6) δ: 161.4, 157.1, 154.2 (br, C-B), 136.9, 136.8, 134.4, 134.0, 133.7, 133.6, 129.3, 128.2, 127.8, 127.5, 127.0, 124.0, 114.3, 107.3. FTIR (Nujol): 2945, 2908, 2869, 1633, 1549, 1464, 1376, 1267, 1186, 960, 860, 800, 742. *Anal*. Calcd. for $C_{34}H_{22}B_2N_2O_3$ (528.20): C, 77.31; H, 4.21; N, 5.30. Found: C, 76.85; H, 4.09; N, 5.18.

Compound 2. An EtOH (5 mL) solution of 2-formylphenylboronic acid (303 mg, 2.02 mmol) was added to an EtOH (45 mL) solution of 3-amino-4-hydroxybenzoic acid (306 mg, 2.00 mmol). The reaction was heated at reflux for 3 h then stirred at RT for an additional 16 h. Following removal of the solvent under vacuum the residual solid was redissolved in MeOH (10 mL) and stored at RT. A yellow precipitate was collected by suction filtration and washed with MeOH (2 x 2 mL) to give **2**. Yield: 228 mg (44 %). Mp = 286 - 288 °C. ^{1}H NMR (DMSO-d_6) δ: 9.63 (s, 2H, Ar), 8.65 (s, 2H, C(H)N), 7.98 (d, *J* = 8.4 Hz, 2H, Ar), 7.80 (d, *J* = 6.9 Hz, 2H, Ar), 7.33 - 7.28 (ov m, 4H, Ar), 7.07 (d, *J* = 6.9 Hz, 2H, Ar), 6.95 (d, *J* = 8.4 Hz, 2H, Ar); ^{11}B NMR (DMSO-d_6/MeOH) δ: 7 (br); ^{13}C{^{1}H} NMR (DMSO-d_6) δ: 167.5, 163.4, 160.6, 152.6 (br, C-B), 136.6, 134.4, 134.3, 133.5, 133.4, 132.2, 128.3, 121.5, 117.6, 114.0. FTIR (Nujol): 3113, 2943, 2908, 2860, 1674, 1600, 1552, 1458, 1377, 1300, 1198, 1105, 970, 918, 758, 665. *Anal*. Calcd. for $C_{28}H_{18}B_2N_2O_7$ (516.10): C, 65.16; H, 3.52; N, 5.43. Found: C, 65.43; H, 3.39; N, 5.21.

Compound 3. An EtOH (5 mL) solution of 2-formylphenylboronic acid (506 mg, 3.37 mmol) was added to an EtOH (25 mL) solution of 2-amino-4-chlorophenol (477 mg, 3.32 mmol). The reaction was heated at reflux for 2 h and the solution stored at RT. The resulting yellow precipitate was collected by suction filtration and washed with cold EtOH (2 x 2 mL) to afford **3**. Yield: 455 mg (55 %). Mp = 205 - 208 °C. ^{1}H NMR (DMSO-d_6) δ: 9.48 (s, 2H, Ar), 8.17 (d, *J* = 2.0 Hz, 2H, C(H)N), 7.69 (d, *J* = 6.7 Hz, 2H, Ar), 7.38 (dd, *J* = 8.9, 2.0 Hz, 2H, Ar), 7.33 - 7.27 (ov m, 4H, Ar), 7.08 (d, *J* = 6.7 Hz, 2H, Ar), 6.89 (d, *J* = 8.9 Hz, 2H, Ar); ^{11}B NMR (DMSO-d_6/MeOH) δ: 7 (br); ^{13}C{^{1}H} NMR (DMSO-d_6) δ: 160.4, 158.7, 152.7 (br, C-B), 136.4, 134.3, 133.7, 133.5, 133.0, 132.2, 128.3, 122.4, 116.2, 115.6. FTIR (Nujol): 2943, 2897, 2864, 1622, 1599, 1550, 1464, 1377, 1302, 1265, 1097, 964, 798, 688. *Anal*. Calcd. for $C_{26}H_{16}B_2Cl_2N_2O_3$ (497.06): C, 62.82; H, 3.25; N, 5.64. Found: C, 62.69; H, 3.11; N, 5.42.

Compound 4. An EtOH (5 mL) solution of 2-formylphenylboronic acid (303 mg, 2.02 mmol) was added to an EtOH (45 mL) solution of 2-amino-4-methylphenol (252 mg, 2.05 mmol). The reaction was heated at reflux for 2 h and then stored at RT. A yellow precipitate was collected by suction filtration and washed with cold EtOH (2 x 2 mL) to give **4**. Yield: 140 mg (30 %). Mp = 210 - 214 °C. ^{1}H NMR (DMSO-d_6) δ: 9.34 (s, 2H, Ar), 7.82 (s, 2H, C(H)N), 7.67 (d, *J* = 6.7 Hz, 2H, Ar), 7.32 - 7.21 (ov m, 4H, Ar), 7.17 (d, *J* = 8.2 Hz, 2H, Ar), 7.06 (d, *J* = 6.7 Hz, 2H, Ar), 6.76 (d, *J* = 8.2 Hz, 2H, Ar), 2.36 (s, 6H, CH_3); ^{11}B NMR (CH_2Cl_2) δ: 7 (sharp); ^{13}C{^{1}H} NMR (DMSO-d_6) δ: 158.1, 157.8, 153.4 (br, C-B), 135.8, 134.6, 133.4, 133.3, 132.9, 131.8, 127.9, 127.7, 115.7, 114.0, 21.2. FTIR (Nujol): 2945, 2896, 2864, 1622, 1550, 1502, 1460, 1377, 1281, 1105, 921, 805, 733. *Anal*. Calcd. for $C_{28}H_{22}B_2N_2O_3$ (456.14): C, 73.72; H, 4.87; N, 6.14. Found: C, 73.49; H, 4.67; N, 6.03.

Compound 5. An EtOH (5 mL) solution of 2-formylphenylboronic acid (303 mg, 2.02 mmol) was added to an EtOH (45 mL) solution of 2-amino-4-phenylphenol (371 mg, 2.00 mmol). The reaction was heated at reflux for 3 h then stirred at RT for an additional 16 h. Following removal of the solvent under vacuum the residual solid was redissolved in MeOH (10 mL) and stored at RT. A dark yellow precipitate was collected by suction filtration and washed with MeOH (2 x 2 mL) to afford **5**. Yield: 216 mg (37 %). Mp = 220 - 222 °C. ^{1}H NMR (DMSO-d_6) δ: 9.60 (s, 2H, Ar), 8.42 (s, 2H, C(H)N), 7.78 - 7.72 (ov m, 8H, Ar), 7.51 - 7.48 (ov m, 4H, Ar), 7.37 - 7.33 (ov m, 6H, Ar), 7.17 (m, 2H, Ar), 6.98 (m, 2H, Ar); ^{11}B NMR (DMSO-d_6/$CDCl_3$) δ: 7 (br); ^{13}C{^{1}H} NMR (DMSO-d_6/$CDCl_3$) δ: 159.7, 158.3, 152.6 (br, C-B), 140.4, 135.7, 134.5, 133.6, 132.8, 132.4, 131.5, 131.0, 129.1, 127.8, 127.2, 126.8, 114.6, 113.6. FTIR (Nujol): 2951, 2929, 2922, 2912, 2863, 2852, 1630, 1606, 1552, 1514, 1481, 1464, 1377, 1306, 1265, 1195, 1124, 1105, 960, 908, 758. *Anal*. Calcd. for $C_{38}H_{26}B_2N_2O_3$ (580.28): C, 78.65; H, 4.53; N, 4.83. Found: C, 79.02; H, 4.27; N, 4.65.

Compound 6. An EtOH (10 mL) solution of 2-formylphenylboronic acid (450 mg, 3.00 mmol) was added to an EtOH (10 mL) solution of ethanolamine (183 mg, 3.00 mmol). The reaction was heated at reflux for 3 h, at which point the solvent was removed under vacuum and the residual solid dissolved in $CHCl_3$ (5 mL). A white precipitate was collected by suction filtration to afford **6**. Yield: 102 mg (20 %). Mp = 196 - 198 °C. ^{1}H NMR (CD_3OD) δ: 8.71 (s, 2H, C(H)N), 7.64 (d, *J* = 7.4 Hz, 2H, Ar), 7.52 - 7.50 (ov m, 4H, Ar), 7.40 - 7.32 (ov m, 2H, Ar), 3.87 (t, *J* = 5.5 Hz, 4H, CH_2), 3.74 (t, *J* = 5.5 Hz, 4H, CH_2); ^{11}B NMR (CD_3OD) δ: 10 (sharp); ^{13}C{^{1}H} NMR (CD_3OD) δ: 170.3, 150.1 (br, C-B), 138.2, 132.5, 129.7, 127.7, 126.7, 59.1, 51.9. FTIR (Nujol): 2972, 2945, 2881, 2839, 1631, 1562, 1460, 1377, 1170, 1107, 1070, 968, 746, 723. *Anal*. Calcd. for $C_{18}H_{18}B_2N_2O_3$ (332.00): C, 65.11; H, 5.48; N, 8.44. Found: C, 64.81; H, 5.27; N, 8.39.

Compound 7. An EtOH (10 mL) solution of 2-formylphenylboronic acid (450 mg, 3.00 mmol) was added to an EtOH (10 mL) solution of 2-amino-1-phenylethanol (412 mg, 3.03 mmol). The reaction was heated at reflux for 3 h at which point the solvent was removed under vacuum. The residual solid was dissolved in $CHCl_3$ (5 mL) to which hexane (5 mL) was added

and the solution stored at RT. An off-white solid precipitated, was collected by suction filtration and washed with $CHCl_3$ (2 x 1 mL) to give **7**. Yield: 293 mg (40 %). Mp = 236 - 238 °C. ^{1}H NMR (CD_3OD) δ: 8.68 (s, 2H, C(*H*)N), 7.64 (d, *J* = 7.4 Hz, 2H, Ar), 7.54 - 7.48 (ov m, 8H, Ar), 7.40 - 7.27 (ov m, 8H, Ar), 5.06 (dd, *J* = 9.4, 2.7 Hz, 2H, C*H*), 3.86 (dd, *J* = 12.6, 2.7 Hz, 2H, CH_2), 3.70 (dd, *J* = 12.6, 9.4 Hz, 2H, CH_2); ^{11}B NMR (CD_3OD) δ: 9 (sharp); ^{13}C{^{1}H} NMR (CD_3OD) δ: 171.1, 150.5 (br, *C*-B), 142.2, 138.1, 132.6, 129.8, 128.2, 127.7, 127.6, 126.8, 125.8, 71.0, 57.2. FTIR (Nujol): 3025, 2931, 2906, 2862, 1666, 1631, 1563, 1456, 1377, 1167, 1097, 1059, 953, 746, 700. *Anal*. Calcd. for $C_{30}H_{26}B_2N_2O_3$ (484.20): C, 74.41; H, 5.42; N, 5.79. Found: C, 74.63; H, 5.13; N, 5.61.

X-Ray Crystallography. Crystals of **1**·**2CH$_2$Cl$_2$** were grown from a CH_2Cl_2 solution at 5 °C. Single crystals were mounted using a glass fibre and Paratone-N oil and frozen in the cold stream of the goniometer. Data were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and ϕ scans with a scan width of 0.3° and 20 s exposure times. The detector distance was 6 cm. The data were reduced (SAINT) [9] and corrected for absorption (SADABS) [10]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 680452). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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