Supporting Information

Hetero-arylboroxines: The First Rational Synthesis, X-ray Crystallographic and Computational Analysis

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General. NMR data was acquired on either a 400 MHz Varian Mercury or a 500 MHz Varian INOVA system. ^{1}H NMR spectra are referenced to the deuterated solvent; ^{19}F chemical shifts are referenced to CCl$_3$F. The relaxation delay for ^{19}F acquisition was set to ten seconds. 4-Fluorophenylboronic acid, 2-((dimethylamino)methyl)phenylboronic acid, 4-methoxyphenylboronic acid, 4-acetylphenylboronic acid were purchased from Frontier Scientific and used as received. CDCl$_3$ was stored over 4 Å molecular sieves and K$_2$CO$_3$.

*General procedure for the preparation of **3a-c**.* To a 25 mL round bottom flask was added 0.6 mmol of 2-((dimethylamino)methyl)phenylboronic acid (**1**) and 1.2 mmol of either **2a**, **2b**, or **2c**. Anhydrous toluene was added to the solids to give a 0.05 M solution relative to compound **1**. Magnesium sulfate (approximately 200-300 mg) was added and the heterogeneous solution refluxed for 24 hours. The reaction mixture was cooled, filtered, and concentrated to dryness yielding a white solid. The white solid was taken up in hot anhydrous 1,2-dichloroethane (3 mL) and transferred into culture tubes (6 x 50 mm) that were subsequently placed inside a 20 mL scintillation vial containing pentane. The 20 mL scintillation vial was capped and the crystals were left to grow over a period of one to two weeks.

Computational Methods. All calculations were carried out using Jaguar 6.0[1] at the B3LYP[2-5] flavor of density functional theory with a 6-311+G* basis set. We chose to run our calculations at a similar level of theory and basis set to complement our previous studies.[6, 7] As in our previous studies, the Poisson-Boltzmann (PB) continuum approximation[8, 9] was used to describe the effect of solvent. The parameters used for the dielectric constant and probe radius are ε = 4.8 and R_{solv} = 2.50 Å for chloroform. Zero-point vibration and thermal enthalpy corrections were included based on calculating the analytical Hessian. Thus, our calculated ΔH values represent the solution phase enthalpy. Entropy and free-energy corrections are not included for reasons discussed previously.[6]

Crystal Data **3a.** The data were integrated using the Brüker SAINT software program and scaled using the SADABS software program.[10] Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97).[11] All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. CCDC-671272 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Crystal Data **3b.** The data were integrated using the Brüker SAINT software program and scaled using the SADABS software program.[10] Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97).[11] All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. CCDC-671273 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Crystal Data **3c.** The data were integrated using the Brüker SAINT software program and scaled using the SADABS software program.[10] Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97).[11] All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. CCDC-671274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Figure S1. ^{1}H NMR (CDCl$_3$, 25°C) spectra showing the room temperature scrambling of hetero-arylboroxine **3c** upon addition of 4-methoxyphenylboronic acid.
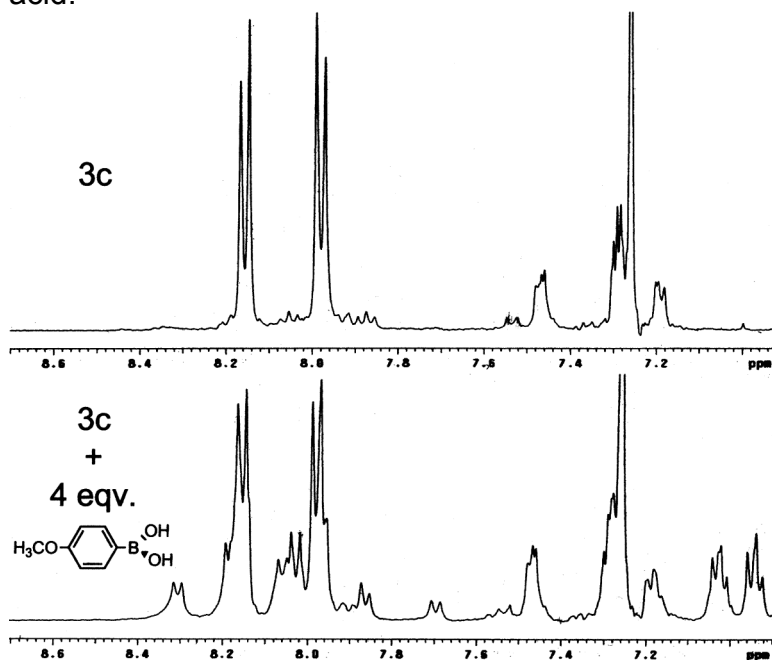

Table S1. Comparison of X-ray crystallographic properties of **3a**, **3b**, and **3c**.

	3a	3b	3c
sp^{3}B-N Bond Length (Å)	1.695 (3)	1.701 (2)	1.680 (4)
B$_3$O$_3$ –Phenyl Ring Dihedral Angles (°)	4.8/2.1	10.7/12.0	6.1/3.6
O-sp^{3}B-O Bond Angle (°)	113.19 (17)	113.18 (13)	112.90 (2)
Avg O-sp^{2}B-O Bond Angle (°)	120.69	120.57	121.28
Avg sp^{3}B-O Bond Length (Å)	1.45	1.45	1.45
Avg sp^{2}B-O Bond Length (Å)	1.36	1.37	1.37

Table S2. Enthalpy for the formation of arylboroxines of the structural type B_3, AB_2, A_2B, and A_3 where A is arylboronic acid monomer **1** and B represents non-coodinating arylboronic acid monomers **2a-c**.

Reaction	ΔE_{elec} (kcal/mol)	ΔE_{solv} (kcal/mol)	ΔE_{corr} (kcal/mol)	ΔH°_{soln} (kcal/mol)
$3B \rightarrow B_3$ (**4a**) $+ 3H_2O$	12.59	-5.44	-2.77	4.38
$A + 2B \rightarrow AB_2$ (**3a**) $+ 3H_2O$	7.12	-7.37	-2.31	-2.56
$2A + B \rightarrow A_2B$ (**5a´**) $+ 3H_2O$	11.80	-7.50	-2.24	2.06
$2A + B \rightarrow A_2B$ (**5a**) $+ 3H_2O$	7.86	-5.78	-2.18	-0.10
$3A \rightarrow A_3$ (**6´**) $+ 3H_2O$	24.61	-5.37	-3.99	15.25
$3A \rightarrow A_3$ (**6**) $+ 3H_2O$	13.90	-5.00	-2.40	6.50
$3B \rightarrow B_3$ (**4b**) $+ 3H_2O$	12.43	-5.55	-2.80	4.09
$A + 2B \rightarrow AB_2$ (**3b**) $+ 3H_2O$	8.48	-7.37	-2.38	-1.26
$2A + B \rightarrow A_2B$ (**5b´**) $+ 3H_2O$	13.08	-7.73	-2.29	3.06
$2A + B \rightarrow A_2B$ (**5b**) $+ 3H_2O$	9.73	-6.16	-2.35	1.22
$3B \rightarrow B_3$ (**4c**) $+ 3H_2O$	14.69	-5.57	-1.05	8.07
$A + 2B \rightarrow AB_2$ (**3c**) $+ 3H_2O$	7.72	-7.64	-1.07	-0.99
$2A + B \rightarrow A_2B$ (**5c´**) $+ 3H_2O$	11.68	-7.64	-1.57	2.47
$2A + B \rightarrow A_2B$ (**5c**) $+ 3H_2O$	8.19	-6.54	-1.55	0.11

Table S3. Standard enthalpies for products and reactants in boronic trimer formation adjusted to 298 K solvated in chloroform.

Molecule	E_{elec} (kcal/mol)	E_{solv} (kcal/mol)	E_{corr} (kcal/mol)	H°_{soln} (kcal/mol)
2a	-318551.09	-9.17	79.09	-318481.16
1	-365012.94	-9.78	150.59	-364872.12
2b	-328142.50	-10.41	105.79	-328047.12
2c	-352070.62	-11.88	108.74	-351973.76
4a	-811733.00	-7.46	187.45	-811553.01
4b	-840507.38	-11.29	267.52	-840251.16
4c	-912289.49	-15.74	278.12	-912027.11
3a	-858200.32	-10.00	259.41	-857950.91
3b	-877381.77	-12.48	312.74	-877081.52
3c	-925238.78	-15.70	319.95	-924934.53
5a´	-904657.49	-10.74	330.98	-904337.25
5a	-904661.43	-9.02	331.04	-904339.40
5b´	-914247.62	-12.21	357.63	-913902.20
5b	-914250.97	-10.65	357.57	-913904.04
5c´	-938177.14	-13.60	361.30	-937829.44
5c	-938180.62	-12.50	361.32	-937831.80
6´	-951106.53	-9.22	400.73	-950715.02
6	-951117.24	-8.84	402.32	-950723.76
H_2O	-47969.22	-8.49	15.68	-47962.03

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