Favoring Heterotrimeric Boroxine Formation Using an Internal Lewis Base: A Computational Study

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Heterotrimeric arylboroxines can be favorably formed by designing one of the arylboronic acid monomers to contain a pendant Lewis base. Using density functional theory (B3LYP//6-311+G*) calculations including Poisson−Boltzmann implicit solvent, we found that AB_2 trimeric arylboroxines were thermodynamically favored over A_2B, A_3, or B_3, where A and B are monomeric arylboronic acids with and without a pendant Lewis base, respectively. The most stable AB_2 trimers were formed when the B monomer contained electron-withdrawing substituents, particularly halogens in the para-position or π-acceptors in the meta-position. On the other hand, adding different para-substituents to the A monomer did not significantly change the energetics. Our calculations also suggest that ABC trimers with three different monomers will not be significantly favored over AB_2 trimers when making small electronic perturbations, by changing the substituents on each monomer.

Introduction

Boroxines, the dehydration product of organoboronic acids,[1] have found commercial use in such diverse areas as flame-retardant materials,[2] dopants for lithium ion transference in polymer electrolytes,[3−5] acid alternatives in Suzuki−Miyaura coupling reactions,[6] and nonlinear optical materials.[7] Arylboroxines are also finding increased utility in material science applications, such as covalent organic frameworks,[8,9] borane-end functionalized polymers,[10] nanoscale molecular scaffolds,[11] and in generating dynamic combinatorial libraries.[12,13]

Boroxines are known to form stable adducts with many nitrogen donor compounds including amines,[14−18] pyridines,[19] hydrazines,[20] azaindoles,[21] and even salen-type ligands.[22] However, in all these cases, the boroxines formed are all *homo*trimers. In contrast, there are only two very recent published reports containing *hetero*trimeric boroxines. The first study, by Tokunaga et al.,[13] used ^1H NMR to measure the equilibrium constants between pairs of arylboronic acid monomers and their corresponding boroxines. Lewis bases were not present, and the purpose of that study was not to preferentially synthesize heteroboroxines but to determine the thermodynamic parameters for their formation. Although we have not examined identical molecules, our present enthalpic calculations on structurally related molecules are in excellent agreement with the experimental results.

The second study was a successful collaborative experimental and computational effort at designing and synthesizing heterotrimeric boroxines by the Iovine group and ours.[23] For the reaction shown in Figure 1, the AB_2 trimer was the dominant product (~90%) over all others formed (A_2B, A_3, B_3). The design of the pendant amine group on A and the *p*-fluoro substituent on B were predicated on two of our previous studies,[24,25] where we found that (i) 1:1 adducts between boroxine and Lewis base were favored over 1:2 or even 1:3 adducts and (ii) electron-withdrawing aryl substituents favor formation of the boroxine•amine adduct. The focus of that study was to describe the synthesis, ^1H and ^{19}F NMR analysis, and X-ray crystallographic data for the three AB_2 trimers synthesized. For all three, the same A monomer was reacted with B monomers with three different para-substituents: fluoro (as shown in Figure 1), methoxy, and acetyl. We presented our thermodynamic calculations for just these three systems in that work.[23]

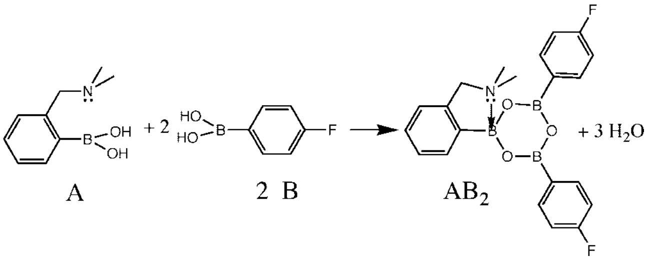

Figure 1. Formation of heterotrimeric AB_2 from monomers.

Our aim in the present study is to explore the limits of this approach by making small perturbations to both the A and B monomers. We have purposefully limited the scope of the present study to include only a range of monosubstitutions, primarily in the para-position (with the exception of two π-acceptors in the meta-position), and minor changes to the pendant group. We chose our template monomers to be *o*-aminomethyl phenylboronic acid ($X = CH_2NH_2$, $Y = H$) and *p*-fluoro phenylboronic acid ($Z = F$), similar to the reaction in Figure 1. Modifications to X, Y, Z were done separately to study the independent contribution of each perturbation. The pendant-containing monomers are designated A, and the nonpendant monomers are designated B (or C where appropriate), as shown in Figure 2. Under these strictures, as will be shown in our results, there was no obviously easy way to thermodynamically favor ABC heterotrimers containing three different monomers. Current and future work includes larger perturbations to this system, including the use of steric effects, to control the architecture of the boroxines formed.

In calculating the solution phase enthalpy for boroxine formation from its monomers, we found that the most stable

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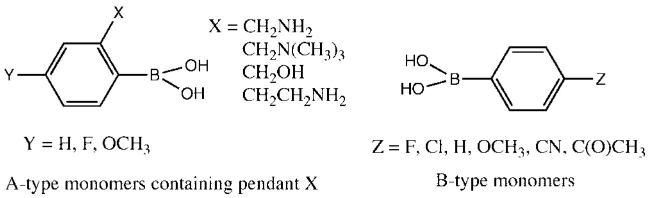

Figure 2. Pendant (A) and nonpendant (B) containing boronic acid monomers in this study.

AB_2 trimers were formed when the B monomer had electron-withdrawing substituents, particularly halogens in the para-position or π-acceptors in the meta-position. On the other hand, adding different para-substituents to the A monomer did not significantly change the overall picture. Adding a methylene spacer in the pendant group contributed to further enthalpic stabilization of AB_2, but replacing the nitrogen with oxygen disfavored intramolecular adduct formation. We have not included any calculations of activation barriers; in a previous computational study of the kinetics of boroxine formation (including all intermediates),[26] we found that the barriers were low and track well with the relative enthalpies of the reactants, intermediates, and products.

Computational Methods

All calculations were carried out using Jaguar 6.0[27] at the B3LYP[28−31] flavor of density functional theory (DFT) 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.[23−26] The Poisson−Boltzmann (PB) continuum approximation[32,33] was used to describe the effect of solvent. In this approximation, a smooth solvent-accessible surface of the solute is calculated by rolling a sphere of radius R_{solv} over the van der Waals surface. The solvent is represented as a polarizable continuum surrounding the molecule with dielectric constant ε. Charges are allowed to develop on the surface according to the electrostatic potential of the solute and ε; then the polarized reaction field of the solvent acts back on the quantum mechanical description of the solute. The wave function of the complex is relaxed self-consistently with the reaction field to solve the PB equations. Although the forces on the quantum mechanical solute atoms due to the solvent can be calculated in the presence of the solvent, in this work, the solvation energy was calculated at the optimized gas-phase geometry for all structures at minima. This is because there is little change between the gas-phase and implicit solvent optimized geometries. The parameters used for the dielectric constant and probe radius are $\varepsilon = 4.8$ and $R_{solv} = 2.50$ Å for chloroform.

The analytical Hessian was calculated for each optimized geometry in the gas phase. The DFT gas-phase energy was then corrected for zero-point vibrations. Negative eigenvalues in transition state calculations were not included in the zero-point energy. The temperature-dependent enthalpy correction term is straightforward to calculate from statistical mechanics. Assuming that the translational and rotational corrections are a constant times kT, that low-frequency vibrational modes will generally cancel out when calculating enthalpy differences, and that the vibrational frequencies do not change appreciably in solution, we can calculate H_{298K}.

The corresponding free-energy corrections in solution are much less reliable.[34−36] Changes in free-energy terms for translation and rotation are poorly defined in solution, particularly as the size of the molecule increases. Additional corrections to the free energy for concentration differentials among species (to obtain the chemical potential) can be significant, especially if the solubility varies among the different species in solution. Furthermore, since the reactions being studied are in solution, the free energy being accounted for comes from two different sources: thermal corrections and implicit solvent. Neither of these parameters is easily separable, nor do they constitute all the required parts of the free energy under our approximations of the system.

TABLE 1: Enthalpies of Boroxine Formation Comparing X = $CH_2N(CH_3)_2$ and X = CH_2NH_2

	$\Delta H°_{soln}$ (kcal/mol)	
Y = H, Z = F	X = $CH_2N(CH_3)_2$[a]	X = CH_2NH_2
$3B \rightarrow B_3 + 3H_2O$	4.38	4.38
$A + 2B \rightarrow AB_2 + 3H_2O$	−2.56	−2.83
$2A + B \rightarrow A_2B$ (syn) $+ 3H_2O$	2.06	0.19
$2A + B \rightarrow A_2B$ (anti) $+ 3H_2O$	−0.10	−0.15
$3A \rightarrow A_3$ (syn−syn) $+ 3H_2O$	15.25	9.82
$3A \rightarrow A_3$ (syn−anti) $+ 3H_2O$	6.50	3.61

[a] Numbers from this column are from ref 23.

Our reported ΔH values are calculated from the difference in solution phase enthalpy between the reactants and products. These are calculated by adding to the electronic energies (1) zero-point energy, (2) enthalpic thermal corrections to 298 K, and (3) the free energy due to solvation. It is important to note that even though the solvation energy contribution is to some extent a free-energy correction, it certainly does not account for all of the free energy. Hence, we will retain the symbol ΔH and refer to this quantity as the solution phase enthalpy in our results and discussion.

Results and Discussion

This section is organized as follows. We have divided our results into three groups according to the three separate perturbations shown in Figure 2: (1) To study changes in the pendant group, we fix Y = H and Z = F while varying X, (2) to study the effect of the nonpendant group, we fix X = CH_2NH_2 and Y = H while varying Z, and (3) to study the effect of changing the electronic properties of the pendant monomer, we fix X = CH_2NH_2 and Z = F while varying Y. We then explored the feasibility of forming ABC heterotrimers based on what we learned from the perturbations. Finally, we compared our computational results for heterotrimers formed solely by monomers without pendant groups, with the recent experimental work by Tokunaga et al.[13] Although these latter reactions are enthalpically unfavorable, the good agreement between our results and the experimentally extracted enthalpies gives us confidence that our choice of computational methods is quite reasonable for these systems.

Altering the Pendant Group. In our previous study, we had used the larger pendant group X = $CH_2N(CH_3)_2$ with Y = H and Z = F to design AB_2 structures that would be favored over A_2B, A_3, and B_3 trimers.[23] We found that the AB_2 heterotrimer is indeed the enthalpically favored product from our calculations, in good agreement with ^1H and ^{19}F NMR data; we were also able to obtain crystal structures of AB_2 trimers. The first order of business was to compare the computationally less expensive X = CH_2NH_2 pendant to our previous results. The calculated solution phase enthalpies are shown in Table 1, and the optimized structures are shown in Figure 3.

The overall energetic trends are the same for the less bulky pendant group (X = CH_2NH_2), i.e., AB_2 is most favored thermodynamically. The difference in enthalpy for forming AB_2

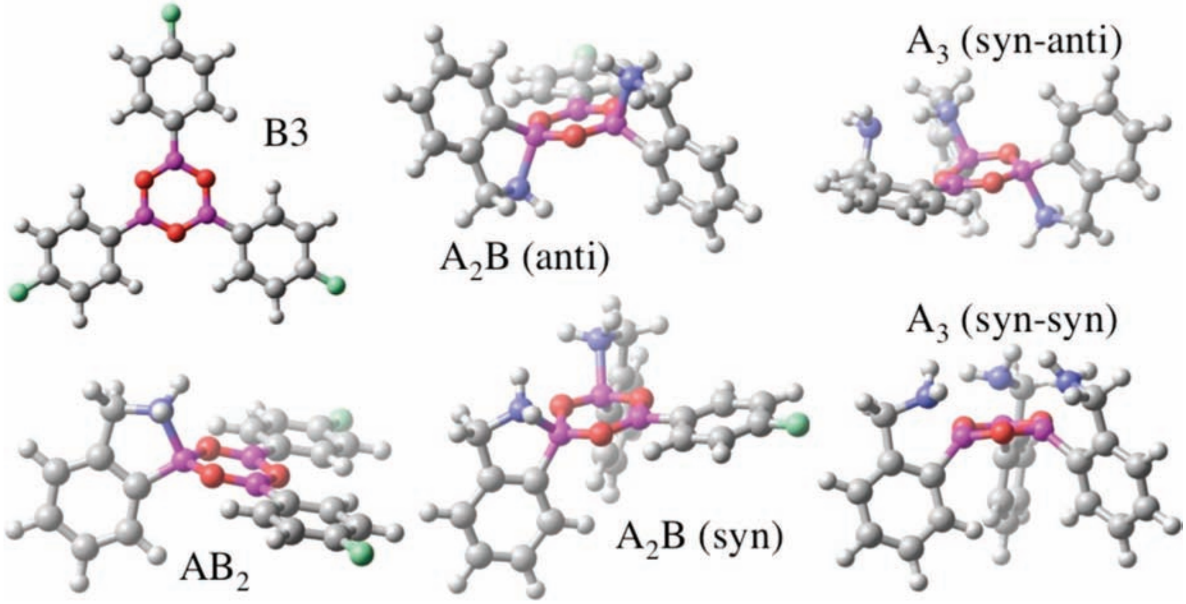

Figure 3. Optimized structures of B_3, AB_2, A_2B, and A_3 for X = CH_2NH_2, Y = H, Z = F.

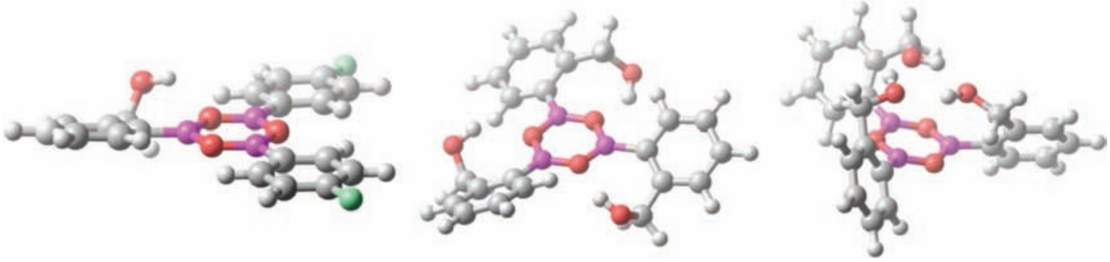

Figure 4. AB_2 and A_3 structures for X = CH_2OH, Y = H, Z = F.

TABLE 2: Enthalpy of AB_2 Formation When Varying Z

X = CH_2NH_2, Y = H reaction: A + 2B → AB_2 + $3H_2O$	$\Delta H°_{soln}$ (kcal/mol)	in the meta- instead of para-position
Z = Cl	−3.99	
Z = F	−2.83	
Z = CN	−2.38	−2.88
Z = H	−1.96	
Z = C(O)CH_3	−1.65	−2.69
Z = OCH_3	−1.32	

TABLE 3: Enthalpy of AB_2 Formation When Varying Y

X = CH_2NH_2, Z = F reaction: A + 2B → AB_2 + $3H_2O$	$\Delta H°_{soln}$ (kcal/mol)
Y = F	−2.76
Y = H	−2.83
Y = OCH_3	−3.11

(−2.56 vs −2.83 kcal/mol) is about the same, certainly within the computational error. When more than one pendant group is present on the same side of the ring (designated syn) in A_2B and A_3, the bulkier pendant groups results in unfavorable steric clashes, increasing ΔH values. The B−N bond distances are 1.71 Å for AB_2 and 1.73−1.76 Å for A_2B. In the syn−anti A_3 structure, one B−N bond is shorter at 1.73 Å, whereas the other is longer at 1.79 Å; the third pendant group swings away. In the syn−syn A_3 structure, the B−N bonds are longer (>1.8 Å), but all three pendant groups are oriented to maximize the dipole of the molecule. More detailed comparisons to crystal structure data for this system and work by others where intramolecular B−N coordination is observed[37−39] are found in our previous work.[24]

Since the overall trends are very similar for the computationally less expensive X = CH_2NH_2 pendant group compared to the larger X = $CH_2N(CH_3)_2$ that has been validated experimentally, we chose to use X = CH_2NH_2 (and Y = H) as the template pendant monomer.

When replacing N with O in the pendant (X = CH_2OH), keeping Y = H and Z = F, we find that forming the AB_2 trimer is no longer favorable: $\Delta H = +6.31$ kcal/mol. In fact, no trimer is favorably formed and the equilibrium favors the monomers. Of the trimers, B_3 is now the most favorable ($\Delta H = +4.38$ kcal/mol). The structure of AB_2 shows that the oxygen does not act as a Lewis base toward the boron. Rather, the most favorable structure (Figure 4, left), has a hydrogen bond formed between the pendant OH and an oxygen in the boroxine ring. The hydrogen bond is a little longer at 2.12 Å and not colinear (the OH−O angle is 136°). The two lowest energy A_3 structures are rather interesting. The lower energy structure ($\Delta H = +10.72$ kcal/mol) has three hydrogen bonds formed between the three pendant groups and the three oxygens in the boroxine ring (Figure 4, middle). The other structure, 0.94 kcal/mol higher in enthalpy (Figure 4, right), has hydrogen bonds formed between the three pendant groups above the boroxine ring.

If an additional methylene spacer is added to the pendant (X = $CH_2CH_2NH_2$) to form six-membered rather than five-membered rings in the adduct, forming AB_2 is now more enthalpically favorable: $\Delta H = -3.39$ kcal/mol, compared to −2.83 kcal/mol for the shorter pendant. Although we have not explicitly calculated the solution phase entropy for reasons described in the Computational Methods section, we think that this difference is not large enough to overcome the entropic

TABLE 4: Enthalpy of Formation of ABC Heterotrimer

	reaction: A + B + C → ABC + 3H$_2$O			
no.	A	B	C	$\Delta H°_{soln}$ (kcal/mol)
1	X = CH$_2$NH$_2$, Y = H	Z = F	Z = OCH$_3$	−2.11
2	X = CH$_2$NH$_2$, Y = H	Z = F	Z = CN	−2.67
3	X = CH$_2$NH$_2$, Y = H	Z = OCH$_3$	Z = CN	−2.28
4	X = CH$_2$NH$_2$, Y = H	Z = F	Z = meta-CN	−3.04
5	X = CH$_2$NH$_2$, Y = H	Z = Cl	Z = meta-CN	−4.05
6	X = CH$_2$NH$_2$, Y = OCH$_3$	Z = F	Z = meta-CN	−3.12

TABLE 5: Enthalpy of Boroxine Formation with No Pendant Groups in Monomeric Species

reaction: A + B + C → ABC + 3H$_2$O			
Z (A)	Z (B)	Z (C)	$\Delta H°_{soln}$ (kcal/mol)
CN	CN	CN	8.07
CN	CN	H	6.79
CN	H	H	5.62
CN	H	OCH$_3$	5.11
H	H	H	5.06
H	H	OCH$_3$	4.65
H	OCH$_3$	OCH$_3$	4.37
OCH$_3$	OCH$_3$	OCH$_3$	3.76

penalty of decreasing the flexibility of a longer pendant. A crude approximation for the entropic (contribution to the free energy) difference between the shorter and longer pendant groups to form AB$_2$ is ~2.5 kcal/mol. This is based on the suggestion of Wertz[40] and Abraham[41] that, upon dissolving in water, molecules lose a constant fraction (~0.5) of their entropy. Although this method has been applied to smaller molecules in implicit water,[42,43] it is not yet clear how well it works for our current system; our study of the limits of this approximation is currently a work in progress. Therefore, we still expect the shorter pendant to be optimal for forming AB$_2$ heterotrimers.

Altering the Electronic Properties of the Nonpendant Monomer. To examine the effect of changing the electronic properties of the nonpendant monomer, we kept X = CH$_2$NH$_2$ and Y = H constant for the pendant monomer and calculated the enthalpies of AB$_2$ formation for various para-substituents Z on the nonpendant monomer. We know that the AB$_2$ structures will be favored over A$_3$ ($\Delta H°_{soln}$ = +6.50 kcal/mol) and B$_3$ ($\Delta H°_{soln}$ ranges from +3.57 to +8.15 kcal/mol).[25] We also know that if Z was electron-donating (such as methoxy), the AB$_2$ structure is still favored over A$_2$B.[23] Thus, we report only our calculations on the AB$_2$ trimer, as shown in Table 2.

We see the same two trends as found for homotrimeric boroxines adducts with an external Lewis base:[24,25] (1) Z substituents that are overall electron-withdrawing favor boroxine formation with a Lewis base adduct, and (2) π-donors stabilized formation of the trimer relative to its monomers, whereas π-acceptors destabilized the trimer. As expected for this series, the halide substituents are the most favorable for formation of AB$_2$. Although CN is a π-acceptor, it is strongly electron-withdrawing overall. Acetyl is also a π-acceptor but not as strongly electron-withdrawing. The overall electron-donating methoxy substituent is the least favorable for AB$_2$ formation in the series. If the electron-withdrawing π-acceptor is instead in the meta-position, the enthalpy of AB$_2$ formation is more exothermic compared to the para-position.

Altering the Electronic Effects of the Pendant Monomer via a Para-Substituent. Starting with the template monomers (X = CH$_2$NH$_2$, Y = H, Z = F), to study the effect of modifying the electronic properties of the pendant monomer, we replaced Y with electron-withdrawing (Y = F) and electron-donating (Y = OCH$_3$) substituents. From Table 3, we see that the electron-donating methoxy substituent favors AB$_2$ formation, whereas the electron-withdrawing fluorine is less favorable. However, these differences are rather small and much less significant than varying Z. This is not a surprising result because the pendant-containing monomer results in a tetrahedral boron center upon adduct formation; therefore, any electronic effects communicated through the phenyl π-system are attenuated in a tetrahedral boron compared to a planar sp^2 boron.

Can We Favor Formation of ABC Heterotrimers? Perturbing the three groups (X, Y, Z) suggests that heterotrimer formation is favored by a short nitrogen Lewis base pendant (X = CH$_2$NH$_2$), potentially with an electron-donating group Y on the pendant monomer. The Z group should be overall electron-withdrawing but also a π-donor. However, perhaps there is an optimal balance between the electronic characteristics of the Y and Z groups. After all, AB$_2$ formation is favored through a balance of electron-withdrawing and electron-donating groups influencing the electronic character of the boroxine ring (including the fact that the Lewis base donates electron density). Therefore, we used a combinatorial approach to examine if there were any cases where the formation of a heterotrimer from three different monomers (ABC) would be favored over one from just two different monomers (AB$_2$). In the ABC trimer, A is a pendant-containing monomer, whereas B and C are both nonpendant-containing monomers.

After calculating over 30 structures, no ABC heterotrimer emerges as being strongly favored. The only examples where formation of ABC is marginally more favorable than AB$_2$ or AC$_2$ is when B contains a para-halide and C contains a meta-π-acceptor; however, the favorable enthalpic difference is within the computational error. The enthalpies for a selection of ABC heterotrimers are shown in Table 4. These examples serve to highlight the lack of selectivity we observe.

In entry nos. 1−3 of Table 4, ΔH values are in between those calculated for the AB$_2$ (or AC$_2$) trimers. From Table 2, these are −1.32, −2.38, and −2.83 kcal/mol for Z = OCH$_3$, CN, and F, respectively. Interestingly, entry no. 3 is marginally more exothermic than entry no. 1; however, the difference is not large enough to be significant. In entry no. 4, the ABC heterotrimer is more stable compared to AB$_2$ (−2.83 kcal/mol) and AC$_2$ (−2.88 kcal/mol) although the difference is still rather small. Entry no. 5 looks particularly favorable, but recall that AB$_2$ for Z = Cl has ΔH = −3.99 kcal/mol, so once again the difference is not significant. If an electron-donating Y was included, such as in entry no. 6, there is still no difference since AB$_2$ has practically the same value of ΔH (−3.11 kcal/mol). We therefore conclude that making small perturbations will not significantly favor ABC heterotrimers over their AB$_2$ counterparts in a mixture of monomers. Current work includes making larger perturbations to the monomers both electronically and sterically.

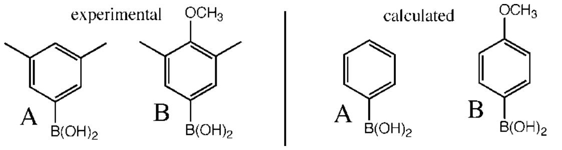

Figure 5. Comparison of boronic acid monomers used in experiment vs calculation.

TABLE 6: Comparison of Experimental and Calculated Δ*H* values for A_3, A_2B, AB_2, and B_3 Formation Comparing Z = H and Z = OCH_3[a]

	ΔH°_{soln} (kJ/mol)	
	exptl[b]	calcd
A_3	18 ± 2	21.2
A_2B	14 ± 5	19.5
AB_2	12 ± 2	18.3
B_3	11 ± 2	15.7

[a] Note the energies are in kJ/mol. [b] Values from ref 13.

Heterotrimers with No Pendant Groups. If no Lewis base is present, the formation of boroxine from monomeric boronic acids is unfavorable, and the equilibrium lies toward the monomers. If a mixture of monomers is present, the enthalpy of boroxine formation simply follows the additive nature of the para-substituent. The observed results are expected based on our previous work[24] and also that observed by Tokunaga et al.[13,44] Table 5 shows a subset of our calculations for formation of boroxine from three monomers that do not contain pendant groups (only the para-substituent Z varies). We find that in the absence of Lewis base, electron-donating substituents are less endothermic for boroxine formation, whereas electron-withdrawing substituents are more endothermic.

Very recent ^{1}H NMR experiments by Tokunaga et al. determined the separate thermodynamic parameters of the boronic acid−boroxine equilibrium mixture.[13] Although we did not choose the same monomers, the closest system in their work compared to ours is shown in Figure 5. Tokunaga's binary mixture of boronic acid monomers is very similar to our system with the exception of the additional methyl substituents in the meta-positions. Since methyl is mildly electron-donating, we expect the experimental Δ*H* for trimer formation to be slightly less endothermic compared to our calculated results. Since the experimental numbers and error bars were reported in kilojoules per mole, we have converted our numbers and included them in a side-to-side comparison in Table 6. There is very good agreement between the two values taking into account that our calculated structures are missing the *m*-methyl substituents.

Conclusion

From our DFT calculations, we find that heterotrimeric arylboroxines can be favorably formed when one of the arylboronic acid monomers contains an internal pendant Lewis base. When A and B are monomeric boronic acids with and without a pendant Lewis base, respectively, we found that AB_2 boroxines were thermodynamically favored over A_2B, A_3, or B_3. The most stable AB_2 trimers were formed when the B monomer contained electron-withdrawing substituents, particularly halogens in the para-position or π-acceptors in the meta-position. Adding different para-substituents to the A monomer, however, did not significantly change the energetics of boroxine construction. Adding a methylene spacer in the pendant group contributed to further enthalpic stabilization of AB_2 (but at an entropic cost), whereas replacing the nitrogen with oxygen disfavored intramolecular adduct formation. Our calculations also suggest that ABC trimers cannot be selectively accessed over AB_2 trimers simply by changing the electronic properties of monosubstituted arylboronic acid monomers. In the absence of a Lewis base, boroxine formation is endothermic; however, we do find good agreement between our calculated results and experimental measurements for Δ*H*.

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