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Formation of Para-Substituted Triphenylboroxines: A Computational Study

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Density functional theory (B3LYP//6-311+G*) calculations including Poisson−Boltzmann (PB) implicit solvent were applied to study the relative stability of triphenylboroxine $(PhBO)_3$ with respect to its phenylboronic acid monomers. In solution, formation of $(PhBO)_3$ is thermodynamically unfavorable; however, addition of an amine base results in the formation of stable 1:1 adducts of $(PhBO)_3$ and amine. Formation of 1:2 adducts is energetically unfavorable. We find that adduct formation is more exothermic than cleavage of the boroxine ring back to its monomers. π-Electron-withdrawing groups in the para-position of the phenyl ring destabilize the boroxine ring with respect to its monomers. However, para-substituents that are net electron-withdrawing are found to stabilize formation of the 1:1 adduct.

Introduction

Boroxines are the dehydration product of organoboronic acids. Boroxines have found commercial use in such diverse areas as flame retardant materials,[1] dopants that enhance lithium ion transference in polymer electrolytes,[2−4] and recently as boronic acid alternatives in Suzuki−Miyaura coupling reactions.[5] Alcaraz et al. has also investigated boroxine-based compounds as nonlinear optical materials.[6]

It is well-known that boroxines form isolatable adducts with many nitrogen donor compounds including amines,[7−11] pyridines,[12] hydrazines,[13] azaindoles,[14] and even salen type ligands.[15] At room temperature, amine and pyridine type ligands are in fast exchange and NMR spectra are therefore time averaged. Activation parameters for several different ligands have been experimentally established.[16]

In contrast to the ligand exchange kinetics, there are few studies delineating the thermodynamics of the two-step reaction sequence:[17] boroxine construction from monomeric boronic acids (Step 1, Figure 1) and subsequent boroxine complexation by nitrogen donor compounds (Step 2, Figure 1). This computational study examines the thermodynamics of both reaction steps individually. From these individual results we are able to draw some general conclusions regarding the overall energetics of an equilibrating mixture of boronic acid, boroxine, and ligand.

As our starting point, we examined a series of para-substituted phenylboronic acids in equilibrium with their corresponding boroxines. Several of the para-substituents were chosen to parallel experimental data published by Tokunaga et al. in which they studied the impact of electron-donating or electron-withdrawing groups on the equilibrium constants.[17] Good agreement was found between experimental trends in boroxine formation constants and our computational results.

We then turned our attention to boroxine ligation (Step 2, Figure 1). Curiously, the vast majority of known solid-state structures are 1:1 adducts.[9,10,14,16,18,19] There are several examples of difunctional ligands generating 2:3 boroxine:ligand complexes, but in these cases, two of the ligands are filling space not actually binding.[9] The preponderance of 1:1 stoichiometries begs the question: Why is the 1:1 complex favored over any other stoichiometric permutation? Beckmann et al. have postulated that binding one ligand (and not two or three) affords the largest reduction in boroxine ring strain.[19] Our calculations do not support this hypothesis fully and point to the sensitivity of calculation on a suitable choice of model compound.

Last, it is worthwhile to make some conclusions regarding the overall thermodynamics of the two-step reaction sequence. Is the energetic favorability of the ligand binding (Step 2) large enough to counteract the unfavorable nature of the boroxine ring construction (Step 1)? Can one reliably generate, in high yield, boroxine complexes starting from a mixture of monomeric boronic acid and ligand? As we begin to explore functional materials derived from organoboroxines, a full understanding of the solution-state properties will be important.

We have applied density functional theory (DFT) at the B3LYP//6-311+G* level including Poisson−Boltzmann (PB) implicit solvent for all our calculations. The layout of the paper is as follows. After the section on computational methods, we discuss the choice of model system used to support the ring strain argument proposed by Beckmann et al.[19] We then present the results of our calculations for the two equilibrium steps and the effect of different para-substituents (X = H, CH_3, Cl, OMe, CF_3, CHO, $C(O)CH_3$, $SiMe_3$) on the relative stabilities of the boronic acid, boroxine, and 1:1 adducts of boroxine•NH_3. Finally, we present results investigating the effects of replacing NH_3 with pyridine, and the relative energetics for forming 1:2 adducts with $(PhBO)_3$.

Computational Methods

All calculations were carried out using Jaguar 5.5[20] at the B3LYP[21−24] 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 as Beckmann et al.[19] as to facilitate comparative analysis. The electronic energy of the optimized gas-phase structures is designated E_{elec}. The PB continuum approximation[25,26] 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

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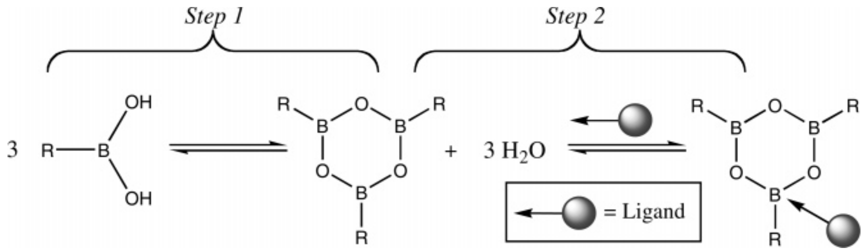


Figure 1. Two-step reaction sequence of boroxine construction followed by adduct formation.

polarizable continuum surrounding the molecule with dielectric constant ϵ. For water as a solvent we used the default Jaguar 5.5 values of $\epsilon = 80.37$ and $R_{\mathrm{solv}} = 1.40$ Å for the dielectric constant and probe radius, respectively. 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. This is because there is little change between the gas-phase and implicit solvent-optimized geometries. The difference in energy between the unsolvated and solvated structures is designated E_{solv}. It is important to note that in these calculations, water as an implicit solvent is *nonreactive*. We chose to use water because the implicit solvent parameters are well tested in the Jaguar program.[27]

The analytical Hessian was calculated at each optimized geometry in the gas phase. The DFT gas-phase energies are then corrected for zero-point vibrations. 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 enthalpy differences are calculated, and that the vibrational frequencies do not change appreciably in solution, we can calculate $H_{298\mathrm{K}}$. The sum of the zero point energy and enthalpy corrections to 298 K are collectively designated E_{corr}. The calculated values of E_{elec}, E_{solv} and E_{corr} are available in the Supporting Information. The corresponding free-energy corrections in solution are much less reliable.[28,29] 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 solvent (water) participates in the reaction and is present in much higher concentration than the other species in solution. Furthermore, because 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.

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. Even though the solvation energy 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 in our results and discussion.

Previous Computational Work on Ring Strain

Previous computational work on boroxines has focused on the aromaticity, localization of electron pairs, and ionicity of the B−O bonds in the ring. These studies are referenced by Beckmann et al.[19] To our knowledge, only the study by Beckmann et al. has addressed the question of adduct formation computationally.

Two of the questions that Beckmann et al. aim to answer are (1) why $(\mathrm{RBO})_3$ rings are susceptible to cleavage compared to their 1:1 amine adducts and (2) why addition of amines to $(\mathrm{RBO})_3$ rarely proceeds beyond 1:1 stoichiometry. Both arguments hinge on how much the B−O−B and O−B−O angles in the ring differ from their ideal "unstrained" or "unconstrained" counterparts. To find these ideal angles, calculations at the B3LYP//6-311+G* level were performed on $\mathrm{O(BH_2)_2}$ and $\mathrm{HB(OH)_2}$ respectively. The ideal angles were found to be ∼125° in both cases. Relaxed potential energy (PE) scans were used to map the "energy cost" of deviating from the ideal angle. Based on the *experimental* bond angles of $(\mathrm{PhBO})_3$, the total strain energy was determined to be 19.5 kJ/mol on the basis of the PE scan. In the adduct $(\mathrm{PhBO})_3$·pyr, there is a *net increase* for five out of the six angles (the exception being the O−B−O angle of the tetrahedral B). Because the ideal angle being compared to is 125°, the result is a reduction of ring strain from 14.7 to 8.7 kJ/mol on the basis of the PE scan. This decrease in strain energy is used to explain why the 1:1 amine adduct is less susceptible to cleavage. No quantification is made of the energy cost in the reduction of the O−B−O angle (down to 113.3°) of the tetrahedral B. It may have been excluded because of the tetrahedral nature of the B. This would require some justification because it is part of the ring. A better treatment might be to compare this angle to a reference compound such as $\mathrm{HB(OH)_2(NH_3)}$, keeping in line with the model hydrides. We calculated this compound to have an O−B−O angle of 113.6°, so perhaps the justification may be that there is little contribution to the ring strain from the tetrahedral B.

To explain the observation of 1:1 preferred stoichiometry in the amine adduct, the authors claim that 1:2 and 1:3 adducts would "necessitate a decrease in the corresponding O−B−O angles and may not be feasible because this would force an unfavorable widening of B−O−B angles". It would have to depend on how much the angles would widen (e.g., strain would actually be relieved if the B−O−B angles widened from a number lower than the ideal up to the ideal). No numbers were used to support it even though PE scans were done.

The problem with the ring strain argument is that if the H attached to B in $\mathrm{O(BH_2)_2}$ and $\mathrm{HB(OH)_2}$ is replaced by a carbon-containing group, the reference B−O−B and O−B−O "unstrained" angles change significantly. Because the boroxine of interest is $(\mathrm{PhBO})_3$ rather than $(\mathrm{HBO})_3$, the corresponding boronic acid model used should have been phenylboronic acid, or at least methylboronic acid. We repeated the calculations of the model compounds chosen by Beckmann et al., at the same

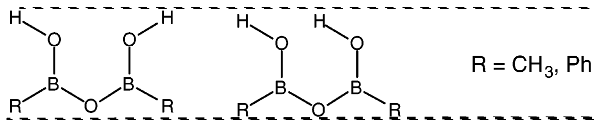


Figure 2. Reference compounds for the B−O−B angle.

level of theory and basis set, but replaced the H with CH_3 and Ph. Although the optimized O−B−O angle in $HB(OH)_2$ is 125.8° in agreement with the previous work, the optimized angles decrease to 116.5° and 116.7° for $CH_3B(OH)_2$ and $PhB(OH)_2$. The optimized B−O−B angle in $O(BH_2)_2$ is also 125.8° in agreement with the previous work, but when the following model compounds shown in Figure 2 are used, the optimized angles increase to an average of 133°. If no hydrogen bond is formed between the hydroxyl groups, the optimized B−O−B angles are 136.1° and 135.4° for CH_3 and Ph, respectively. If a hydrogen bond is formed, these angles are 131.3° and 130.8°. We also calculated the O−B−O angle to be 115.7 and 114.3° in the model compounds $(CH_3)B(OH)_2(NH_3)$ and $PhB(OH)_2(NH_3)$, representing the unstrained tetrahedral B. These angles are quite close to the crystallographic 113.3° O−B−O angle for the tetrahedral B in the $(PhBO_3)$·pyr adduct.

The ring strain argument is predicated on the following. From the more precise of two sources of crystallographic data,[30,31] the O−B−O and B−O−B angles of $(PhBO)_3$ are 119.3° and 120.3°, respectively. (Our calculated angles are quite close: 118.5° and 121.5°, respectively.) Note that these angles are 5−6° below the "ideal" reference angle of 125°. Upon binding of pyridine to form the 1:1 adduct, there is an overall increase in five of the six bond angles, not counting the tetrahedral B (where the O−B−O angle decreases to 113.1°) according to crystallographic data. The result is that these five angles are now in the 120−122° range and thus closer to the ideal of 125°. This is interpreted as a decrease in strain energy, quantified by the PE scan as 6.0 kJ/mol.

Because ring strain is defined with reference to ideal unstrained reference compounds, the choice of the reference compound becomes a very important factor. Because the compounds being studied are organoboroxines where R ≠ H, we think that the reference compounds incorporating the methyl group are a better choice. Now, on the basis of the crystallographic data, it is no longer clear that the overall increase in the five bond angles (excluding tetrahedral B) will lead to an overall decrease in strain energy. Though increasing the B−O−B angle brings it closer to the ideal, increasing the O−B−O angle brings it further away from the ideal. The two nontetrahedral O−B−O bond angles from the crystallographic data of the 1:1 adduct are 120.7 and 122.4°. The three B−O−B angles are 122.4, 121.3, and 119.2°. Recall that in $(PhBO)_3$ the crystallographic angles for O−B−O and B−O−B were 119.3 and 120.3°, respectively. Therefore three out of the five angles are moving away from the ideal while two are moving toward the ideal. The sixth angle for the tetrahedral B remains close to the ideal.

On the basis of the different ideal "unstrained" angles from our proposed model compounds, though we do not discount that some release of ring strain may have a stabilizing effect on the 1:1 adduct, we think that ring strain may be a less important effect than previously suggested. Although no crystallographic data were found for the 1:2 adduct, we calculated the O−B−O and B−O−B angles in $(PhBO_3)$·2pyr. We considered both possible adducts with two pyridines bound to the same face or to opposite faces of the ring. The nontetrahedral angles are all between 121.1 and 123.1° and the tetrahedral O−B−O angles have a range of 116.0−116.7°. Because these angles are close to those found in the 1:1 adduct, we think ring strain does not play a major role in determining the lower stability of the 1:2 adduct.

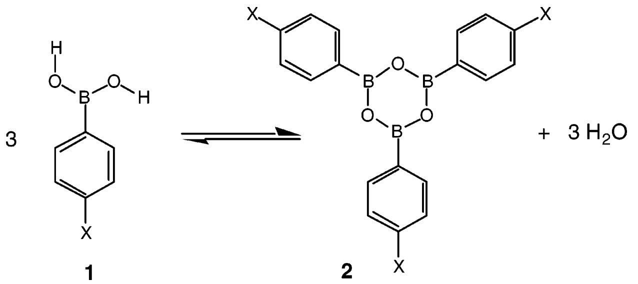


Figure 3. Formation of triphenylboroxine from the trimerization of phenylboronic acid.

TABLE 1: Energetics of Boroxine Trimer Formation

X	ΔE_{elec} 1(kcal/mol)	ΔE_{corr} (kcal/mol)	ΔE_{solv} (kcal/mol)	ΔH (kcal/mol)
OMe	12.45	−2.76	−3.67	6.02
Cl	12.91	−3.90	−3.63	5.38
CH_3	13.11	−4.55	−3.53	5.03
H	13.21	−2.74	−3.68	6.79
$SiMe_3$	13.51	−1.01	−3.82	8.68
CF_3	14.58	−2.78	−4.17	7.63
$C(O)CH_3$	14.67	−1.00	−4.17	9.50
CHO	14.76	−1.01	−4.03	9.72

Results and Discussion

Equilibrium between Boronic Acid Monomers and Boroxine Trimer. The trimerization of phenylboronic acid (**1**) to form triphenylboroxine (**2**) is shown in Figure 3. The equilibrium generally lies to the left; i.e., formation of the trimer is disfavored.

Calculated energies for the trimerization of boronic acid monomers are compiled in Table 1. The results are sorted by magnitude of ΔE_{elec}. The solution-phase enthalpy for trimerization is given by $\Delta H = \Delta E_{elec} + \Delta E_{corr} + \Delta E_{solv}$, where ΔE_{elec} is the change in electronic energy, ΔE_{corr} is the change in energy when zero point energy and enthalpy corrections to 298 K are taken into account, and ΔE_{solv} is the change in solvation energy.

All ΔE_{elec} values are positive for the trimerization. Substituents in the para-position of the phenyl ring that are electron-withdrawing in the π-system (CHO and $C(O)CH_3$) have ΔE_{elec} values that are more positive (14.76 and 14.67 kcal/mol, respectively) than that for H (13.21 kcal/mol). The CF_3 substituent is strongly electron-withdrawing in the σ-framework. Its effect in the π-system, via hyperconjugation of the F atoms, is expected to be smaller because the F atoms have low polarizability and are not directly connected to the ring. ΔE_{elec} for CF_3 is calculated to be 14.58 kcal/mol. $SiMe_3$ is not expected to have much effect on the electronic properties of the system; as ΔE_{elec} is 13.51 kcal/mol, it may be mildly electron-withdrawing. Because ring cleavage of the trimer (the reverse reaction in the equilibrium) begins with water donating its lone pair into the p-orbital of B perpendicular to the plane of the ring, it is no surprise that electron-withdrawing substituents destabilize the trimer. The effect is most dramatic when the electron-withdrawing substituent acts through the π-system.

On the basis of the argument above, electron-donating groups are expected to stabilize the boroxine ring, particularly if they can do so through the π-system. This is true of both Cl and OMe with ΔE_{elec} values that are less positive (12.91 and 12.45

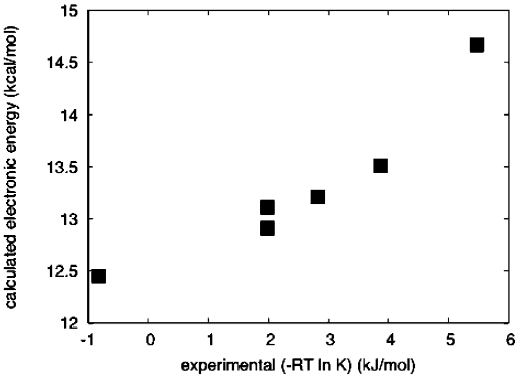
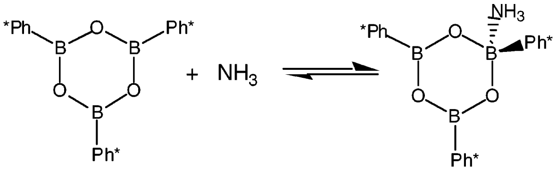


Figure 4. Relative comparison of calculated ΔE_{elec} and experimental $-RT \ln K_{\text{eq}}$ for trimerization.



2 **3**

Figure 5. Formation of the triphenylboroxine:ammonia adduct.

kcal/mol, respectively) compared to the value for H. OMe is generally classified as an electron-donating group and the O atom can certainly donate electron density into the π-system. Although Cl is generally considered an electron-withdrawing group, it is electron-withdrawing via the σ-framework but electron-donating via the π-system. CH_3, which is electron-donating through the σ-framework, and perhaps very mildly through the π-system via hyperconjugation, also has a less positive ΔE_{elec} value of 13.11 kcal/mol compared to that for H.

Zero point energy and thermal enthalpic corrections decrease the energy gap between reactants and products. Solvation energies also favor trimerization. After taking these into account, all the solution-phase enthalpy ΔH values are still positive. If the different substituents were ordered from least to most endothermic, there are some changes in the order comparing ΔH and ΔE_{elec}; however, none of them change qualitatively in comparison to the values for H. A substituent with ΔE_{elec} more positive than that for H also has ΔH more positive than H and vice versa. ΔS is also positive because three molecules of water are released per trimerization; thus $-T\Delta S$ is negative.

The equilibrium constant in Figure 3 has been measured via NMR spectroscopy (in $CDCl_3$) by Tokunaga et al. for six out of the eight cases we have studied.[17] CF_3 and CHO were not included in the experimental study. Because we have not calculated free energies in solution, our calculated energies are not directly comparable to experimental values. However, it is encouraging that the trends we observe in terms of the electron-donating and -withdrawing capability of different substituents are in good agreement with experiment. Figure 4 compares our calculated ΔE_{elec} values with $-RT \ln K_{\text{eq}}$ from experiment. In particular, we find that the π-donating capability of Cl is more important than its σ-withdrawing ability. The same is observed in experiment; i.e., Cl has a higher equilibrium constant than H.

Formation of 1:1 Boroxine·Amine Adducts. The reaction between triphenylboroxine and NH_3 to form a 1:1 adduct is shown in Figure 5 where Ph* indicates a para-substituted phenyl group. The equilibrium generally lies to the right, i.e., formation of the 1:1 adduct is favored.

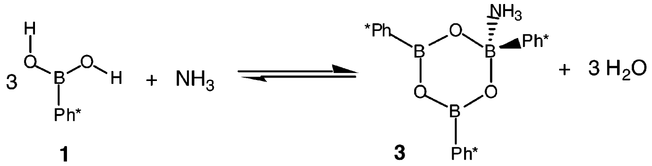


Figure 6. Net reaction for forming 1:1 adduct from boronic acid monomers when NH_3 is present.

TABLE 2: Energetics of 1:1 Adduct Formation

X	ΔE_{elec} (kcal/mol)	ΔE_{corr} (kcal/mol)	ΔE_{solv} (kcal/mol)	ΔH (kcal/mol)
OMe	−4.46	2.10	−3.81	−6.17
CH_3	−5.60	2.22	−2.96	−6.34
$SiMe_3$	−6.40	2.23	−4.16	−8.33
H	−6.45	2.20	−4.34	−8.59
Cl	−7.51	2.29	−4.89	−10.11
C(O)CH_3	−8.63	2.29	−5.40	−11.74
CHO	−9.53	2.33	−5.62	−12.82
CF_3	−9.78	1.79	−4.80	−12.79

In the adduct, the “tetrahedral” B has a calculated O−B−O angle of 115.0°, the two N−B−O angles are 102.7°, and the N−B−C angle is 105.0°. The B_3O_3 boroxine ring remains relatively planar. Calculated ΔH values for the addition of ammonia to **2** to form the adduct **3** are shown in Table 2. ΔH is partitioned into contributions from electronic energies, zero point energies and thermal corrections, and solvation energies, in the same way as discussed for Table 1.

All ΔE_{elec} values are negative for formation of the adduct. There is little difference in ΔE_{elec} (or ΔH for that matter) for the $SiMe_3$ substituent compared to H. The electron-donating groups, CH_3 and OCH_3, have ΔE_{elec} less negative (−5.60 and −4.46 kcal/mol, respectively) than the value for H (−6.45 kcal/mol). This is not surprising because electron-donating groups are expected to destabilize the buildup of negative charge on the B due to dative covalent bonding from the lone pair in ammonia. The distinction between σ and π effects is not important once the adduct is formed from a thermodynamic standpoint (although it is expected to have an effect on the kinetics). Hence, we see that Cl does act primarily in its electron-withdrawing capacity, stabilizing the buildup of negative charge on B. Its ΔE_{elec} value is more negative (−7.51 kcal/mol) than for H. The same is true for the other electron-withdrawing groups: CF_3, CHO, and C(O)CH_3.

ΔE_{corr} is positive because zero point energy corrections are positive (and larger than the thermal enthalpic correction) for adduct formation. Solvation energies favor adduct formation. The net result is that all ΔH values are negative. As observed for the trimerization equilibrium above, there are some minor differences in the order when ΔH and ΔE_{elec} are compared; however, none of them change qualitatively in comparison to H. Once again we see that a substituent with ΔE_{elec} more negative than H also has ΔH more negative than H and vice versa. Note that ΔS is negative for adduct formation; thus, $-T\Delta S$ will be positive.

In all eight cases, the exothermic ΔH for adduct formation is larger in magnitude than the endothermic ΔH for trimerization; i.e., the second equilibrium lies further to the right than the first equilibrium lies to the left. This overall net reaction is shown in Figure 6. The sum of the two ΔH values is shown in Table 3.

The net ΔH values are all negative. Our results suggest that formation of the boroxine·NH_3 adduct is stable with respect to a solution of boronic acid monomers and free NH_3 in solution. Because the number of moles of reactants and products are equal

TABLE 3: Net Δ*H* for Formation of 1:1 Adduct from Boronic Acid Monomers When NH_3 Is Present

R	net Δ*H* (kcal/mol)
OMe	−0.15
$SiMe_3$	−0.35
CH_3	−1.31
H	−1.80
$C(O)CH_3$	−2.24
CHO	−3.10
Cl	−4.73
CF_3	−5.16

in this net reaction, the entropic terms cancel out to some extent (although not necessarily completely). Hence, for this net reaction, we expect a closer correspondence between our calculated Δ*H* values and experimentally measured equilibrium constants. There are no experimental measurements for these thermodynamic data to our knowledge.[27] Note, however, that the net Δ*H* values are also much smaller; therefore even small differences in the entropic terms may contribute more significantly.

The most exothermic net Δ*H* values come from the σ-framework electron-withdrawing substituents (CF_3 and Cl), although the other electron-withdrawing substituents (CHO and $C(O)CH_3$) are also more exothermic than H. The electron-donating substituents (and $SiMe_3$) have net Δ*H* values less exothermic than H. Because some of these latter values are close to zero, using a different solvent may tip the balance in favor of the boronic acid monomers over the 1:1 adduct.

Formation of 1:2 Adducts. Two possible 1:2 adducts can be formed. The second NH_3 can be added to the same face on the same boroxine as the first NH_3, or it can be added to the opposite face. The net reactions for 1:2 adduct formation are shown in Figure 7. If both NH_3 molecules attach to the same face (**4a**), the boroxine ring puckers on the NH_3-bound side of the ring. If NH_3 attaches to opposite faces (**4b**), the ring remains relatively planar.

Relative energies for forming the 1:2 adducts are compiled in Table 4. ΔE_{elec} for binding two NH_3 to the same face is −4.10 kcal/mol (or an average of −2.05 kcal/mol per NH_3). To the opposite face, $\Delta E_{\mathrm{elec}} = -8.69$ kcal/mol (or −4.35 kcal/mol per NH_3). This suggests that **4b** is more stable than **4a** in terms of gas-phase binding. Solvation, however, favors **4a** over **4b** because binding two NH_3 molecules to the same face results in a more polar adduct. The net result is that $\Delta H = -5.43$ and −5.23 kcal/mol for the formation of **4a** and **4b**, respectively, from boroxine. This is less exothermic than forming the 1:1 adduct ($\Delta H = -8.59$ kcal/mol); i.e., the 1:2 adduct is less stable than the 1:1 adduct. (Loss in entropy would further destabilize the 1:2 adduct.) In addition, because the formation of boroxine from boronic acid monomers has $\Delta H = +6.79$ kcal/mol, we expect that formation of the 1:2 adduct is thermodynamically disfavored and is expected not to be observed in solution, except perhaps when a huge excess of ligand is present.

Substituting Pyridine as the Amine Base. If pyridine is used as the amine base instead of NH_3, $\Delta H = -7.18$ kcal/mol for formation of the 1:1 adduct. Pyridine does not bind as strongly to boroxine compared to NH_3; however, it still stabilizes the 1:1 adduct with respect to monomers and free base in solution. Binding two pyridine molecules is clearly unfavorable. The structures of the 1:2 adducts with pyridine are similar to those with NH_3. The same trends are observed; i.e., binding to the same face is less stable but has favorable ΔE_{solv} compared to binding to opposite faces. ΔE_{solv} is clearly unfavorable for the hydrophobic pyridine adducts leading to positive Δ*H* values.

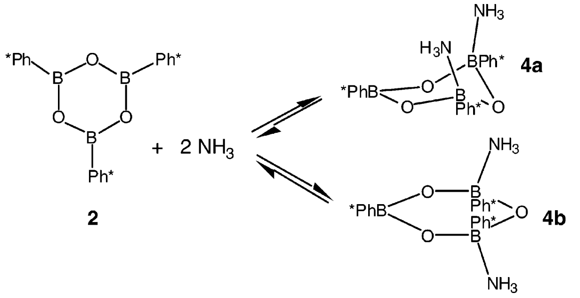


Figure 7. Net reaction for 1:2 adduct formation.

TABLE 4: Formation of 1:1 and 1:2 Adducts between Boroxine and NH_3 or Pyridine

amine	ΔE_{elec} (kcal/mol)	ΔU_{corr} (kcal/mol)	ΔE_{solv} (kcal/mol)	Δ*H* (kcal/mol)
NH_3	−6.45	2.20	−4.34	−8.59
2 NH_3 (fac)	−4.10	4.00	−5.33	−5.43
2 NH_3 (opp)	−8.69	3.44	+0.02	−5.23
pyr	−4.51	1.10	−3.97	−7.18
2 pyr (fac)	0.36	1.62	12.34	14.32
2 pyr (opp)	−4.56	2.45	16.41	14.30

Conclusions

From our DFT calculations we find that the trimerization of phenylboronic acids to form boroxine rings is thermodynamically unfavorable. The formation of stable 1:1 adducts, but not 1:2 adducts, in the presence of amine, however, is found to be highly favorable. These two observations are in good agreement with experimental results. In addition, we find that substitution of π-electron-withdrawing groups in the para-position of the phenyl ring further destabilizes the trimer with respect to its monomers, whereas the opposite is observed from π-electron-donors. To form the adduct, we find that net electron-withdrawing and electron-donating ability of the para-substituents is important in stabilizing or destabilizing the boron that binds the amine.

We are in the process of identifying key intermediates in the equilibrium mixture of boronic acids, boroxines, amine, and adducts via both NMR spectroscopy and further calculations. These calculations will include studying the effects of different solvents and determining activation energy barriers between intermediates.

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Supporting Information Available: Calculated values of E_{elec}, E_{solv} and E_{corr}, and Cartesian coordinates of all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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