Experimental Work Guided by Computational Results: Reactions of Boronic Acids and Amines Give Structurally-Diverse B←N Adducts

Marina Juribašić Kulcsár and Mario Pajić

Marina.Juribasic@irb.hr

Ruđer Bošković Institute, Division of Physical Chemistry, Bijenička cesta 54, HR-10000 Zagreb, Croatia

Boronic acids $(RB(OH)_2, R \text{ is aryl or alkyl})$ are important building blocks employed from organic synthesis, materials science to medicine [1]. Boroxines $(RBO)_3$, cyclotrimeric anhydrides of boronic acids, are formed by a reversible entropically-favorable dehydration of boronic acids [1]. Boron atoms in boroxines are Lewis acidic sites with a high affinity toward amines [2]. Synthesis of stable boroxine-amine adducts proceeds *via* ligand-facilitated trimerization [2]. The boronic acid first gives the corresponding boroxine, which reacts with the ligand (amine) usually forming one dative boron-nitrogen (B \leftarrow N) bond, *i.e.* an adduct A31, Figure 1.

Herein, we describe a computational analysis of the structure, stability and spectra of $B \leftarrow N$ adducts of the phenylboronic acid (PBA) and a series of amines, Figure 1 [3]. Calculations guided the experimental work toward a successful isolation of adducts A31, A32 and/or A61 depending on the amine structure. Competitive binding experiments indicated that the exchange of the amines in adducts A31 follows the computed adduct stabilities that increase with the amine basicity. Following the DFT prediction, the first adduct with two different amines, DMAP and pip, bound to one boroxine moiety was isolated and structurally characterized. The correlation of the calculated stabilities of adducts with pK_a values suggests that amines with pK_a larger than about 8 could form both A31 and A32 adducts. Less basic amines with pK_a lower than 8 would form only adducts A31. Results show that calculations can be used to predict possible and preferred product(s) and their spectral characteristics.





References:

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