

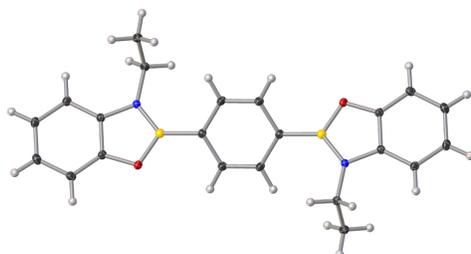
56004-UNII

Benzodiazaboroles as Potential Dynamic Covalent Functional Groups for New Molecular Architectures  
Dustin E. Gross, Department of Chemistry, Sam Houston State University

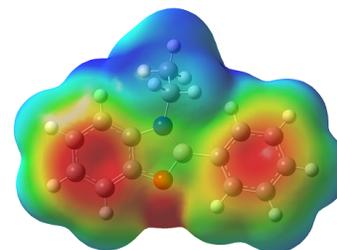
In the last year, we have continued to investigate nitrogen containing boronate ester-based derivatives. Specifically, we have wrapped up our project on the  $\text{BF}_3 \cdot \text{OEt}_2$  catalyzed interchange of boronate esters, characterized newly synthesized benzoxazaboroles and benzodiazaboroles, continued to investigate diazaborole based macrocycles, and furthered our knowledge regarding the kinetics and thermodynamics of boronate ester derivative interchange.

*Boronate ester interchange:* At the beginning of the most recent funding year, we wrapped up and published our work on the transesterification of boronate esters with selected diols using  $\text{BF}_3 \cdot \text{OEt}_2$  as a catalyst.

*Benzoxazaboroles and benzodiazaboroles:* We have taken previously synthesized benzoxazaboroles and characterized them using UV-vis and fluorescence spectroscopies, computations, and X-ray crystallography to provide further structural information for several benzoxazaborole derivatives.

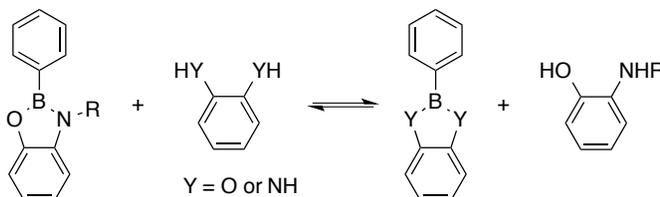


X-ray crystal structure of 1,4-phenylene-bis-[3-(ethyl)benzoxazaborole]

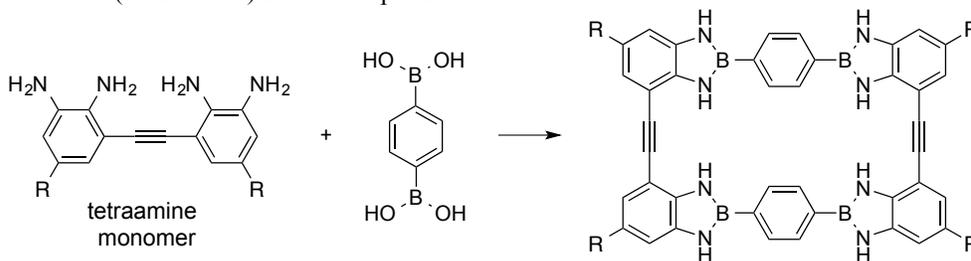


Electrostatic potential map of 2-ethyl-3-phenylbenzoxazaborole

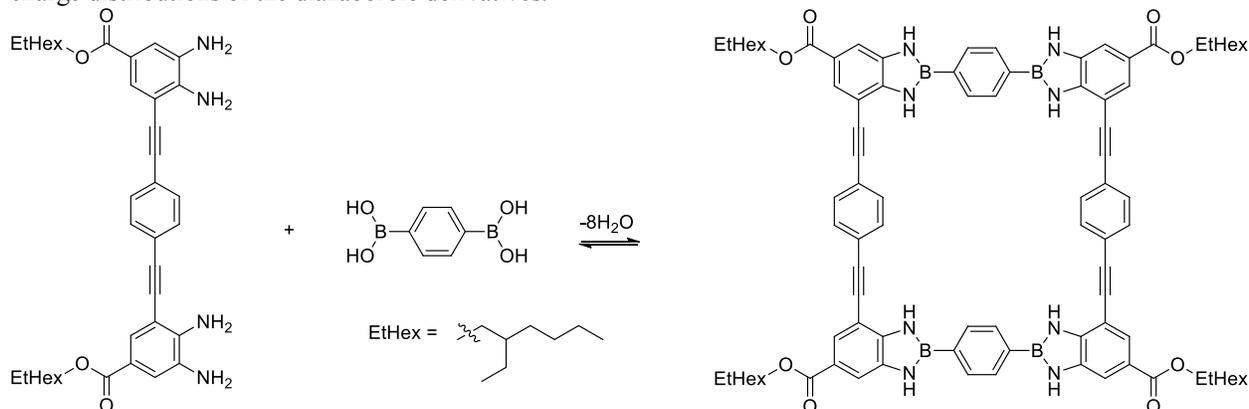
Previously, our research group has explored the preliminary synthesis and characterization of several benzoxazaboroles. In the current work, we have synthesized several new benzoxazaboroles using 2-(alkylamino)phenols and phenylboronic acid derivatives. bis(Benzoxazaborole)s were synthesized using 2-aminophenol or 2-(alkylamino)phenols and diboronic acids. Characterization of benzoxazaboroles and bis(benzoxazaborole)s was carried out using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-visible, and fluorescence spectroscopic methods. X-ray crystallographic analysis was also used for structural identification. Furthermore, dynamic covalent exchange reactions were conducted with 3-(alkyl)benzoxazaboroles and benzodioxaboroles to determine equilibrium constants and Gibbs free energy values for the benzoxazaborole exchange reactions. Specifically, solution studies concerning the dynamic covalent nature of the oxazaboroles and the relative stability compared to the well-established benzodioxaboroles were carried out using  $^1\text{H}$  NMR in  $\text{CDCl}_3$ . The results of these studies revealed that oxazaboroles exhibit dynamic covalent nature. The reaction with dioxaborole ( $\text{Y} = \text{O}$ ) reached a seemingly steady state much faster than diazaborole ( $\text{Y} = \text{NH}$ ) (<5 min versus 7 d, respectively). Additionally, the stability of benzoxazaborole was also found to be similar to benzodioxaboroles and about an order of magnitude more stable than benzodiazaboroles. Finally, computational calculations of benzoxazaboroles and bis(benzoxazaborole)s were utilized to support and add to the experimental results. This includes calculations of bond lengths, HOMO-LUMO energies, and Gibbs free energy values for benzoxazaborole exchange reactions.



*Diazaborole-based macrocycles:* We have now synthesized several rectangular shaped diazaborole-based macrocycles from a tetraamine monomers having methyl groups, triethylene glycol ester [ $\text{R} = \text{CO}_2\text{Tg}$ ,  $\text{Tg} = -(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ ] or ethylhexyl ester side chains and bis(boronic acid)s. Solubility continues to be a limitation on the synthesis and characterization of oligomeric/macrocylic products. We have also investigated an expanded system and several bis(diazaborole) model compounds.



An expanded macrocycle has been synthesized by incorporating an additional phenylene ethynylene linker into the tetraamine monomer. In addition to the synthetic work these systems have undergone computational analysis of along with various diazaborole-containing molecules. The primary objective of this study was to obtain further understanding of the molecular geometry, the electronic properties, HOMO-LUMO energy differences, and electronic charge distributions of the diazaborole derivatives.



*Impact on students:* Over the last year, two Master's students and six undergraduate students have contributed to the above described work. These students have gained experience with synthesis and characterization. Specifically, students have become proficient at NMR, IR, Raman, UV-vis, X-ray crystallography, and computational chemistry. Their work was presented at the ACS Southwest Regional Meeting (3 poster presentations). PRF funds were used to support student travel. We have also submitted three abstracts to the upcoming ACS Southwest Regional Meeting. Two of the Master's students have graduated and one is now enrolled in a PhD program in chemistry. Two of the undergraduate students have graduated, one of which is now enrolled in a PhD program in chemistry. One of them presented at the undergraduate research symposium, graduated with honors, and completed an undergraduate thesis based on research supported by this grant. The funds from this grant have also been used to support one graduate and two undergraduate students over the summer and two undergraduate students during the fall and spring semesters. The other students that were involved in these projects were supported through our Welch summer research program.