# DIAZABOROLES: EXPERIMENTAL INVESTIGATIONS OF THEIR DYNAMIC COVALENT NATURE AND COMPUTATIONAL CHEMISTRY 

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by
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## DEDICATION

To my wife, parents, brothers and sister.


#### Abstract

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Diazaboroles have interesting optical and electronic properties. They are soluble in many organic solvents, electrochemically active, and thermally stable. The understanding of diazaboroles' dynamic covalent behavior is important for the synthesis and incorporation in complex molecular architectures like fully p-conjugated, noncollapsible, and shape-persistent macromolecules.

The present study involves the influence of solvent on diazaborole formation and its dynamic covalent behavior under various conditions. XRD structural determination was carried out for structural identification of diazaborole; moreover, computational calculations were used to compare experimental and theoretical results.

The investigation of the solvent effect on diazaborole formation is important when synthesizing more complex diazaborole based molecular architectures. Therefore, the effect of the solvent on diazaborole formation was investigated and identified that only solvent evaporation time was sufficient to obtain greater diazaborole formation in high boiling solvents. Even though high reaction temperature leads to high diazaborole production, the functional groups of the solvents show less impact on the reaction.

The reversibility of diazaborole formation was examined by considering diazaborole transamidation and exchange reactions with different diazaborole substituents. The results illustrate that transamidation reactions of diazaboroles are reversible.


Computational calculations reveal the bond angle and bond length deviation of diazaborole isostructures (analogues). Further, electrostatic potential maps disclose the existence of an electron rich phenyl ring in diazaborole. The Gibbs free energy values of diazaborole formation in the solvent phase reveal the reaction favorability of diazaborole formation in some solvents under appropriate conditions.

KEY WORDS: Diazaborole, Solvent effect, Computational chemistry, Dynamic covalent chemistry

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## CHAPTER I

## Introduction

### 1.2 Molecular Architectures

Porous solids (amorphous or crystalline) are widely spread around the world and have found use in many applications. A crystalline solid can be identified as a complex structure that grows from basic structural units called "unit cells". These unit cells assemble to make complex or regular structures called "molecular architectures". Exploration of crystalline porous solids has gained significant interest due to their wide variety of uses in gas storage, catalysis, molecular sensing, host materials for drug distribution and molecular separation, and gas and water purification.

Porous solids in nature are primarily classified into two categories, amorphous or crystalline, according to their structural orientation and atomic distribution. Amorphous solids have an irregular structure, which makes their properties difficult to reproduce and/or characterize. In contrast, crystalline solids exhibit well-ordered microscopic pores, well-defined pore structure, and topology, reproducible patterns, high mechanical and thermal stability, and easy characterization. ${ }^{1}$

Zeolites are naturally occurring porous inorganic solids based on silica. One area in which they have found utility is in the form of molecular sieves for applications of water adsorption, molecular adsorption, and separation. The zeolite framework consists of oxygen connected corner-sharing tetrahedral silicon or aluminum atoms. ${ }^{2}$ Because of their limited ability to undergo structural alterations, the application scope of zeolites is limited.

### 1.2 Synthetic Molecular Architectures

J. M. Lehn introduced the concept of supramolecular chemistry in the 1980s. He defined this new phenomenon as "Chemistry beyond the molecule, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces. Its development requires the use of all resources of molecular chemistry combined with the designed manipulation of noncovalent interactions so as to form supramolecular entities, supramolecules possessing features as well defined as those of molecules themselves." ${ }^{3}$

In supramolecular chemistry, non-covalent interactions occur between molecular components in order to make larger molecular architectures through intermolecular interactions such as hydrogen bonding, ${ }^{4}$ metal-ligands coordination bonds, ${ }^{5}$ van der Waals forces, ${ }^{6}$ pi-pi interactions, ${ }^{7}$ and electrostatic interactions. ${ }^{8}$ The non-covalent interactions are weak but dynamic by nature. ${ }^{9}$ Molecular self-assembly, molecular recognition, ${ }^{10}$ mechanically interlocked molecular architectures, ${ }^{11}$ host-guest chemistry ${ }^{12}$ and dynamic covalent chemistry ${ }^{13-20}$ are some of the concepts whose importance to the chemistry community has grown with the advent of supramolecular chemistry.

Large supramolecular architectures can be subdivided into three major types, metal organic frameworks (MOFs), supramolecular organic frameworks (SOFs), and covalent organic frameworks (COFs), according to the intermolecular interactions of the building blocks.
1.2.1 Metal-organic frameworks (MOFs). MOFs are coordination networks that consist of metal ions and rigid functionalized organic ligands. The components selfassemble to give one, two, or three-dimensional molecular architectures. An interesting
feature of these frameworks is their tunable pores and channels. The geometry of MOFs depend on the metal ion coordination number, functional group, and the length of organic ligands. MOFs have many potential uses, such as gas separation and gas storage, ${ }^{21,22}$ gas purification, molecular recognition, ${ }^{23}$ and heterogeneous catalysis. ${ }^{24}$ However, the associated high density of metals hinders the versatility of MOFs and prohibits certain applications, where light material is desired.
1.2.2 Supramolecular organic frameworks (SOFs). SOFs are constructed from large organic components through weak interactions such as hydrogen bonding, ${ }^{4}$ van der Waals forces, ${ }^{6}$ pi-pi interactions, ${ }^{7}$ and electrostatic interactions. ${ }^{10}$ The weaker nonbonding interactions favor the reversible formation of SOFs, which leads to kinetically stable, high energy mispaired products that reorient rapidly until the most thermodynamically stable product is achieved. Although these materials possess some of the qualities of MOFs, such as crystallinity, high porosity, and surface area, they are typically soft porous architectures, due to the weak intermolecular interactions, and instability at higher temperatures. Despite this, SOFs have been used in the fields of catalysis, gas separation/absorption, ${ }^{25}$ and drug delivery. ${ }^{26,27}$
1.2.3 Covalent organic frameworks (COFs). COFs are another type of wellestablished molecular architecture. COFs are composed of large, rigid and noncollapsible structures. COFs share many properties with MOFs and SOFs such as extraordinary adsorption capacity. COFs are different in that they have very low density due to being composed of light elements ( $\mathrm{C}, \mathrm{N}, \mathrm{O}, \mathrm{S}$ etc.) and high thermal stability from covalent bonding. ${ }^{28,29}$ The first COF (COF-1) was synthesized by Yaghi and co-workers by the self-condensation of three boronic acid moieties into its planar six-membered $\mathrm{B}_{3} \mathrm{O}_{3}$
(boroxine) ring (Figure 1). ${ }^{30}$ COF-8 (Figure 2) has been reported as the least dense crystalline material. ${ }^{30}$


Figure 1. The structure and formation of COF-1.

Even though gaseous hydrogen has been accepted as an efficient energy source for the automotive industry, efficient hydrogen storage methods are still being explored. MOFs and SOFs cannot be successfully used as hydrogen storage materials due to their high density and weaker bonding strength. However, some of the unique characteristics of COFs (i.e., strong covalent bonds) open the way toward using them as efficient hydrogen storage materials.


Figure 2. The structure of COF-8.

COFs are being used for various applications in the fields of gas storage, ${ }^{30-32}$ catalysis, ${ }^{33,34}$ optoelectronics, ${ }^{35-37}$ and charge storage. ${ }^{38}$ However, insolubility and structural deformation during synthesis have been reported as the major drawbacks of COFs. To date, few studies have been carried out to find a solution for these drawbacks. ${ }^{39,40}$ Developing more soluble monomers, discovering more suitable solvents and introduction of functional groups to the monomers may be suitable solutions for avoiding the aforementioned issues of COFs.

### 1.3 Dynamic Covalent Chemistry (DCC)

Dynamic covalent chemistry involves the reversible formation of covalent bonds. Dynamic covalent reactions (DCR) typically occur with a relatively low activation barrier
between the starting materials and the products. That is overcome by providing appropriate conditions. ${ }^{41}$ Due to the reversibility of DCR, the desired products can be obtained in high yield by adjusting the reaction conditions such as solvent, reaction temperature, reaction pressure, reaction time, ${ }^{17}$ and the presence of stabilization sources (templates, metal ions, protons, etc.). ${ }^{14}$
1.3.1 Dynamic covalent bonds. There are two types of DCR, dynamic covalent bond formation and bond exchange reactions. Further, dynamic covalent reactions can be divided into three subcategories according to the atoms, which are present in the dynamic covalent bond: carbon-carbon, carbon-heteroatom, and heteroatom-heteroatom.

Carbon-carbon dynamic covalent reactions. Typically, the C-C bond formation occurs along a high activation barrier. Therefore, most of the time, the $\mathrm{C}-\mathrm{C}$ bond formation is irreversible. However, certain catalysts can reduce the activation energy of C-C bond to a breakage level where the reaction becomes reversible. The Diels-Alder, ${ }^{41}$ aldol, and metathesis reactions ${ }^{42,43}$ are well-known C-C dynamic covalent bond forming reactions.

Carbon-heteroatom dynamic covalent reactions. Replacing a carbon atom with a heteroatom such as $\mathrm{O}, \mathrm{N}$ or S can lead to weaker covalent bonds between the heteroatom and its adjacent carbon. Consequently, these weaker covalent bonds tend to undergo reversible reactions. Ester exchange and imine formation (Figure 3) ${ }^{20}$ are well-known examples for this category.


Figure 3. Carbon-nitrogen bond formation through imine synthesis.

Heteroatom-heteroatom dynamic covalent reactions. The formation of dynamic bonds between heteroatoms are the most employed DCR. The self-condensation of boronic acid, and the esterification to form dioxaborole (1.2) via the reaction of boronic acid (1.1) with alcohols (Figure 4) are two examples.


Figure 4. The formation of dioxaborole 1.2

### 1.4 Boron in Dynamic Covalent Chemistry

Boron chemistry has contributed to many important inventions. Three Nobel prizes have been awarded to William Lipscomb (1976), Herbert C. Brown (1979), and Akira Suzuki (2010) for their uncompromising commitment to boron chemistry. ${ }^{44}$ Boroncontaining molecular systems have received attention in the field of supramolecular chemistry because of the superior structure-directing property of boron based interactions. ${ }^{45}$ Further, the significance of boron in DCR has been shown by the inclusion of boron in many designed COF architectures.
1.4.1 Boronic acids. Boronic acids contain one alkyl/aryl group and two hydroxyl groups bonded to a central trivalent boron. The boron is $\mathrm{sp}^{2}$ hybridized, and the empty p orbital on boron allows the delocalization of $\pi$ electrons. The electron accepting ability also allows these boron compounds to behave as Lewis acids.
1.4.2 Boronate Esters. Boronate esters are boronic acid derivatives in which the hydroxyl groups are replaced by alkoxy groups. They have been recognized as a very
useful chemical class that has found application in polymers, ${ }^{46}$ blue emissive materials, ${ }^{47}$ sensors, ${ }^{48}$ and covalent organic frameworks. ${ }^{30,49,50}$
1.4.3 B-N Bond. Recently, the substitution of $\mathrm{C}=\mathrm{C}$ bonds in conjugated organic molecules with the B-N moiety has received considerable attention. Even though the B-N moiety is isoelectronic and isosteric to the $\mathrm{C}=\mathrm{C}, \mathrm{B}-\mathrm{N}$ containing organic compounds have different reactivity and photo physical properties. ${ }^{51}$ The B-N bond strength strongly depends on the steric effects of the bulky substituents on boron or nitrogen. ${ }^{52}$ Thus, B-N bonds can be used to tune the structural properties of large molecular architectures via the changes of substituents on the nitrogen. ${ }^{53}$ Höpfl and his group have shown that the capability of dative B-N bonds to provide rigidity to boronate ester-based structures. ${ }^{54,55}$

### 1.5 2-Phenyl-1,3,2-diazaborole (diazaborole)

Diazaborole $\mathbf{1 . 3}$ is a molecule that consists of two aromatic phenyl rings and a five-membered borole ring (Figure 5). Even though most organoborane molecules show instability in air and moisture, diazaborole $\mathbf{1 . 3}$ exhibits exceptional stability to hydrolysis due to the stable B-N bonds. ${ }^{56,57}$


Figure 5. The structure of diazaborole 1.3.
The synthesis of diazaborole was first reported in 1958 with parallel and subsequent investigations by Dewar's, ${ }^{58}$ Letsinger's, ${ }^{59-61}$ Snyder's, ${ }^{62}$ and Soloway's groups. ${ }^{63}$ In 1962, Marvel reported the first diazaborole polymer. ${ }^{64}$ The synthesis of diazaborole based materials has been ongoing since the 1970s. ${ }^{65,66,67}$ During this time,
researchers have studied the potential applications of diazaborole. ${ }^{48,58-62}$ Recently, rapid and waste-free methods for diazaborole formation in solvent free conditions were introduced. ${ }^{68,69}$ In addition to the study of diazaborole monomers, the applications, and properties of diazaborole containing oligomers ${ }^{61,70,45}$ and polymers ${ }^{64,71,72,73,74}$ have been studied.

Diazaborole preparation can be divided into two categories: solvent and solvent free. Diazaborole formation in solution can be further classified by considering the starting materials: phenylboronic acid (1.4), phenylboron dihalide, boronate ester, and boroxine. Microwave irradiation, ball milling, and the heating of starting materials were used as solvent free diazaborole formation methods.

The condensation of phenylboronic acid 1.4 and benzenediamine (1.5) is the most commonly used synthetic method. Condensation reactions are typically carried out in a solvent under reflux conditions. Toluene, ${ }^{70,74}$ benzene, ${ }^{59}$ ether, ${ }^{75}$ and N-methyl-2pyrrolidone ${ }^{72}$ are common solvents for diazaborole synthesis. Further, reflux of starting materials in dimethylacetamide, ${ }^{64}$ and toluene, ${ }^{76}$ have also been reported as diazaborole synthetic methods. Emery Nyilas and A. H. Soloway reported the first diazaborole condensation reaction from phenylboronic acid 1.4 and benzenediamine 1.5 in xylene using simple distillation (Figure 6). ${ }^{77}$ They obtained a number of diazaborole derivatives from this method.


Figure 6. Substituted diazaboroles prepared by Nyilas and Soloway.

The first diazaborole oligomer preparation was reported by Letsinger and Nazy in 1959. ${ }^{61}$ They formed bis-phenylboradiazole $\mathbf{1 . 6}$ by boiling $2,2^{\prime}$-tolanediboronic acid (1.7) and diamine $\mathbf{1 . 5}$ for few minutes in ethanol (Figure 7).


Figure 7. Tolane-based bis-diazaborole prepared by Letsinger and Nazy.

The reaction of phenylboron dichloride (1.8) and diamine 1.5 forms gaseous hydrogen chloride as the byproduct and this can be easily removed from the system. ${ }^{58}$ Various diazaborole analogues (dioxaborole 1.9, oxazaborole 1.10, dithiaborole 1.11, and thiazaborole 1.12) have been synthesized using this method (Figure 8). ${ }^{58}$


Figure 8. Synthesis of diazaborole from phenyl boron dichloride.

The first evidence of diazaborole formation using boronate esters was reported by Letsinger and Hamilton. They investigated the reaction of benzenediamine $\mathbf{1 . 5}$ and ethyl tartrate ester of benzeneboronic acid $\mathbf{1 . 1 3}$ as the starting materials for the formation of diazaborole 1.3 in benzene at room temperature and obtained a series of substituted diazaboroles, including 1.3 and its bromo and methoxy derivatives (1.14 and 1.15) (Figure 9). ${ }^{60}$


Figure 9. Synthesis of diazaborole from a tartrate ester.

Brotherton and group introduced diazaborole preparation from the condensation reaction of boroxine $\mathbf{1 . 1 6}$ and diamine $\mathbf{1 . 5}$ (Figure 10). ${ }^{78}$


Figure 10. Synthesis of diazaborole from boroxine.

In 2003, Kaupp and group used a waste free, facile solid-state reaction for the formation of diazaborole 1.3 (Figure 11). The major advantage of the ball-milling method is that catalysts and other auxiliaries are not needed (Figure 11). In this study, a stoichiometric mixture of reactants was ball milled in a mortar at room temperature and heated at $40^{\circ} \mathrm{C}$ under vacuum for 1 h to remove the water that forms in this reaction. ${ }^{69}$


Figure 11. The formation of diazaborole $\mathbf{1 . 3}$ using a ball mill.

Slabber and his group synthesized diazaborole derivatives 1.3a-1.3d using microwave irradiation. They obtained diazaborole in high yield within 15 min and without any side products except water under solvent-free conditions (Figure 12). ${ }^{68}$


Figure 12. Synthesis of diazaborole using microwave irradiation.

The $\pi$-conjugation of diazaborole 1.3 extends through the borole ring, which contributes to its interesting optoelectronic properties (Figure 13). The $\pi$-conjugation expansion of the phenyl rings through the five-membered borole ring of diazaborole $\mathbf{1 . 3}$ leads interesting properties. Due to boron's limited valence electrons, it acts as a $\pi$ accepter and stabilizes the LUMO of the adjacent conjugated $\pi$-electron system. Thus, the HOMO-LUMO gap of $\mathbf{1 . 3}$ is lowered, and $\mathbf{1 . 3}$ shows a blue luminescence when it is irradiated with UV light. ${ }^{79}$ Furthermore, diazaborole $\mathbf{1 . 3}$ can act as an electron transporting material because of the extended $\pi$-electron conjugation. ${ }^{80}$


Figure 13. The $\pi$-electron expansion of diazaborole 1.3.

In 2010, Kubo and his group synthesized a diazaborole appended resorcin[4]arene cavitand (1.17) (Figure 14). Diazaborole facilitates guest recognition based on the hydrogen bonding capability of NH that stabilizes the accommodation of guest molecule and the $\pi$-donor character of diazaborole which participates in $\mathrm{CH}-\pi$ interactions with guest molecules. This cavitand can serve as a fluorescence receptor by emitting blue in the absence of guest and quenching of fluorescence upon addition of guest. ${ }^{45}$


Figure 14. Diazaborole appended resorcin[4]arene cavitand (1.17).

In 2011, Kojima and his group revealed the p-type semiconducting behavior of $\pi$ conjugated diazaborole containing oligomers 1.18a-c, and 1.19a-b (Figure 15). ${ }^{80}$ Compounds 1.18a-c and 1.19a-b show good p-type semiconducting behavior with hole mobilities ranging from $10^{-7}$ to $10^{-2} \mathrm{~cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$.

1.18a $\mathrm{Ar}=$ phenyl
1.18b Ar = naphthyl
1.18c Ar = biphenyl

1.19a $\mathrm{Ar}=$ phenyl
1.19b Ar = biphenyl

Figure 15. Diazaborole derivatives having p type semiconducting behavior prepared.

In the same year, Nishida and his group showed the n-type field-effect transistor (FET) characteristics of some trifluoromethyl substituted diazaborole derivatives (1.20, 1.21, 1.22a) with an electron mobility of $10^{-2} \mathrm{~cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$. Further, they have shown ambipolar FET characteristic of biphenyl diazaborole derivative, $\mathbf{1 . 2 2 b}$ to have $2.3 \times 10^{-5}$ $\mathrm{cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$ (n-type) and $1.5 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$ (p-type) electron and hole mobilities, respectively (Figure 16)..$^{81}$

1.20

1.21

1.22a $R=\mathrm{CF}_{3}$
1.22b $\mathrm{R}=\mathrm{Ph}$

Figure 16. n-Type field-effect transistor characterized diazaborole derivatives.

Son and his group synthesized diazaborole appended polymer 1.23. This polymer can be used as a probe to selectively detect anions. They identified that cyanide anion quenches the fluorescence of diazaborole polymer 1.23, while other anions display fluorescence improvement upon exposure to UV light. ${ }^{74}$

1.23

Figure 17. Diazaborole cyanide detector.

### 1.6 Aims of this Study

The understanding of the solvent influence upon diazaborole formation is of interest for effective diazaborole synthesis. Solvents may affect the reaction by stabilizing reactants, intermediates, or products, which can limit reversibility of the reaction. Even though many studies have been carried out on the synthesis at diazaborole in the solution, none have shown the real impact of solvent on the reaction. Furthermore, the reported diazaborole formation studies have been limited to a few solvents. Therefore, in the first project (chapter II of this thesis), the solvent influence on diazaborole formation was examined and investigated to find the mildest reaction conditions in various solvents.

Determination of the reversibility of the diazaborole formation is essential to categorize diazaborole formation as a dynamic covalent reaction (DCR). The dynamic nature of this reaction could allow self-assembly and self-healing (error-checking and proofreading) capabilities. This could contribute to the synthesis of molecular architectures involving diazaborole monomer units while limiting unfavorable byproduct formation. However, the reversibility of diazaborole formation has yet to be reported. Therefore, the reversibility was studied as the second project (chapter III).

Lastly, computational chemistry gives insight to properties that cannot be confirmed experimentally. In this project (Chapter IV), some important aspects of diazaborole and its analogues were computationally investigated.

## CHAPTER II

## Formation of diazaboroles

### 2.1 Background

About a century ago, it was discovered that the solvent can dramatically change the rate of chemical reactions. Since then, the generality and the importance of the solvent effects on the chemical reactivity (rate constants or equilibrium constants) have been widely acknowledged. Therefore, solvent effects are one of the most central topics of chemistry and remain an ever-increasingly active area of study. ${ }^{82}$

Solvents are widely used in chemical reactions as facilitators because of the high solubility of most reagents, and to be readily removed by evaporation. Some reaction solvents provide favorable solubility, stability, and kinetics. In some cases, the solvent mediates the reaction by providing electrophiles or nucleophiles, whereas, most often, the solvent is unreactive towards the reagents and provide only the media for reaction progress.

Solvents are typically classified, based on their dielectric constants, into two main categories, polar and non-polar. Solvents with dielectric constants greater than 15 are considered as polar and below 15 as non-polar. Polar solvents are further divided into protic and aprotic, based on the hydrogen bond donating capability. Protic solvents have the ability to donate hydrogen bonds, while polar aprotic solvents do not.

The condensation reaction of benzenediamine $\mathbf{2 . 1}$ and phenylboronic acid 2.2, as mentioned in Chapter I, in appropriate solvents is the main method employed for the formation of diazaborole 2.3 while using a Dean-Stark apparatus. During the reflux, water, which is a byproduct of the reaction is azeotropically removed from the system to
facilitate a shift in the equilibrium towards the products. Although diazaborole has mainly been produced using toluene ${ }^{60,62,68,70,74,80,81,83}$ as the solvent. The use of xylene, ${ }^{78}$ benzene, ${ }^{58,59}$ and ether ${ }^{75}$ have also been reported. In addition, diazaborole has been prepared from phenylboronic acid and benzene-1,2-diamine by the distillation of xylene and toluene, ${ }^{77}$ heating in toluene at $80{ }^{\circ} \mathrm{C}$ for $8 \mathrm{~h},{ }^{76}$ heating in dry dimethylacetamide at $230{ }^{\circ} \mathrm{C}$ bath temperature, ${ }^{64}$ or heating in dimethylformamide under nitrogen atmosphere at $130{ }^{\circ} \mathrm{C}$ for three days..$^{84}$

Our research group has qualitatively examined the kinetics of diazaborole formation through the condensation of starting materials in $\mathrm{CDCl}_{3}$ and DMSO-d6. The formation reaction was carried out in $\mathrm{CDCl}_{3}$ at $50^{\circ} \mathrm{C}$ using unsubstituted phenylboronic acid (2.2a), an electron withdrawing substituted (bromide 2.2b) phenylboronic acid, and an electron donating substituted (methoxy 2.2c) derivative (Figure 18). All three reactions approached equilibrium within nearly 200 h with conversions of $72 \%$ for $\mathbf{2 . 3 a}, 72 \%$ for $\mathbf{2 . 3 b}$, and $41 \%$ for $\mathbf{2 . 3} \mathbf{c}$ (Figure 19). ${ }^{85}$


Figure 18. The formation of diazaboroles 2.3a-c in $\mathrm{CDCl}_{3}$ at $50^{\circ} \mathrm{C}$.


Figure 19. The formation of diazaborole derivatives in $\mathrm{CDCl}_{3}$ at $50{ }^{\circ} \mathrm{C} .{ }^{85}$

The relatively slow formation of $\mathbf{2 . 3} \mathbf{c}$ was presumed to be due to decreased rate of boron-nitrogen bond formation due to the reduction in electrophilicity at boron that is induced electrophilicity by the electron rich methoxy group substituent of the phenylboronic acid 2.2c. The reaction temperature was limited due to the relatively low boiling point of chloroform $\left(61^{\circ} \mathrm{C}\right)$. So, the reaction was then repeated in DMSO-d $\mathrm{d}_{6}$ at $100{ }^{\circ} \mathrm{C}$ (Figure 20)..$^{85}$


Figure 20. The formation of diazaborole 2.3a in DMSO-d 6 at $100{ }^{\circ} \mathrm{C} .{ }^{85}$

Eighty percent conversion was observed after 60 h reaction time (Figure 21). The results disclosed an increase in diazaborole formation rate and product formation in DMSO-d 6 at $100{ }^{\circ} \mathrm{C} .{ }^{85}$


Figure 21. The reaction kinetic of diazaborole formation in DMSO-d ${ }_{6}$ at $100{ }^{\circ} \mathrm{C} .{ }^{85}$

### 2.2 Objectives

The first objective of the current study was to identify the minimum reaction time for diazaborole formation under reflux reaction conditions in toluene. Previously, the reflux of $\mathbf{2 . 1}$ and 2.2a using a Dean-Stark apparatus has been widely used for diazaborole formation in different solvents. However, most of the time the reaction has been carried out for 24 h , which is likely more than enough time for the reaction to reach completion. Despite this, a thorough study of the time-dependency of the reaction has yet to be reported.

The second objective of this study was to ascertain the impact of solvent on diazaborole formation by applying a wide range of polar protic and polar aprotic organic solvents (Figure 22). Further reaction conditions were tuned according to the solvents’ properties (solvation and boiling point) until the mildest conditions were obtained.


Figure 22. The general reaction of diazaborole formation.
The third objective of the study was to grow X-ray quality crystals of diazaborole and its derivatives from solvent evaporation, solvent diffusion, and vapor diffusion techniques and obtain their crystallographic images.

### 2.3 Results and Discussion

2,4,6-Triphenylcyclotriboroxane (boroxine) (2.4) formation from the selfcondensation of phenylboronic acids adversely affects the formation of diazaborole 2.3a, by removing free boronic acids from the reaction system (Figure 23 and Figure 24). This leads to low product yields. Therefore, ideal solvents should favor diazaborole formation, while suppressing boroxine formation.


Figure 23. Boroxine formation.


Figure 24. Partial ${ }^{1} \mathrm{H}$ NMR spectrum of boroxine. ${ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.

Refluxing and azeotropic removal of water in suitable solvents has been used to help facilitate diazaborole synthesis. However, no systematic study has been reported about the precise influences of the time and the temperature on the completion of 2.3a formation under these conditions. Researchers have implemented 2-24 h reaction times. Therefore, as the first task, the kinetics of diazaborole formation in toluene under reflux conditions was investigated (Figure 26).


Figure 25. The formation of diazaborole 2.3a in toluene under reflux conditions.
${ }^{1} \mathrm{H}$-NMR analysis of the products illustrates that the amount of diazaborole formation increases with time while the amount of boroxine decreases. After 8 h of reaction, the majority of boroxine/phenylboronic acid was consumed. The results confirm that 8 h reaction time sufficient to obtain virtually quantitative diazaborole formation in toluene by using phenylboronic acid (2.2a) and benzenediamine $\mathbf{2 . 1}$ as the starting materials under reflux reaction conditions in toluene.

2.4

2.3a

2.1
$\mathrm{H}_{\mathrm{b}}, \mathrm{H}_{\mathrm{c}}$

$\begin{array}{llllllllllllllllll}8.4 & 8.3 & 8.2 & 8.1 & 8.0 & 7.9 & 7.8 & 7.7 & 7.6 & 7.5 & 7.4 & 7.3 & 7.2 & 7.1 & 7.0 & 6.9 & 6.8 & 6.7\end{array}$ $\delta$ (ppm)
Figure 26. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of diazaborole formation under reflux conditions. ${ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.

The ${ }^{1} \mathrm{H}$-NMR spectra showed a boroxine peak shift at $\approx 8.2 \mathrm{ppm}$. The peak shift was likely due to the different amount of water and different amount of benzene-1,2diamine presence in the separate reactions. These two species may also form hydrogen bonds with boroxine.

Northrop and Goldberg have shown that room temperature condensation of diazaborole 2.3a in $\mathrm{CDCl}_{3}$ is relatively slow. ${ }^{76}$ They observed the diazaborole formation reaction over the course of 24 h and reported that after 24 h the reaction has no substantial changes. To further explore the solvent effect on the diazaborole formation, benzenediamine 2.1 and phenylboronic acid 2.2a were dissolved in four other solvents (Table 1) and stirred for two weeks at room temperature. Solvents having different functional groups (ester, ethers, and nitrile) were selected in the initial studies to investigate their effect on the progress of the reaction. Then, the solvents were removed from the sample using reduced pressure. Tetrahydrofuran (THF), ethyl acetate, and acetonitrile were removed at room temperature to obtain the crude product. However, the minimum temperature needed for the rotary evaporation of 1,4-dioxane was $45^{\circ} \mathrm{C}$.

Table 1
Solvents and their polar/non-polar characteristics

| Solvent | Polar or non-polar | Boiling Point* $\left({ }^{\circ} \mathrm{C}\right)$ | Lewis acid/base |
| :--- | :---: | :---: | :---: |
| 1,4-dioxane (dioxane) | Non-polar | 101.2 | base |
| acetonitrile | Polar aprotic | 82.0 | base |
| ethyl acetate (EtOAc) | Polar aprotic | 77.1 | base |
| tetrahydrofuran (THF) | Polar aprotic | 66.0 | base |

*Note: The boiling points of solvents were obtained from CRC Handbook

After two weeks, ${ }^{1} \mathrm{H}-\mathrm{NMR}$ analysis of the crude reactions in acetonitrile, ethyl acetate and tetrahydrofuran revealed incomplete formation of diazaborole and the persistence of boroxine. However, $100 \%$ formation of diazaborole was observed in 1,4dioxane (Figure 30).


Figure 27. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of diazaborole prepared by two-week reaction in different solvents: tetrahydrofuran, ethyl acetate, acetonitrile, and 1,4-dioxane. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ was taken in $\mathrm{CDCl}_{3}$.

Diazaborole formation in 1,4-dioxane was further examined by reducing the reaction time. Finally, it turned out that only solvent evaporation time ( 15 min ) and drying under vacuum was needed for the reaction to go to completion (Figure 28 and

Figure 29). The results obtained from this experiment indicate that the reaction time at room temperature has less of an effect than the higher temperature needed during solvent removal.


Figure 28. The reaction conditions of diazaborole formation 2.3a in 1,4-dioxane.


Figure 29. The formation of Diazaborole 2.3a in 1,4-dioxane at $45{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.

A similar time dependent study was carried out with tetrahydrofuran at room temperature (Figure 30). The reaction progress was monitored from ${ }^{1} \mathrm{H}$ NMR spectra.

However, the presence of boroxine at each reaction time indicated that tetrahydrofuran was not as favorable of a solvent compared to dioxane (Figure 31).


Figure 30. The formation of diazaborole 2.3a in tetrahydrofuran.


2.4

$\begin{array}{lllllllllllllllll}8.2 & 8.1 & 8.0 & 7.9 & 7.8 & 7.7 & 7.6 & 7.5 & \begin{array}{c}\text { (ppm })\end{array} & 7.3 & 7.2 & 7.1 & 7.0 & 6.9 & 6.8 & 6.7 & 6.6\end{array}$

Figure 31. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction of benzenediamine 2.1 and phenylboronic acid (2.2a) in THF. ${ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.

Water is a byproduct of this reaction and the removal of tetrahydrofuran at room temperature may not provide sufficient heating to remove water. One way to shift the equilibrium in the forward direction is to remove byproducts from the reaction medium. So, diazaborole formation in tetrahydrofuran was performed in the presence of molecular sieves in various amounts (1, 2, 3, and 4 equivalents by mass) relative to phenylboronic acid 2.2a (Figure 32). However, the integration values of the ${ }^{1} \mathrm{H}$-NMR signals reveal that the addition of molecular sieves resulted in the formation of more boroxine $\mathbf{2 . 4}$ compared to diazaborole 2.3a (Table 2).


Figure 32. The formation of diazaborole in the presence of molecular sieves in THF.

Table 2
Ratio of diazaborole 2.3a and boroxine 2.4 in THF with varying amounts of molecular sieves

| Molecular <br> sieves (equiv) | \% diazaborole <br> $\mathbf{2 . 3 a}$ | \% boroxine <br> $\mathbf{2 . 4}$ |
| :---: | :---: | :---: |
| 1 | 37 | 63 |
| 2 | 37 | 63 |
| 3 | 18 | 82 |
| 4 | 14 | 86 |

During diazaborole formation, the removal of water is required to form diazaborole. However, water removal also facilitates boroxine formation. According to
the data in Table 2, water removal from the system more greatly affects boroxine formation in tetrahydrofuran (Figure 23).

After determining that diazaborole formation in 1,4-dioxane only required solvent evaporation time ( 15 min ), the solvent scope was expanded to include solvents with similar functional groups but different boiling points (Figure 33). Phenylboronic acid 2.2a and benzenediamine $\mathbf{2 . 1}$ were mixed in each of the solvents in a round bottom and connected to the rotary evaporator. Aspirator vacuum was applied (27 in Hg ) and the temperature was gradually increased from room temperature to the temperature that the solvent started to condense in order to have the mildest reaction conditions for that solvent. The temperature was kept constant until all the solvent was removed from the system.

Aromatic hydrocarbons


diethyl ether


dimethoxyethane




1,2-dichloroethane



2-methoxyethyl acetate
Amides

$\mathrm{N}, \mathrm{N}$-dimethylacetamide

Figure 33. The solvents used to study diazaborole formation.

Table 3
The solvents, boiling points, evaporation bath temperatures, and evaporation time for diazaborole formation

| Solvent | Boiling Point* <br> ${ }^{\circ} \mathrm{C}$ | Evaporation <br> temperature <br> ${ }^{\circ} \mathrm{C}$ | Evaporation <br> time <br> $(\mathrm{min})$ |
| :--- | :---: | :---: | :---: |
| diethyl ether | 34.4 | RT | $<5$ |
| dichloromethane | 39.8 | RT | $<5$ |
| methanol | 64.5 | RT | 14 |
| tetrahydrofuran | 66.0 | RT | 20 |
| ethyl acetate | 77.1 | RT | 17 |
| ethanol | 78.2 | 26 | 10 |
| 1,2-dichloroethane | 84.0 | RT | 13 |
| dimethoxyethane | 85.0 | 25 | 14 |
| 1,4-dioxane | 101.2 | 45 | 15 |
| toluene | 110.6 | 45 | 15 |
| 1-butanol | 117.6 | 50 | 20 |
| xylene | 140.4 | 61 | 13 |
| 2-methoxyethyl acetate | 145.0 | 74 | 60 |
| 1,3,5-trimethylbenzene | 164.7 | 85 | 20 |
| $N, N$-dimethylacetamide | 165.9 | $90-100$ | 30 |

*Note: The boiling points of the solvents were obtained from CRC Handbook

The percent formation of diazaborole was determined from the integration values of the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of boroxine and diazaborole (Figure 34, Figure 35, and Figure 36)


Figure 34. ${ }^{1} \mathrm{H}$-NMR spectra of diazaborole formation in low boiling solvents. ${ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.


Figure 35. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of diazaborole formation in high boiling solvents. ${ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.


Figure 36. The percent of diazaborole formation in different solvents.

The data reflects that the formation of diazaborole in higher boiling solvents is more favorable. The reactions in 1-butanol, 2-methoxyethyl acetate and $\mathrm{N}, \mathrm{N}$ dimethylacetamide reached $100 \%$ conversion and the presence of boroxine was not detected. In this experiment, the results in dioxane were different than what was observed previously. This may be due to the fact that a new bottle of dioxanes was used for these experiments, and the amount of water in dioxanes might affect the outcome of these reactions. However, further experiments are needed to support this conclusion. All of the other higher boiling point solvents tested $\left(>100^{\circ} \mathrm{C}\right)$ gave greater than $85 \%$ diazaborole formation. The lower boiling solvents evaporate at or near room temperature under aspirator pressure. The results of this experiment indicate that the impact of reaction temperature has an influence on diazaborole formation. The water removal, which formed in the diazaborole formation, with the solvent at high temperature under reduced pressure may lead to have high diazaborole production.

X-ray crystallographic characterization. For further characterization of the diazaborole system, we attempted to grow X-ray quality crystals via solvent evaporation, solvent diffusion, and vapor diffusion techniques using various solvent systems.

Vapor diffusion. Slow diffusion of vapor of one solvent into another solvent was carried out to obtain X-ray quality crystals. Two solvents were selected according to their boiling points (vaporization) and the sample dissolution. Solvents able to dissolve diazaboroles and having high boiling points were used in the inner vial as a "good solvent" and a relatively low boiling, a low solubilizing solvent was added to the outer vial ("bad solvent"). The inner vial was kept open to allow the solvent vapors to diffuse. However, the outer vial was kept closed to prohibit the solvent loss from the system. The
low boiling solvent diffuses into the high boiling solvent, and consequently, the outer vial solvent level gradually decreases, while the solvent level in inner vial increases. With the "bad solvent" diffusing into the "good solvent", diazaborole solubility in the inner vial gradually decreases and finally it reaches a saturation point. Further solvent diffusion into the inner vial results in either precipitation or crystal formation. See Table 4 for examples of the solvent systems that were tried.

Table 4
Crystal formation from vapor diffusion

| Solute | "Good" <br> solvent | "Bad" <br> solvent | Crystal <br> formation | Color | X-ray <br> quality |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1,4-dioxane <br> 1,4-dioxane | hexane <br> hexane | yes | no colorless | yes |
| diazaborole 2.3a | DCM | hexane | yes | colorless | yes |
|  | $\mathrm{CHCl}_{3}$ | hexane | yes | colorless | no |
| ethyl acetate | hexane | yes | yellow | no |  |
| bromodiazaborole 2.3b | 1,4-dioxane | hexane | no | - | no |
| methoxydiazaborole 2.3c | 1,4-dioxane | hexane | no | - | no |
| boroxine 2.4 | 1,4-dioxane | hexane | no | - | no |
|  | 1,4-dioxane | hexane | no | - | no |
| methyldiazaborole 2.5 | CHCl |  |  |  |  |
|  | hexane | no | - | no |  |
| ethyl acetate | hexane | no | no | no | no |

We were able to obtain large colorless crystals from the 1,4-dioxane-hexane. The obtained crystals were analyzed using an X-ray diffractometer (Figure 37). The X-ray image reveals that H -bonding exists between the diazaborole NH and oxygen in 1,4dioxane in the solid state (Figure 38).


Figure 37. X-ray crystal structure of diazaborole single molecule.


Figure 38. X-ray crystal structure packing of diazaborole 2.3a. The crystals were grown in dioxane-hexane solvent system

Solvent diffusion followed by solvent evaporation. We realized that solvent evaporation after vapor diffusion was a good method to grow diazaborole crystals. With the intention of setting the system at low temperature $\left(-20^{\circ} \mathrm{C}\right)$ and as a "very bad" solvent for diazaborole dissolution, 1-pentane was used. In this technique, two solvents were allowed to penetrate each other in solvent phase. First, the sample was dissolved in "good solvent" in a vial, and then the "bad" solvent was carefully layered on the "good solvent" without disturbing the "good" solvent. This system was stored for three days in a closed vial to allow the bad solvent to diffuse into the good solvent. Then, the cap of the vial was opened and solvents were slowly evaporated (Table 5).

Table 5
Crystal formation from solvent diffusion

| Solute | "Good" <br> solvent | "Bad" <br> solvent | Crystal <br> formation | Color | X-ray <br> quality |
| :--- | :---: | :---: | :---: | :---: | :---: |
| diazaborole 2.3a | DCM | 1-pentane | Yes | colorless | Yes |
| bromodiazaborole 2.3b | DCM | 1-pentane | Yes | brown | No |
| methoxydiazaborole 2.3c | DCM | 1-pentane | Yes | White | No |
| boroxine 2.4 | DCM | 1-pentane | Yes | White | No |
| methyldiazaborole 2.5 | DCM | 1-pentane | No | - | No |

This method was more successful than the vapor diffusion and we were able to obtain larger diazaborole crystals. Other diazaborole derivatives gave needle shape or very tiny crystals, which were not appropriate for XRD structure determination.

### 2.4 Conclusions

The $100 \%$ diazaborole formation can be obtained in toluene under reflux conditions within minimum 8 h reaction time. Boroxine is always present below the 8 h reaction time. The reaction of phenylboronic acid and benzene-1,2-diamine in 1,4dioxane revealed that the reaction time at room temperature is not a significant factor compared to the solvent removal temperature. Further, high boiling solvents contribute to increased diazaborole formation compared to low boiling solvents. Among the high boiling solvents 1-butanol, 2-methoxyethyl acetate and $N, N$-dimethylacetamide show $100 \%$ diazaborole formation. The results indicate that reaction temperature/solvent boiling point affects the diazaborole formation more than the solvent functional groups or polarity. The 1,4-dioxane-hexane, dichloromethane-hexane, ethyl acetate-hexane and $\mathrm{CHCl}_{3}$-hexane solvent systems yielded diazaborole 2.5 single crystals in vapor diffusion technique.

### 2.5 Experimental

Chemicals and reagents. All starting materials and reagents were purchased from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar, and J.T. Baker) and used without further purification. The $\mathrm{CDCl}_{3}$ was stored over activated $4 \AA$ molecular sieves.

NMR spectroscopy. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra were collected on a JEOL Eclipse $300^{+}$ spectrometer. Chemical shifts were reported in $\delta(\mathrm{ppm})$ relative to residual solvent protons $\left(\mathrm{CHCl}_{3}: 7.26\right)$ or (DMSO-d6: 2.50). The splitting patterns are designated as s (singlet); d (doublet); t (triplet); m (multiplet)
2.5.1 Synthesis of diazaboroles 2.5. Commercially available phenylboronic acids (2.2) and benzene-1,2-diamine (2.1) were used for the following synthetic work.

Reflux in toluene. An equimolar amount of benzene-1,2-diamine 2.1 ( 54.0 mg , $0.5 \mathrm{mmol}, 1$ equiv) and phenylboronic acid $\mathbf{2 . 2 a}$ ( $61.1 \mathrm{mg}, 0.5 \mathrm{mmol}, 1$ equiv) were mixed in toluene $(20 \mathrm{~mL})$ in a round bottom flask. The reaction mixture was refluxed (20 $\min , 1 \mathrm{~h}, 2 \mathrm{~h}, 3 \mathrm{~h}$, and 8 h ). Then, the solvent was removed under reduced pressure ( 27 in Hg ) at $45^{\circ} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ NMR was obtained. $100 \%$ diazaborole formation was observed for 8 h reaction (A tan color solid ( $67.9 \mathrm{mg}, 78 \%$ ) ). The $20 \mathrm{~min}, 1 \mathrm{~h}, 2 \mathrm{~h}, 3 \mathrm{~h}$ refluxed reactions resulted in $13.8 \%, 54.3 \%, 74.2 \%, 87.3 \%$ conversion of diazaborole, respectively, compare to boroxine. ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right) \delta: 7.74(\mathrm{~d}, 2 \mathrm{H}), 7.43(\mathrm{t}, 3 \mathrm{H}), 7.14-7.08$ (m, 2H), 7.00-6.94 (m, 3H), 6.76 (s, 2H), 6.73 (s, 2H).

Two weeks reaction. An equimolar amount of benzene-1,2-diamine 2.1 ( 108 mg , $1 \mathrm{mmol}, 1$ equiv) and phenylboronic acid $\mathbf{2 . 2 a}(121 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) were mixed in the solvent $(5 \mathrm{~mL})$ in a vial. The reaction mixture was stirred for 2 weeks at room temperature. Then, the solvent was removed under reduced pressure ( 27 in Hg ) at room temperature. The resultant dried sample was mixed to get homogeneous sample and ${ }^{1} \mathrm{H}$ NMR was obtained.

Reaction in 1,4-dioxane. An equimolar amount of benzene-1,2-diamine 2.1 (108 $\mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) and phenylboronic acid $\mathbf{2 . 2} \mathbf{2}$ ( $121 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) were mixed in 1,4-dioxane ( 5 mL ) in a vial and connected to the rotary evaporator. Aspirate vacuum was applied ( 27 in Hg ) and heated at $45^{\circ} \mathrm{C}$ for 10 min and ${ }^{1} \mathrm{H}$ NMR was obtained.

Reaction in tetrahydrofuran. An equimolar amount of benzene-1,2-diamine 2.1 ( $108 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) and phenylboronic acid $\mathbf{2 . 2 a}(121 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) were mixed in tetrahydrofuran $(5 \mathrm{~mL})$ in a vial. The reaction mixture was kept at room temperature ( $30 \mathrm{~min}, 1 \mathrm{~h}$, and 5 h ). Then, vial was connected to the rotary evaporator. Aspirator vacuum was applied (27 in Hg ) and heated at $45^{\circ} \mathrm{C}$ for 10 min and ${ }^{1} \mathrm{H}$ NMR was obtained. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction time $30 \mathrm{~min}, 1 \mathrm{~h}$ and 5 h revealed that $58.8 \%, 38.7 \%, 29.1 \%$ percent formation of diazaborole, respectively, compared to boroxine in the resultant product.

Reaction in tetrahydrofuran with molecular sieves. An equimolar amount of benzene-1,2-diamine 2.1 ( $108 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) and phenylboronic acid 2.2a (121 $\mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv), were mixed in tetrahydrofuran ( 5 mL ) in a vial. Then, molecular sieves ( $3 \AA$ : $200 \mathrm{mg}, 403 \mathrm{mg}, 601 \mathrm{mg}$, and 802 mg ). The reaction mixture was kept at room temperature for 1 h . Then, the solvent was removed under reduced pressure (27 in Hg ) at room temperature and ${ }^{1} \mathrm{H}$ NMR was obtained. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction with $200 \mathrm{mg}, 403 \mathrm{mg}, 601 \mathrm{mg}$ and 802 mg revealed that $37 \%, 37 \%, 18 \%$, and $14 \%$ percent conversions of diazaborole formation, respectively, compare to the boroxine in the resultant product.

Reaction in different solvents. An equimolar amount of benzene-1,2-diamine $\mathbf{2 . 1}$ ( $108 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) and phenylboronic acid $\mathbf{2 . 2}$ ( $121 \mathrm{mg}, 1 \mathrm{mmol}, 1$ equiv) were mixed in solvents ( 5 mL ) in a vial. Then, solvent was removed under reduced pressure $(27$ in Hg$)$ at the indicated temperature and time. The crude product was a solid. It was ground with a metal spatula to a powder and ${ }^{1} \mathrm{H}$ NMR was analyzed.
2.5.2 Growing of X-ray quality crystals. The growth of crystals for the x-ray diffraction studies were attempted using solvent evaporation, vapor diffusion, and solvent diffusion methods.

X-ray crystallography. Diffraction data were collected on a Rigaku XtaLABmini diffractometer using $\operatorname{Mo} \mathrm{K} \alpha(\lambda=0.71075)$ radiation. The crystal was kept at 180 K during collection time. Using Olex2, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimization.

## CHAPTER III

## Reversibility of diazaborole formation

### 3.1 Background

Supramolecular chemistry consists of noncovalent interactions (Van der Waals, hydrogen bonding, etc.) and therefore, rapid and reversible equilibrium can occur. ${ }^{86}$ Supramolecular interactions result in the self-assembly of molecules into architectures that typically become unstable when the temperature is increased or when competing species or solvents are introduced. Consequently, although supramolecular chemistry can be used to build up many molecular architectures, they will likely collapse under certain temperature and solvent conditions. On the other hand, conventional synthetic organic chemistry involves the formation of strong covalent bonds, which are often formed irreversibly under the kinetically controlled reaction conditions. ${ }^{17}$ Due to this irreversibility, once the products are formed they do not revert to the starting materials. The combination of dynamic covalent bonds and self-assembly brings robustness and reversibility to reaction systems. This process is recognized as dynamic covalent chemistry (DCC). The bonds that result from dynamic covalent reactions (DCR) are covalent and stable when removed from the reaction system. Therefore, it is possible to undergo reverse transformations while showing error-checking and proof-reading characteristics under the reaction conditions. ${ }^{14}$ DCRs give thermodynamically stable products and ensure the capability of designing rational large-scale molecular architectures. ${ }^{87}$ Even though dynamic covalent chemistry resembles supramolecular chemistry in the sense of reaction reversibility, ${ }^{13}$ the equilibrium process can be very slow due to the associated slow reaction kinetics. ${ }^{14}$ In this project, we attempted to
answer the following question, "under what condition is diazaborole formation dynamic?"

The preliminary step for building up desirable, rational diazaborole molecular architectures would be the understanding of its dynamic covalent nature. Even though the dynamic covalent nature of dioxaborole has been widely accepted, there is no solid evidence that diazaborole possesses dynamic covalent character. In over 50 years of diazaborole history, only one study has shown the hydrolysis of diazaborole. ${ }^{88}$ In that study, diazaborole was shown to readily hydrolyze under acidic or basic reaction conditions (Figure 39).

3.1

Figure 39. Hydrolysis of diazaborole 3.1.

Previously, our research group observed the ring opening of diazaborole 3.1 using methanol to give benzenediamine 3.3 and the phenylboronate dimethyl ester (Figure 40). Those experiments also revealed the potential reversibility of diazaborole formation. ${ }^{85}$



$+$

3.1

Figure 40. Methanolysis of diazaborole 3.1.

Furthermore, our research group demonstrated, qualitatively, the dynamic reversibility of diazaborole formation by treating diazaborole 3.1 with
bromophenylboronic acid (3.4) and methoxyphenylboronic acid (3.5) in $\mathrm{CDCl}_{3}$ at $50^{\circ} \mathrm{C}$ to give diazaborole 3.6 and 3.7, respectively (Figure 41). ${ }^{85}$


Figure 41. The exchange reaction of diazaborole 3.1 with bromo and methoxysubstituted boronic acids 3.4 and $\mathbf{3 . 5}$.

### 3.2 Objectives

The objective of the current work is to explore the reversibility of diazaborole formation, and through that, establish the dynamic covalent character of diazaborole derivatives. This goal was pursued by two main pathways; i) by reacting differently substituted phenylboronic acids with diazaboroles or ii) by reacting differently substituted benzene-1,2-diamines with diazaboroles. If the formation is dynamic, the reaction mixture should consist of differently substituted diazaboroles upon reaching equilibrium.

### 3.3 Results and Discussion

### 3.3.1 Stability of diazaborole in solution.

Even though diazaborole $\mathbf{3 . 1}$ is well-known to be stable at room temperature for months/years on the bench, the stability in solution phase is lesser known. The
understanding of the stability of $\mathbf{3 . 1}$ at high temperatures in the solution phase is important before studying the reversibility of diazaborole formation. If unwanted side reactions or hydrolysis occurs with simple diazaborole under these conditions, then experiments regarding diazaborole interchange may also involve the same unwanted side reactions. The stability of $\mathbf{3 . 1}$ in solution was examined by monitoring the changes in its ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (DMSO-d $\mathrm{d}_{6}$ ) at $100{ }^{\circ} \mathrm{C}$ (Figure 42). The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra reveal that peaks corresponding to 3.1 remain over 15 days without serious change (Figure 43). However, an unknown peak at 8.0 ppm appeared over time. Moreover, the absence of the peaks assignable to phenylboronic acid $\mathbf{3 . 2}$ and benzenediamine $\mathbf{3 . 3}$ discloses the stability of $\mathbf{3 . 1}$ to hydrolysis even under these harsh conditions.


Figure 42. Heating diazaborole $\mathbf{3 . 1}$ in DMSO at $100^{\circ} \mathrm{C}$.


Figure 43. Partial ${ }^{1} \mathrm{H}$ NMR spectra of diazaborole $\mathbf{3 . 1}$ in DMSO- $\mathrm{d}_{6}$ at $100{ }^{\circ} \mathrm{C}$ at varied time intervals.

Once the stability of diazaborole was confirmed under these conditions, diazaborole 3.1 and its derivatives were subjected to transamidation and phenylboronic acid exchange reactions to ascertain the dynamic nature of the reaction in applicable solvents at various reaction temperatures. The solvents for the reaction were determined from the results in Chapter II and the literature. ${ }^{64}$

The exchange reaction of diazaborole 1 (DAB 1) with phenylboronic acid 1 (PBA 1) should in theory produce diazaborole 2 (DAB 2) and phenylboronic acid 2 (PBA 2) (Figure 44). Additionally, the self-assembly of PBA 1 and PBA 2 may form boroxines (Boroxine 1-4). For example, when phenylboronic acid 3.2 and bromophenylboronic acid 3.4 were mixed in 1-butanol at $50^{\circ} \mathrm{C}$. Peaks assignable to all four boroxines were observed in the ${ }^{1} \mathrm{H}$ NMR spectrum (Figure 45).


Figure 44. The exchange reaction of diazaborole with phenylboronic acid.


Figure $45 .{ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of boroxine 3.8-3.11

### 3.3.2 Exchange reactions of diazaborole.

First, the exchange diazaborole $\mathbf{3 . 1}$ with bromophenylboronic acid $\mathbf{3 . 4}$ ( 1 mmol each) was examined in 1,4-dioxane ( 5 mL ) at $50^{\circ} \mathrm{C}$ (Figure 46).


Figure 46. The reaction of diazaborole 3.1 and bromophenylboronic acid 3.4 in 1,4dioxane at $50^{\circ} \mathrm{C}$.

The reaction was monitored by observing the signals for $\mathbf{3 . 1}\left(\mathrm{H}_{\mathrm{a}}\right)$ and $\mathbf{3 . 6}\left(\mathrm{H}_{\mathrm{d}}, \mathrm{H}_{e}\right)$. However, due to the peak overlap of boroxines (7.5 ppm) 3.8-3.11 and bromodiazaborole
3.6, the exchange reaction of $\mathbf{3 . 1}$ with $\mathbf{3 . 4}$ could not be examined quantitatively (Figure 47). A clear decrease in intensity for $\mathbf{3 . 1}$ and an increase in the signals for $\mathbf{3 . 6}$ was observed.


Figure 47. ${ }^{1} \mathrm{H}$ NMR spectra of the reaction of diazaborole 3.1 and bromophenylboronic acid 3.4 in 1,4-dioxane at $50^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR spectra were obtained in $\mathrm{CDCl}_{3}$.

The reaction was then studied in 1-butanol with same reaction time (1.33 h), but at two different temperatures in order to understand the impact of the temperature on the reaction. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the products of the reaction at two different temperatures apparently show that at high temperatures, conversion to bromodiazaborole 3.6 was greater (Figure 48).

3.1

3.6

3.8

3.11

Figure 48. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction of diazaborole 3.1 and bromophenylboronic acid 3.4 in 1-butanol at $50^{\circ} \mathrm{C}$ and $70^{\circ} \mathrm{C}$.

The literature shows that reflux conditions have been widely used for diazaborole formation. Therefore, 1-butanol under reflux conditions was tested for this reaction to understand the reaction progress at high temperature. The reaction was carried out at 140 ${ }^{\circ} \mathrm{C}$. Figure 49 reveals that reaction reached equilibrium within 2 h with $58 \%$ conversion of 3.1 and remains constant with time (even after 8.5 h ).


3.6

3.8

3.11


Figure 49. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction of diazaborole 3.1 and bromophenylboronic acid 3.4 in 1-butanol under reflux conditions.

### 3.3.1 Investigation of the ability of diamines to undergo exchange.

Diazaborole 3.1 was reacted with methylbenzenediamine $\mathbf{3 . 1 2}$ in different
solvents at varying temperatures (Figure 50). In this situation, the diamine component of diazaborole was in excess and therefore the presence of boroxines was expected to be reduced.


Figure 50. The transamidation reaction of diazaborole 3.1 with methylbenzenediamine 3.11.

The transamidation of $\mathbf{3 . 1}$ and $\mathbf{3 . 1 2}$ was first studied in $\mathrm{CDCl}_{3}$ at room temperature (Figure 51). The reaction progress was monitored by integrating the ${ }^{1} \mathrm{H}$ NMR signals associated with the methyl protons of $\mathbf{3 . 1 2}$ ( 2.21 ppm ) and $\mathbf{3 . 1 3}$ ( 2.39 ppm ).


Figure 51. The reaction of diazaborole $\mathbf{3 . 1}$ and methylbenzenediamine $\mathbf{3 . 1 2}$ in $\mathrm{CDCl}_{3}$ at room temperature.

Under these conditions, the reaction was very slow reaching $22 \%$ conversion after 7 days (Figure 52) However, even after 7 days the reaction did not reach its equilibration point.


Figure 52. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction of diazaborole $\mathbf{3 . 1}$ and methylbenzenediamine 3.15 in $\mathrm{CDCl}_{3}$ at room temperature.

Due to the slow equilibration of the reaction in $\mathrm{CDCl}_{3}$ at room temperature, the transamidation reaction of $\mathbf{3 . 1}$ and $\mathbf{3 . 1 2}$ was studied in DMSO-d $\mathrm{d}_{6}$ at $100^{\circ} \mathrm{C}$ (Figure 53).


Figure 53. The reaction of diazaborole $\mathbf{3 . 1}$ and methylbenzenediamine $\mathbf{3 . 1 2}$ in DMSO-d6 at $100^{\circ} \mathrm{C}$.


Figure 54. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction of diazaborole $\mathbf{3 . 1}$ and methylbenzenediamine 3.12 in DMSO-d 6 at $100^{\circ} \mathrm{C}$.

The initial equilibration rate was slow. However, the increase of $\mathbf{3 . 1 3}\left(\mathrm{H}_{\mathrm{a}}\right)$ and decrease of $\mathbf{3 . 1 2}\left(\mathrm{H}_{\mathrm{b}}\right)$ in the ${ }^{1} \mathrm{H}$-NMR spectra indicated the formation and consumption of 3.12 and 3.13, respectively (Figure 54). After 372 h , the reaction reached $54 \%$ conversion (Figure 55).


Figure 55. Percent conversion of diazaborole $\mathbf{3 . 1}$ to methyldiazaborole $\mathbf{3 . 1 3}$ in DMSO-d 6 at $100^{\circ} \mathrm{C}$.

Concurrent with the above, the reverse reaction of $\mathbf{3 . 1 3}$ and $\mathbf{3 . 3}$ was investigated in DMSO-d6 at $100^{\circ} \mathrm{C}$ (Figure 56).


Figure 56. The reaction of methyldiazaborole $\mathbf{3 . 1 3}$ and benzenediamine $\mathbf{3 . 3}$ in DMSO-d ${ }_{6}$ at $100^{\circ} \mathrm{C}$.

The reaction was monitored by following the consumption and formation of $\mathbf{3 . 1 3}$ $\left(\mathrm{H}_{\mathrm{b}}\right)$ and $\mathbf{3 . 1 2}\left(\mathrm{H}_{\mathrm{a}}\right)$, respectively. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra revealed that methylbenzenediamine $\mathbf{3 . 1 2}$ began forming within 5 h and increased with time, whereas peaks associated to methyldiazaborole $\mathbf{3 . 1 3}$ gradually decreased (Figure 57 and Figure 58). The reaction was allowed to equilibrate for 125 h at which point $48 \%$ conversion
was observed. This was similar to the transamidation reaction of $\mathbf{3 . 1}$ with $\mathbf{3 . 1 2}$ where $56 \%$ conversion was observed, but the equilibration time was significantly shorter.


Figure 57. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the reaction of methyldiazaborole $\mathbf{3 . 1 3}$ and benzenediamine $\mathbf{3 . 3}$ in DMSO- $\mathrm{d}_{6}$ at $100^{\circ} \mathrm{C}$.


Figure 58. Percent conversion of methyldiazaborole $\mathbf{3 . 1 3}$ to methylbenzenediamine $\mathbf{3 . 1 2}$ in DMSO-d 6 at $100^{\circ} \mathrm{C}$.

While heating in DMSO at $100^{\circ} \mathrm{C}$ provided evidence of interchange, these conditions are not ideal for dynamic covalent reactions. Therefore, the reaction was further investigated in other solvents and at lower temperatures. Dioxane was chosen as the next solvent based on the experiments described in chapter II of this thesis.

Diazaborole 3.1 and methylbenzenediamine $\mathbf{3 . 1 2}$ were mixed in dioxane and heated to 50 ${ }^{\circ} \mathrm{C}$ (Figure 59). Aliquots were taken from the reaction and most of the dioxane was removed. ${ }^{1} \mathrm{H}$ NMR analysis provided qualitative evidence of the conversion of diazaborole 3.1 to diazaborole $\mathbf{3 . 1 3}$ (Figure 60).


Figure 59. The reaction of diazaborole 3.1 and methylbenzenediamine 3.12 in 1,4dioxane at $50^{\circ} \mathrm{C}$.



$\qquad$
$\qquad$



Figure 60. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the transamidation of diazaborole 3.1 and methylbenzenediamine $\mathbf{3 . 1 2}$ in 1,4-dioxane at $50^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}-\mathrm{NMR}$ were taken in $\mathrm{CDCl}_{3}$.

The reverse reaction was carried out under the same conditions (Figure 61).
Aliquots were taken from the reaction of methyldiazaborole $\mathbf{3 . 1 3}$ and benzenediamine $\mathbf{3 . 3}$
in 1,4-dioxane at $50^{\circ} \mathrm{C}$ over a 278 h period and most of the solvent was removed under reduced pressure.


Figure 61. The reaction of methyldiazaborole $\mathbf{3 . 1 6}$ and benzenediamine 3.3 in 1,4dioxane at $50^{\circ} \mathrm{C}$.

The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra (Figure 62) illustrate the formation of methylbenzenediamine $\mathbf{3 . 1 2}\left(\mathrm{H}_{\mathrm{a}}\right)$ and consumption of methyldiazaborole $\mathbf{3 . 1 3}(\mathrm{Hb})$ over time. The reaction is relatively fast and reached $\sim 50 \%$ conversion after 125 h (Figure 62 and Figure 63). However, quantitative analysis was not possible due to overlapping signals that were likely due to oligomeric species or complexes with the solvent, dioxane.


Figure $62 .{ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of aliquots taken from the reaction of methyldiazaborole 3.13 and benzenediamine $\mathbf{3 . 3}$ in 1,4-dioxane at $50^{\circ} \mathrm{C}$ over a 278 h period. ${ }^{1} \mathrm{H}$ NMR were taken in $\mathrm{CDCl}_{3}$.


Figure 63. Percent conversion of methyldiazaborole $\mathbf{3 . 1 3}$ in the reaction of methyldiazaborole 3.13 and benzenediamine 3.3 in 1,4-dioxane at $50^{\circ} \mathrm{C}$.

### 3.4 Conclusions

Diazaborole showed high stability in solvent phase, at $100{ }^{\circ} \mathrm{C}$ in DMSO- $\mathrm{d}_{6}$, for more than 15 days without significant changes. Therefore, it is determined that diazaborole $\mathbf{3 . 1}$ is suitable to use at high temperatures in the reactions.

Although boroxine formation in the reaction prevented the quantitative analysis the reaction exchange was observed qualitatively. The exchange reaction between diazaborole 3.1 and bromophenylboronic acid 3.4 in 1,4-dioxane was confirmed qualitatively. The exchange reaction of $\mathbf{3 . 1}$ and $\mathbf{3 . 5}$ at different temperatures showed higher equilibration rate at high temperatures. The reaction reached equilibrium within 2 h in 1-butanol with $58 \%$ conversion of $\mathbf{3 . 1}$ to $\mathbf{3 . 5}$ in reflux conditions.

The transamidation reaction of diazaborole $\mathbf{3 . 1}$ and methylbenzenediamine $\mathbf{3 . 1 2}$ in $\mathrm{CDCl}_{3}$ was slow and reaction reached $22 \%$ conversion of methyldiazaborole $\mathbf{3 . 1 3}$ after 168 h . However, in DMSO- $\mathrm{d}_{6}$ at $100^{\circ} \mathrm{C}$ the transamidation of diazaborole 3.1 and methylbenzenediamine $\mathbf{3 . 1 2}$ revealed that the reaction reached equilibrium within 220 h , while reaching nearly $55 \%$ conversion of methyldiazaborole 3.13. Further, the reverse reaction of $\mathbf{3 . 1 3}$ and $\mathbf{3 . 3}$ revealed that reaction reached equilibrium within 125 h with 52 $\%$ conversion. In 1,4-dioxane the reaction of diazaborole 3.1 and methylbenzenediamine 3.12 at $50^{\circ} \mathrm{C}$ reached equilibrium within 45 h with $70 \%$ conversion. The reverse reaction of $\mathbf{3 . 1 3}$ and $\mathbf{3 . 3}$ did not apparently reach equilibrium. These results indicate that the reaction is dynamic. However, quantitative analysis has been hindered by overlapping signals and a conclusion cannot be reached regarding the relative stability of the studied diazaborole derivatives.

### 3.5 Experimental

Chemicals and reagents. All starting materials and reagents were purchased from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar, and J.T. Baker) and used without further purification. The $\mathrm{CDCl}_{3}$ was stored over activated $4 \AA$ molecular sieves.

NMR spectroscopy. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra were collected from JEOL Eclipse $300+$ spectrometer. Chemical shifts were reported in $\delta(\mathrm{ppm})$ relative to the ${ }^{1} \mathrm{H}\left(\mathrm{CHCl}_{3}\right.$ : 7.26) or (DMSO-d6: 2.50). The splitting patterns are designated as s (singlet); d (doublet); $m$ (multiplet).

Synthesis of 5-methyl-2-phenyl-2,3-dihydro-1H-benzo[1,3,2]diazaborole 3.13. A mixture of phenylboronic acid $(1.83 \mathrm{~g}, 15.00 \mathrm{mmol})$ and methylbenzenediamine 3.9 (1.83 $\mathrm{g}, 15.00 \mathrm{mmol})$ was dissolved in toluene $(50 \mathrm{~mL})$ and refluxed with a Dean-Stark trap for 24 h . During the reaction period, approximately 35 mL of toluene was removed. The reaction mixture was cooled and the product was allowed to crystallize from toluene. The crystals were collected and washed with cold toluene $(30 \mathrm{~mL})$, then cold hexane $(10 \mathrm{~mL})$. The crude product was recrystallized from toluene and white color crystals ( 2.50 g ) were obtained in $80 \%$ yield. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ analysis of the product was consistent with expectations. ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right) \delta: 7.71(\mathrm{~m}, 2 \mathrm{H}), 7.42(\mathrm{~m}, 3 \mathrm{H}), 6.99(\mathrm{~d}, 1 \mathrm{H})$, $6.93(\mathrm{~s}, 1 \mathrm{H}), 6.77(\mathrm{~d}, 1 \mathrm{H})$.

## Exchange reaction of diazaborole with bromophenylboronic acid. Diazaborole

 3.1 ( $38.8 \mathrm{mg}, 0.2 \mathrm{mmol}$, 1 equiv) and bromophenylboronic acid 3.4 ( $40.3 \mathrm{mg}, 0.2 \mathrm{mmol}$, 1 equiv) were mixed in 1-butanol ( 3 mL ) in a 25 mL round bottom flask. The reaction mixture was heated for 1.33 h at $50^{\circ} \mathrm{C}$. Then, the solvent was removed under reduced pressure at $50{ }^{\circ} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ NMR was obtained.Diazaborole 3.1 ( $38.8 \mathrm{mg}, 0.2 \mathrm{mmol}$, 1 equiv) and bromophenylboronic acid 3.4 ( $40.3 \mathrm{mg}, 0.2 \mathrm{mmol}$, 1 equiv) were mixed in 1-butanol ( 3 mL ) in a 25 mL round bottom flask. The reaction mixture was heated for 1.33 h at $70^{\circ} \mathrm{C}$. Then, the solvent was removed under reduced pressure at $50^{\circ} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ NMR was obtained.

Diazaborole 3.1 ( $9.8 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) and bromophenylboronic acid $\mathbf{3 . 4}$ ( $10.2 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) were mixed in 1-butanol ( 3 mL ) in a 25 mL round bottom flask. The reaction mixture was refluxed 2 h . Then, the solvent was removed under reduced pressure at $50^{\circ} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ NMR was obtained.

Diazaborole 3.1 ( $9.8 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) and bromophenylboronic acid $\mathbf{3 . 4}$ ( $10.2 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) were mixed in 1-butanol ( 3 mL ) in a 25 mL round bottom flask. The reaction mixture was refluxed 8.5 h . Then, the solvent was removed under reduced pressure at $50^{\circ} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ NMR was obtained.

Diazaborole 3.1 ( $0.194 \mathrm{~g}, 1 \mathrm{mmol}, 1$ equiv) and bromophenylboronic acid 3.4 ( $0.201 \mathrm{~g}, 1 \mathrm{mmol}$, 1 equiv) were mixed in 1,4-dioxane ( 15 mL ) in a 50 mL round bottom flask. The reaction mixture was heated at $50^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR was obtained periodically for 101.5 h.

Reaction of diazaborole with methylbenzenediamine. An equimolar amount of diazaborole 3.1 ( $9.7 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) and methylbenzenediamine $\mathbf{3 . 1 2 ( 6 . 1 \mathrm { mg } \text { , }}$ 0.05 mmol , 1 equiv) were mixed in NMR tube in $\mathrm{CDCl}_{3}(0.6 \mathrm{~mL})$. Reaction progress was monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy.

An equimolar amount of diazaborole 3.1 ( $0.194 \mathrm{~g}, 1 \mathrm{mmol}, 1$ equiv) and methylbenzenediamine $\mathbf{3 . 1 2}$ ( $0.122 \mathrm{mg}, 1 \mathrm{mmol}$, 1 equiv) were mixed in 1,4-dioxane ( 15
mL ) in a 50 mL round bottom flask. The reaction mixture was heated at $50{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR was obtained periodically for 119.5 h

An equimolar amount of diazaborole $\mathbf{3 . 1}$ ( $9.7 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) and methylbenzenediamine $\mathbf{3 . 1 2}$ ( $6.1 \mathrm{mg}, 0.05 \mathrm{mmol}, 1$ equiv) were mixed in an NMR tube in DMSO-d $6(0.75 \mathrm{~mL})$. Reaction mixture was heated at $100^{\circ} \mathrm{C}$ in an oil bath. Reaction progress was monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy.

Reaction of methyldiazaborole with benzenediamine. An equimolar amount of benzenediamine $\mathbf{3 . 3}$ ( $0.208 \mathrm{~g}, 1 \mathrm{mmol}, 1$ equiv) and methyldiazaborole $\mathbf{3 . 1 3}(0.108 \mathrm{mg}, 1$ mmol, 1 equiv) were mixed in 1,4-dioxane ( 15 mL ) in a 50 mL round bottom flask. The reaction mixture was heated at $50^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR was obtained periodically for 278 h .

An equimolar amount of benzenediamine $\mathbf{3 . 3}$ ( $5.4 \mathrm{mg}, 0.05 \mathrm{mmol}, 1$ equiv) and methyldiazaborole 3.13 ( $10.4 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1 equiv) were mixed in NMR tube in DMSO ( 0.75 mL ). Reaction mixture was heated at $100^{\circ} \mathrm{C}$ in an oil bath. Reaction progress was monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy.

Table 6
${ }^{1} H$-NMR signals used to determine the percent conversion

| Reaction | starting material | product |
| ---: | :---: | :---: |
| $\mathbf{3 . 1}+\mathbf{3 . 4}$ | $\delta 7.74 \mathrm{ppm}(\mathbf{3 . 1})$ | $\delta 7.57 \mathrm{ppm} \mathrm{( } \mathrm{\mathbf{3.5})}$ |
| $\mathbf{3 . 1}+\mathbf{3 . 1 2}$ | $\delta 2.02 \mathrm{ppm} \mathrm{( } \mathrm{\mathbf{3.12})}$ | $\delta 2.26 \mathrm{ppm} \mathrm{( } \mathrm{\mathbf{3.13})}$ |
| $\mathbf{3 . 3}+\mathbf{3 . 1 3}$ | $\delta 7.26 \mathrm{ppm} \mathrm{( } \mathrm{\mathbf{3.13})}$ | $\delta 2.02 \mathrm{ppm} \mathrm{( } \mathrm{\mathbf{3.12})}$ |

## CHAPTER IV

## Computational study of diazaborole analogues

### 4.1 Background

Computational chemistry can be used to predict the characteristics of novel molecules, identify additional information for synthesized molecules, compare the properties of structurally analogous molecules (isostructural or isosteric), and identify the favorability of product formation in a reaction by calculating thermodynamic parameters. Bond lengths, interatomic distances, molecular geometry, dipole moments, vibrational frequencies, spectroscopic information, solvation results, thermodynamics, and electric charge densities/electrostatic potentials are the some of the types of information that can be estimated using computational calculations.

The blue luminescence and semi-conductor properties of diazaborole depend on the extended $\pi$-conjugation. The $\pi$-accepter characteristics of boron primarily serve to reduce the HOMO-LUMO energy gap. Computational calculations have been utilized to show HOMO-LUMO energies of diazaborole derivatives and thereby explain their different absorption and emission properties. ${ }^{76,81,89-98}$ Furthermore, Weber et al., ${ }^{90,93}$ and Lu-Yi Zou et al., ${ }^{92}$ validated computationally calculated bond lengths and bond angles by comparing them with XRD structure results. Moreover, computational chemistry has been utilized to represent additional information of diazaboroles such as electrostatic potentials, ${ }^{76,94,99}$ dipole moments, ${ }^{94}$ and ring currents in the diazaborole system as indicated by nucleus-independent chemical shift values. ${ }^{96,99}$ Most recently, Northrop and Goldberg used computational calculations to determine thermodynamics of diazaborole and some of its analogues alongside experimental information. ${ }^{76}$

### 4.2 Objectives

In this study, nine diazaborole analogues that have been synthesized and studied in our lab as building blocks for covalent organic framework (COF) development were investigated computationally (Figure 64).

The first objective of this study was to identify the structural alterations of the molecules by comparing their bond lengths and bond angles. The second objective was to investigate the electron density maps and nucleus-independent chemical shift (NICS) values in order to identify how heteroatoms and substituent groups affect to the electron density and chemical environment of the molecules. The third objective was to calculate the Gibbs free energies of formation for the diazaborole analogues in the gas phase and in selected solvents.

DAB derivatives

4.1

4.4

DAB analogues

4.7

4.2

4.5

4.8

4.3

4.6

4.9

Figure 64. Computationally studied diazaborole analogues.

### 4.3 Results and Discussion

### 4.3.1 Bond length and bond angle.

The bond lengths and bond angles of diazaborole analogues were measured computationally to understand the impact of functional groups and heteroatoms on the molecular geometry (Figure 65). In order to obtain the most stable orientation (global minimum), the molecules were first scanned through all possible dihedral angles in the gas phase using a computationally inexpensive Hartree-Fock (HF) method and minimal basis set (3-21G). Then, the obtained geometries were subjected to full convergence geometry optimization using density functional theory (DFT) and B3LYP function with the $6-311++G(d, p)$ basis set. Finally, frequency calculations were performed and the global minimum orientations were confirmed by realizing the absence of any imaginary (negative) vibrational frequencies of the optimized structures using the DFT/B3LYP/6$311++G(d, p)$ method.

The $6-311 \mathrm{G}$ basis set was used to perform all optimization and frequency calculations in order to obtain the most reliable bond lengths and bond angles. The numbers in the basis set (6-311) represent that the six Gaussian functions are summed to describe the inner shell orbital (core electrons) and three Slater orbitals (triple zeta), which are comprised of $3,1,1$ Gaussian functions, respectively, to describe the valence electrons of the molecule. Additional functions are added to describe polarization of the electron density of the atoms in a molecule. The d-characteristics in p-orbitals and the pcharacteristics in s-orbitals of hydrogen were considered for the calculations in order to reach more accurate results. Further, full diffuse function (++) was employed to capture the total electron distribution of atoms including the excited state due to the presence of
lone pair electrons on the heteroatoms of diazaborole analogues. Table 7 shows the bond length data for the diazaborole analogues. The bond lengths of the boron-carbon, the two boron heteroatom, and two heteroatom-carbon bonds were observed because they were expected to be more sensitive to structural changes (Figure 65). Dioxaborole 4.7 possesses the shortest bond lengths ( $1.39 \AA$ ) due to the high electronegativity of the oxygen in the B-O bond. In oxazaborole 4.8, the B-O bond length is $1.40 \AA$ and the N-B bond length is relatively longer ( $1.44 \AA$ ). The other diazaborole derivatives possess similar bond lengths ( $1.44 \AA$ for the B-N bond). The calculated B-N bond length ( $1.44 \AA$ ) in this study for diazaborole 4.1 is the same as Northrop's calculated B-N bond length for tert-butyl substituted diazaborole (1.44 $\AA$ B-N bond). ${ }^{76}$


Figure 65. The isostructural framework of diazaborole.

Table 7
Bond lengths of diazaborole analogues

| Molecule | Bonds |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1-6 | 4-6 | 5-6 | 2-4 | 3-5 |
|  | $\begin{aligned} & 1.56 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \text { N-C } \end{aligned}$ |
|  | $\begin{aligned} & 1.56 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \text { N-C } \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ |
|  | $\begin{aligned} & 1.55 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ |
|  | $\begin{aligned} & 1.56 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ |
|  | $\begin{aligned} & 1.56 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{~N}-\mathrm{C} \end{aligned}$ |


| Molecule | Bonds |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1-6 | 4-6 | 5-6 | 2-4 | 3-5 |
|  | $\begin{aligned} & 1.56 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \mathrm{~N}-\mathrm{B} \end{aligned}$ | $\begin{aligned} & 1.44 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \text { N-C } \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \text { N-C } \end{aligned}$ |
|  | $\begin{aligned} & 1.54 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \mathrm{O}-\mathrm{B} \end{aligned}$ | $\begin{aligned} & 1.39 \\ & \text { O-B } \end{aligned}$ | $\begin{aligned} & 1.38 \\ & \mathrm{O}-\mathrm{C} \end{aligned}$ | $\begin{aligned} & 1.38 \\ & \mathrm{O}-\mathrm{C} \end{aligned}$ |
|  | $\begin{aligned} & 1.55 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.43 \\ & \mathrm{~N}-\mathrm{B} \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \mathrm{O}-\mathrm{B} \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \text { N-C } \end{aligned}$ | $\begin{aligned} & 1.37 \\ & \mathrm{O}-\mathrm{C} \end{aligned}$ |
|  | $\begin{aligned} & 1.55 \\ & \text { C-B } \end{aligned}$ | $\begin{aligned} & 1.43 \\ & \text { N-B } \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \mathrm{O}-\mathrm{B} \end{aligned}$ | $\begin{aligned} & 1.40 \\ & \text { N-C } \end{aligned}$ | $\begin{aligned} & 1.37 \\ & \mathrm{O}-\mathrm{C} \end{aligned}$ |

When considered separately, the two phenyl rings (A and B), and the fivemembered borole ring (C) have planar geometries. However, when they are incorporated into a single molecule, the geometry tends to change due to the steric hindrance of neighboring atoms. Dioxaborole 4.7 and oxazaborole 4.8 have a $0^{\circ}$ dihedral angle between the A and C rings (Figure 65). The H atoms on the N of diazaborole 4.1 have a steric interaction with the ortho-Hs of the A ring, and therefore the lowest energy
conformation has a $20^{\circ}$ dihedral angle between the A and C rings. As expected, the A and B ring substituents $\left(\mathrm{Br}, \mathrm{OCH}_{3}, \mathrm{CH}_{3}\right)$ have little effect on the dihedral angle (bromodiazaborole $4.2=21^{\circ}$, methoxydiazaborole $4.3=18^{\circ}$ and methyldiazaborole 4.4 $=21^{\circ}$ ). As the steric repulsion increases with larger methyl groups, the dihedral angle between the A and C rings increases ( $\mathrm{N}, \mathrm{N}^{\prime}$-dimethyldiazaborole $4.5=53^{\circ}$ and N methyldiazaborole $4.6=43^{\circ}$ ).

Table 8
Rotational barriers of diazaborole analogues

|  | Dihedral angle | $G_{\text {Actual }}$ | GPlanar | $\Delta G_{\text {Difference }}$ | $\Delta G_{\text {Difference }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\alpha$ | $($ Hartrees $)$ | $($ Hartrees $)$ | $($ Hartrees $)$ | $(\mathrm{kJ} / \mathrm{mol})$ |
| $\mathbf{4 . 1}$ | 20 | -598.351 | -598.349 | 0.002 | 5 |
| 4.2 | 21 | -3171.907 | -3171.905 | 0.002 | 5 |
| 4.3 | 18 | -712.879 | -712.877 | 0.002 | 6 |
| $\mathbf{4 . 4}$ | 21 | -637.651 | -637.649 | 0.002 | 5 |
| $\mathbf{4 . 5}$ | 53 | -676.930 | -676.918 | 0.012 | 32 |
| $\mathbf{4 . 6}$ | 43 | -637.640 | -637.635 | 0.005 | 13 |
| $\mathbf{4 . 7}$ | 0 | -638.126 | -638.126 | 0.000 | 0 |
| $\mathbf{4 . 8}$ | 0 | -618.238 | -618.238 | 0.000 | 0 |
| $\mathbf{4 . 9}$ | 29 | -657.527 | -657.525 | 0.002 | 6 |

The energy differences between the optimized geometry and the coplanar geometry of diazaborole analogues are very low ( $5-32 \mathrm{~kJ} / \mathrm{mol}$ ) (Table 8 ) and may be overcome by the thermal energy of the system at the reaction temperature, due to molecular collisions and heat from external sources or the environment. Therefore, planar
geometries were considered for the study of electrostatic potential diagrams and NICS calculations to obtain a rational comparison of diazaborole analogues.

### 4.3.2 Electrostatic potentials.

The electrostatic potential map (EPM) or electron density map reveals the regions of relative electron richness or deficiency in a molecule, and thereby its behavior as an electron acceptor or donor (Figure 66). The electron-rich regions (red) of the map are electron donating, whereas electron poor (blue) regions are accepting. The EPMs of 4.14.9 (iso values:-0.02 to 0.02 ) were obtained using DFT methods at the B3LYP/6$311++G(d, p)$ level.


Figure 66. EPMs of diazaborole analogues 4.1-4.9.

The EPMs show that diazaborole derivatives 4.1-4.6 have electron accumulation on the B ring, which indicates the possibility of diazaboroles being electron donors using
this electron rich site. However, the electron density of dioxaborole 4.7 around the A ring is less intense (Table 9). Further, except for bromodiazaborole 4.2 and dioxaborole 4.7, other all molecules possess high electron density on the A ring. It is clear that the electron affinity of bromine in the diazaborole 4.2 and dioxaborole 4.7 lead to reduced electron density on the A ring.

Table 9
Estimated charge densities/surface mapped values of diazaborole analogues

| Molecule | A ring - Center | B ring - center | C ring - Center |
| :---: | :---: | :---: | :---: |
| $\mathbf{4 . 1}$ | -0.02180 | -0.02976 | -0.01529 |
| $\mathbf{4 . 2}$ | -0.01328 | -0.02631 | -0.01051 |
| $\mathbf{4 . 3}$ | -0.02238 | -0.03165 | -0.01852 |
| $\mathbf{4 . 4}$ | -0.02249 | -0.02958 | -0.01629 |
| $\mathbf{4 . 5}$ | -0.02163 | -0.03017 | -0.01522 |
| $\mathbf{4 . 6}$ | -0.02239 | -0.03072 | -0.01546 |
| $\mathbf{4 . 7}$ | -0.01921 | -0.01599 | -0.07162 |
| $\mathbf{4 . 8}$ | -0.02108 | -0.02358 | -0.00432 |
| $\mathbf{4 . 9}$ | -0.02211 | -0.02355 | -0.00448 |

### 4.3.3 NICS value.

The Hückel $4 n+2$ rule for $\pi$-conjugated molecules indicates aromaticity and the 4 n rule indicates antiaromaticity. ${ }^{100}$ The nucleus-independent chemical shift (NICS) was proposed Schleyer et al. in 1996. NICS is a simple and effective aromatic probe as it measures aromaticity at the desired position by introducing a "theoretical nuclei $(\mathrm{Bq})$ " to probe the electron shielding at that position using modern quantum chemical methods. ${ }^{99}$ Since NICS at a point in space is zero, reference molecules are not required for the calculations and the areas that have high magnetic shielding produce negative NICS
values (stronger diatropic ring currents). In contrast, positive NICS values represent paratropic ring currents (antiaromaticity). ${ }^{99,100}$ Earlier on, only NICS (0) (NICS at the geometric center of the aromatic ring) was the position used to probe for aromaticity, however, it was realized that the sigma frame influences the $\pi$-conjugation at the ring center. ${ }^{101}$ Therefore, the acquisition of many NICS values from a scan at several points has been determined as a better approach as it shows aromaticity attenuation in several directions. ${ }^{100,101}$ Previously, Molander et. al. reported the NICS values of diazaborole 4.1 (Table 10) and its carbon isosteres at the GIAO-B3LYP/6-311+G(2d,p) level of theory. ${ }^{99}$


Figure 67. Pictorial representation of the calculated NICS indices above the borole and phenyl rings.

Table 10
Reported NICS values for diazaborole 4.1 ${ }^{99}$

| Diazaborole | NICS (0) <br> B Ring <br> ppm | NICS (1) <br> B Ring <br> ppm | NICS (0) <br> C Ring <br> ppm | NICS (1) <br> C Ring <br> ppm |
| :---: | :---: | :---: | :---: | :---: |

For the current study, the NICS values of planar diazaborole analogues (4.1-4.9) were calculated using the DFT-GIAO method with the intent of obtaining NICS values along the vertical axis above the mean plane of the five-membered borole ring. In order to ascertain the distribution of aromaticity of the borole ring, five NICS values were calculated in $1 \AA$ increments (Figure 67 and Table 11).

Table 11
NICS values for diazaboroles 4.1-4.9 along the vertical axis above the $C$ ring

| Molecule | NICS (0C) <br> ppm | NICS (1C) <br> ppm | NICS (2C) <br> ppm | NICS (3C) <br> ppm | NICS (4C) <br> ppm |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{4 . 1}$ | -9.50 | -5.88 | -2.21 | -1.25 | -0.73 |
| $\mathbf{4 . 2}$ | -8.03 | -5.73 | -2.27 | -1.29 | -0.74 |
| $\mathbf{4 . 3}$ | -7.92 | -5.61 | -2.20 | -1.25 | -0.73 |
| $\mathbf{4 . 4}$ | -7.69 | -5.53 | -2.18 | -1.25 | -0.72 |
| $\mathbf{4 . 5}$ | -8.40 | -6.18 | -2.66 | -1.42 | -0.87 |
| $\mathbf{4 . 6}$ | -8.03 | -5.77 | -2.37 | -1.24 | -0.76 |
| $\mathbf{4 . 7}$ | -4.16 | -3.64 | -1.94 | -1.23 | -0.74 |
| $\mathbf{4 . 8}$ | -5.31 | -4.28 | -2.06 | -1.2 | -0.75 |
| $\mathbf{4 . 9}$ | -5.54 | -4.37 | -2.37 | -1.25 | -0.76 |

Among diazaborole derivatives, diazaborole 4.1 possesses NICS (1)=-5.88 ppm. Aromaticity on the five-membered ring is decreased by an electron withdrawing group substitution (bromodiazaborole $4.2($ NICS $(1)=-5.73 \mathrm{ppm})$ on the A ring as well as by electron donating group substitution to the A ring (methoxydiazaborole 4.3 (NICS (1) = $5.61 \mathrm{ppm})$ and B ring (methyldiazaborole $4.4(\mathrm{NICS}(1)=-5.53 \mathrm{ppm})$. However, the
substitution of methyl groups on the nitrogen increases the aromaticity. This trend can be seen in diazaborole as well as oxazaborole. Theoretical values predict that dioxaborole 4.7 possesses the lowest and $N, N^{\prime}$-dimethyldiazaborole 4.5 has the greatest NICS (1) value. The analogues that do not have 2 nitrogen atoms $(4.7,4.8,4.9)$ have lower aromaticity than the diazaboroles 4.1-4.6.

Comparison of the obtained NICS values with Molander's results show slightly different in NICS (1) values ( -5.88 ppm and -5.30 ppm ) and greater difference in NICS (0) values ( -9.50 ppm and -6.32 ppm ). The differences might originate from the two different polarization functions that have been used for the calculations.

The two NICS indices at distances of $0.0 \AA$ and $1.0 \AA$ (above the A and B rings) were also calculated to determine the aromaticity above the phenyl rings of diazaborole analogues 4.1-4.9 (Table 12).

Table 12
NICS values for diazaboroles 4.1-4.9 along the vertical axis of $A$ and $B$ rings

| Molecule | Ring A |  | Ring B |  |
| :---: | :---: | :---: | :---: | :---: |
|  | NICS (0) <br> ppm | NICS (1) <br> ppm | NICS (0) <br> ppm | NICS (1) <br> ppm |
| $\mathbf{4 . 1}$ | -6.78 | -9.49 | -9.59 | -10.17 |
| $\mathbf{4 . 2}$ | -7.27 | -9.20 | -9.60 | -10.21 |
| $\mathbf{4 . 3}$ | -7.67 | -9.18 | -9.56 | -10.15 |
| $\mathbf{4 . 4}$ | -6.80 | -9.52 | -9.41 | -9.88 |
| $\mathbf{4 . 5}$ | -6.96 | -9.81 | -9.56 | -10.29 |
| $\mathbf{4 . 6}$ | -6.83 | -9.50 | -9.58 | -10.18 |
| $\mathbf{4 . 7}$ | -6.95 | -9.70 | -10.48 | -10.41 |


|  | Ring A |  |  | Ring B |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Molecule | NICS (0) <br> ppm | NICS (1) <br> ppm | NICS (0) <br> ppm | NICS (1) <br> ppm |  |
| $\mathbf{4 . 8}$ | -6.88 | -9.62 | -9.94 | -10.25 |  |
| $\mathbf{4 . 9}$ | -6.93 | -9.69 | -9.94 | -10.32 |  |

The results in Table 12 show that 4.1-4.9 follow a similar trend. NICS (0) comprises a lower value than NICS (1) and the B ring possesses greater aromaticity than the A ring. Dimethyldiazaborole 4.5 has the highest NICS (1) value ( -9.81 ppm ) on the A ring, whereas methoxydiazaborole $4.3(\operatorname{NICS}(1)=-9.18 \mathrm{ppm})$ possess the lowest aromaticity. When comparing diazaborole derivatives, the aromaticity on the A and B rings increases with $N$-methyl substitution. Aromaticity on the A ring decreases with both bromo and methoxy substitution $(\operatorname{NICS}(1)=-9.20 \mathrm{ppm}$ and 9.18 ppm , respectively) compared to diazaborole $4.1($ NICS $(1)=-9.49 \mathrm{ppm})$. However, methyl substitution on the B ring (methyldiazaborole 4.4) (NICS (1) $=-9.52 \mathrm{ppm})$ does not have any impact on the A ring aromaticity whereas the aromaticity on the B ring decreased $(\operatorname{NICS}(1)=-9.88$ $\mathrm{ppm})$. The highest NICS values on the B ring were found on dioxaborole 4.5 (-10.41 $\mathrm{ppm})$. While the lowest value is obtained with methyldiazaborole $4.4($ NICS $(1)=-9.88$ ppm). Again, the difference of the computational functions, that have been used for the calculation of NICS (0) and NICS (1) in this study (GIAO-B3LYP/6-311++G(d,p)), might result in values different from Molander's (GIAO-B3LYP/6-311+G(2d,p)) (NICS $(1)=-9.34 \mathrm{ppm}$ and $-9.96 \mathrm{ppm})$ and this study $(\mathrm{NICS}(1)=-9.59 \mathrm{ppm}$ and $-10.17 \mathrm{ppm})$.
4.3.4 Thermodynamic calculations. Recently, Northrop and Goldberg reported the Gibbs free energy values of tertiary butyl substituted diazaborole derivatives (Figure
$68)$ in non-aqueous solutions (chloroform ( $\varepsilon=4.7113$ )) in the polarizable continuum model (PCM) reaction field model using four levels of theories: B3LYP/6-311+G(d,p), M06-2X/6-31+G(d,P), CBS-QB3, AND MP2/aug-cc-PVDZ. Besides that report, the computational calculations for thermodynamics of diazaborole analogues in the solvent phase have been unreported. Therefore, the Gibbs free energies of the formation of diazaborole analogues 4.1-4.8 in the solvents and conditions that were used experimentally (Chapter II) were performed. Oxazaborole 4.9 had a very large value for the Gibbs free energy. Initially, the Gibbs free energies of the formation $\left(\Delta \mathrm{G}_{\text {formation }}\right)$ of diazaborole in the gas phase at room temperature ( 298 K ) were calculated using the equation of $\Delta \mathrm{G}_{\text {formation }}=\mathrm{G}_{\text {products- }} \mathrm{G}$ starting materials. (Table 13 shows the $\Delta \mathrm{G}$ calculation of diazaborole in 1,4-dioxane at room temperature) Then, the Gibbs free energies of the formation of diazaborole in solvent phase were recalculated using gas phase optimized structures at the experimental reaction temperatures. (Table 14).







Figure 68. Diazaborole derivatives studied by Northrop and group.

## Table 13

$\Delta G$ calculation of diazaborole analogues in 1,4-dioxane

| Products (P) |  |  |  |  | Starting Materials (SM) |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | DAB <br> isostructure <br> (Hartrees) | $2 \mathrm{H}_{2} \mathrm{O}$ <br> (Hartrees) | PBA <br> derivative <br> (Hartrees) | BDA <br> derivative <br> (Hartrees) | $\Delta$ G (P-SM) <br> (Hartrees) |  |
| $\mathbf{4 . 1}$ | -598.35 | -152.91 | -408.30 | -342.96 | -0.002 |  |
| $\mathbf{4 . 2}$ | -3171.91 | -152.91 | -2981.86 | -342.96 | 0.001 |  |


| Products $(\mathrm{P})$ |  |  |  |  | Starting Materials (SM) |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :---: | :---: |
| $\mathbf{4 . 3}$ | -712.88 | -152.91 | -522.83 | -342.96 | -0.001 |  |  |
| $\mathbf{4 . 4}$ | -637.65 | -152.91 | -408.30 | -382.26 | -0.001 |  |  |
| $\mathbf{4 . 5}$ | -637.64 | -152.91 | -408.30 | -382.25 | 0.001 |  |  |
| $\mathbf{4 . 6}$ | -676.93 | -152.91 | -408.30 | -421.53 | -0.003 |  |  |
| $\mathbf{4 . 7}$ | -638.13 | -152.91 | -408.30 | -382.73 | -0.004 |  |  |
| $\mathbf{4 . 8}$ | -618.24 | -152.91 | -408.30 | -362.84 | -0.001 |  |  |
| $\mathbf{4 . 9}$ | -657.53 | -152.91 | -408.30 | -427.69 | 25.552 |  |  |
| Table 14 |  |  |  |  |  |  |  |

Gibbs free energies of the formation of diazaborole analogues in gas the phase

|  | Gas Phase |  |  |
| :---: | :---: | :---: | :---: |
| Molecule | $25{ }^{\circ} \mathrm{C}$ <br> $(\mathrm{kJ} / \mathrm{mol})$ | $50{ }^{\circ} \mathrm{C}$ <br> $(\mathrm{kJ} / \mathrm{mol})$ | $100^{\circ} \mathrm{C}$ <br> $(\mathrm{kJ} / \mathrm{mol})$ |
| $\mathbf{4 . 1}$ | -5.16 | -8.94 | -16.58 |
| 4.2 | 1.77 | -9.00 | -16.63 |
| 4.3 | -3.31 | -7.70 | -15.39 |
| $\mathbf{4 . 4}$ | -2.78 | -6.80 | -14.44 |
| $\mathbf{4 . 5}$ | -7.45 | -10.88 | -17.69 |
| $\mathbf{4 . 6}$ | 3.67 | 0.56 | -6.30 |
| $\mathbf{4 . 7}$ | -10.31 | -13.40 | -20.16 |
| $\mathbf{4 . 8}$ | -3.25 | -6.50 | -12.98 |

The Gibbs free energies $(\Delta \mathrm{G})$ of diazaborole analogues in the gas phase show an increasing favorability of formation with increased temperature. All the analogues in gas phase possess higher reaction favorability at $100^{\circ} \mathrm{C}$ and lowest at $25^{\circ} \mathrm{C}$. Finally, the optimized structures, which were calculated in gas phase and reaction temperatures, were subjected to optimization and frequency calculations in solvent phase (acetonitrile, tetrahydrofuran, methanol, dioxane, butanol, chloroform, and dimethylsulfoxide) using the Gaussian G09W default SCRF (self-consistent reaction field) method and the default solvation method (IEFPCM) (Table 15).

Table 15
Gibbs free energies of the formation of diazaborole analogues in experimentally studied solvents

|  | Solvent phase |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  | $\mathrm{CH}_{3} \mathrm{CN}$ | THF | methanol | dioxane | butanol | $\mathrm{CHCl}_{3}$ | DMSO |
| $25^{\circ} \mathrm{C}$ | $25^{\circ} \mathrm{C}$ | $25^{\circ} \mathrm{C}$ | $50{ }^{\circ} \mathrm{C}$ | $50^{\circ} \mathrm{C}$ | $50^{\circ} \mathrm{C}$ | $100{ }^{\circ} \mathrm{C}$ |  |
|  | $(\mathrm{kJ} / \mathrm{mol})$ | $(\mathrm{kJ} / \mathrm{mol})$ | $(\mathrm{kJ} / \mathrm{mol})$ | $(\mathrm{kJ} / \mathrm{mol})$ | $(\mathrm{kJ} / \mathrm{mol})$ | $(\mathrm{kJ} / \mathrm{mol})$ | $(\mathrm{kJ} / \mathrm{mol})$ |
| $\mathbf{4 . 1}$ | -7.61 | -5.15 | -7.67 | -14.85 | -9.63 | 3.00 | -2.54 |
| 4.2 | -7.75 | -5.44 | -7.72 | -15.41 | -9.94 | 2.30 | 24.36 |
| $\mathbf{4 . 3}$ | -7.84 | -4.94 | -7.70 | -14.38 | -9.90 | -3.41 | 23.60 |
| $\mathbf{4 . 4}$ | -28.96 | -24.55 | -21.11 | -22.95 | -23.15 | -15.92 | -27.21 |
| 4.5 | -21.59 | -19.12 | -21.55 | -14.74 | -23.67 | -10.58 | -16.29 |
| $\mathbf{4 . 6}$ | -9.04 | -6.53 | -9.00 | -2.54 | -11.16 | 1.96 | -3.84 |
| $\mathbf{4 . 7}$ | -17.77 | -16.63 | -17.76 | -14.74 | -20.23 | -8.83 | -12.44 |
| $\mathbf{4 . 8}$ | -23.87 | -22.74 | -23.85 | -15.08 | -26.91 | -13.71 | -20.01 |

The $\Delta \mathrm{G}$ of formation of diazaborole analogues in THF, acetonitrile, methanol, 1,4-dioxane and 1-butanol have higher Gibbs free energy of formation than gas phase. However, this trend is reversed in $\mathrm{CHCl}_{3}$ and DMSO. In DMSO, all diazaborole analogues had lower $\Delta \mathrm{G}$ of formation values than in the gas phase at $100^{\circ} \mathrm{C}$ except methyldiazaborole 4.4. A similar trend was observed in $\mathrm{CHCl}_{3}$ where methyldiazaborole 4.4 and oxazaborole 4.8 obtained high $\Delta \mathrm{G}$ values in the solvent phase. One of the interesting observations of these calculations was that the methyl substituted analogues, $N, N$-dimethyldiazaborole $4.5, N$-methyldiazaborole 4.6 possess favorable $\Delta \mathrm{G}$ values in all solvent phases.

### 4.4 Conclusions

Bond length comparisons showed that dioxaborole 4.7 comprises the lowest $\mathrm{C}-\mathrm{B}$ bond length, while other all diazaborole analogues are estimated to possess nearly equal N-B bond lengths. Further, dioxaborole 4.7 and oxazaborole 4.8 have zero dihedral angle between ring A and ring C , while all other derivatives have nonplanar optimized structures. This observation can be explained by the steric hindrance of the H atoms or methyl groups of the N and the ortho-H atoms of ring A. Energy difference calculations between the optimized geometry and the coplanar geometry of diazaborole analogues reveal that the energy difference between optimized geometry and planar (restricting the dihedral angle between $A$ and $C$ Rings to 0 ) geometry is small $(5 \mathrm{~kJ} / \mathrm{mol}-32 \mathrm{~kJ} / \mathrm{mol})$.

The electrostatic potential maps of diazaborole analogues 4.1-4.9 revealed that all diazaborole derivatives 4.1-4.6 have an electron rich phenyl ring, whereas dioxaborole 4.7 possesses significantly less electron density. Further, EPMs disclose that the electron density is less due to the bromine and oxygen atoms in bromodiazaborole 4.2 and dioxaborole 4.6, respectively.

NICS calculations show that $N, N^{\prime}$-dimethyldiazaborole 4.5 has the greatest NICS (1) value. Further, aromaticity on the five-membered ring is enhanced with electron withdrawing substituents on ring A and decreases with electron donating substituent on the A and B rings.

The Gibbs free energy calculations show increased favorability for diazaborole formation at higher temperatures. Further, the Gibbs free energies of diazaborole analogues in acetonitrile, tetrahydrofuran, methanol and ethyl acetate at room temperature are higher than they are in gas phase. However, Gibbs free energies of
diazaborole analogues in $\mathrm{CHCl}_{3}$ at $50^{\circ} \mathrm{C}$ and DMSO at $100^{\circ} \mathrm{C}$ have lower values except methyldiazaborole 4.4 in both solvents and oxazaborole 4.8 in $\mathrm{CDCl}_{3}$.

### 4.5 Experimental

All calculations were performed with the Gaussian G09W suite of programs. Initially, the molecular structures were built within the GaussView 5.0 interface and then geometric optimization in the gas phase was carried out to obtain the global minimum orientation by scanning all easily rotating dihedral angles at the computationally cheap Hartree-Fock (HF) level with a minimal basis set (3-21G). Even though HF calculation with a minimal basis set does not approach a realistic result, it was used as a fast and comparative method to obtain the approximate global energy minima from conformational searches. Then, the most stable conformation obtained from the HF scan was subjected to full convergence geometry optimization using density functional theory (DFT) and B3LYP function with the $6-311++G(d, p)$ basis set to obtain a more realistic and reliable orientation. The molecule was then subjected to frequency analysis at the same level of theory to ensure the stationary points are minima in the absence of any imaginary vibrational frequencies.

NICS values were also computed with the DFT-B3LYP/6-311++G(d,p) method through the gauge-including atomic orbital method (GIAO) in Gaussian G09W. The magnetic shielding tensor was calculated for ghost atoms $(\mathrm{Bq})$ which were located at the geometrical centers of the two phenyl rings and the five-membered borole ring. Five NICS indices for the borole ring from the center (NICS (0)) and every $1 \AA$ above and two NICS indices along the center of two phenyl rings in every $1 \AA$ distance were calculated.

For the thermodynamic calculations, first, the $\Delta \mathrm{G}$ values of optimized structures of 4.1-4.9, its starting materials and byproduct $\left(\mathrm{H}_{2} \mathrm{O}\right)$ were obtained using DFT/6$311 \mathrm{G}++(\mathrm{d}, \mathrm{p})$ method and basis sets in gas phase at room temperature. The change in Gibbs free energies at room temperature was calculated using $\Delta \mathrm{G}=\mathrm{G}$ products- G starting materials equation. Then, the optimized structures were exposed to re-optimization and frequency calculations at reaction corresponding temperatures to obtain the $\Delta \mathrm{G}$ values at reaction temperatures in the gas phase. Finally, the molecules were subjected to optimization and frequency calculations at the reaction temperatures and appropriate solvent phase. All optimization and frequency calculations, to obtain thermodynamic parameters, were performed using DFT model with B3LYP/6-311++G(d,p) basis set.

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APPENDIX A - NMR spectra for the synthesized compounds


${ }^{1} H-N M R$ spectra of the products in the exchange reaction of diazaborole with bromophenylboronic acid under reflux Conditions at 2 h and 8.5 h reaction time

${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the products in the exchange reaction of diazaborole with bromophenylboronic acid at $50^{\circ} \mathrm{C}$ in 1,4-dioxane. ${ }^{1} \mathrm{H}$-NMR spectra were taken in $\mathrm{CDCl}_{3}$.

${ }^{1} \mathrm{H}$-NMR spectra of the products in the exchange reaction of diazaborole with methylbenzenediamine at room temperature in $\mathrm{CDCl}_{3}$.






## APPENDIX B - The output data for the computational studies

a) Computational data of optimized structures in gas phase

## 1. Diazaborole (4.1)

\%chk=T:\CHM\deg013\Janaka\Macrocycles\DAB analogous\DAB\DFT Calculations $\backslash$ DFT cal culations.chk


Optimization completed.
-- Stationary point found.

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.208582 (Hartree/Particle)
Thermal correction to Energy $=\quad 0.219963$
Thermal correction to Enthalpy= 0.220907
Thermal correction to Gibbs Free Energy= 0.170112
Sum of electronic and zero-point Energies $=\quad-598.312132$
Sum of electronic and thermal Energies $=\quad-598.300751$
Sum of electronic and thermal Enthalpies $=\quad-598.299806$
Sum of electronic and thermal Free Energies $=\quad-598.350601$

## 2. Bromodiazaborole (4.2)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous $\backslash \mathrm{DAB}$ analogous $\backslash \mathrm{DAB}$ Derivatives $\backslash \mathrm{B}$
r.DAB $\backslash$ DFT Calculations $\backslash$ Recalc $\backslash D F T$ CALCULATIONS.chk


| C | -4.49517 | -0.45902 | -0.40668 |
| :--- | :--- | :--- | :--- |
| C | -5.8906 | 0.42962 | 1.83142 |
| H | -3.97918 | 0.797 | 2.69885 |
| C | -5.88763 | -0.46949 | -0.41846 |
| H | -3.97382 | -0.82393 | -1.28603 |
| C | -6.57355 | -0.02225 | 0.7065 |
| H | -6.43547 | 0.77921 | 2.69909 |
| H | -6.43019 | -0.82274 | -1.28609 |
| Br | -8.49145 | -0.02873 | 0.70656 |

Item Value Threshold Converged?
Maximum Force $0.000214 \quad 0.000450$ YES
RMS Force 0.0000450 .000300 YES
Maximum Displacement $0.001277 \quad 0.001800$ YES
RMS Displacement $0.000260 \quad 0.001200$ YES
Predicted change in Energy=-1.842696D-07
Optimization completed.
-- Stationary point found.

## GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.198333 (Hartree/Particle)
Thermal correction to Energy $=\quad 0.211222$
Thermal correction to Enthalpy= 0.212167
Thermal correction to Gibbs Free Energy $=0.156540$
Sum of electronic and zero-point Energies= -3171.865327
Sum of electronic and thermal Energies $=\quad-3171.852438$
Sum of electronic and thermal Enthalpies $=\quad-3171.851494$
Sum of electronic and thermal Free Energies $=\quad-3171.907121$

## 3. Methoxydiazaborole (4.3)

\%chk=T:\CHM\deg013\Janaka\Macrocycles\DAB analogous\Methoxy DAB\DFT Calculations

```
.chk
```

\# opt=(z-matrix,maxcycle=500) freq b3lyp/6-311++g(d,p) geom=connectivity

```
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1
C
C 1 B1
C 2 B2 1 A1
```

| C |  | B3 |  | A2 |  | D1 | 0 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C | 4 | B4 |  | A3 | 2 | D2 | 0 |
| C | 1 | B5 | 2 | A4 | 3 | D3 | 0 |
| H | 3 | B6 | 2 | A5 | 1 | D4 | 0 |
| H | 4 | B7 | 3 | A6 | 2 | D5 | 0 |
| H | 5 | B8 | 4 | A7 | 3 | D6 | 0 |
| H | 6 | B9 | 1 | A8 | 2 | D7 | 0 |
| H | 1 | B10 | 6 | A9 | 5 | D8 | 0 |
| H | 2 | B11 | 1 | A10 | 6 | D9 | 0 |
| N | 1 | B12 | 6 | A11 | 5 | D10 | 0 |
| N | 2 | B13 | 1 | A12 | 6 | D11 | 0 |
| B | 14 | 4 B14 | 2 | A13 | 1 | D12 | 0 |
| C | 15 | 5 B15 | 14 | 4 A14 |  | 2 D13 |  |
| C |  | 6 B16 | 15 | 5 A15 |  | 14 D14 |  |
| C | 16 | 6 B17 | 15 | 5 A16 |  | 14 D15 |  |
| C | 17 | 7 B 18 | 16 | A17 |  | 15 D16 |  |
| H |  | 7 B19 | 16 | 6 A18 |  | 15 D17 |  |
| C | 18 | 8 B20 | 16 | A19 |  | 15 D18 |  |
| H |  | 8 B21 | 16 | 6 A20 |  | 15 D19 |  |
| C | 19 | B22 | 17 | 7 A 21 |  | 16 D20 |  |
| H |  | 9 B23 | 17 | 17 A22 |  | 16 D21 |  |
| H |  | 1 B 24 | 18 | A23 |  | 16 D22 |  |
| O |  | 3 B25 |  | A24 |  | 17 D23 |  |
| C |  | 6 B26 | 23 | A25 |  | 19 D24 |  |
| H | 27 | 7 B 27 | 26 | 6 A26 |  | 23 D25 |  |
| H | 27 | 7 B 28 | 26 | 6 A27 |  | 23 D26 |  |
| H | 27 | 7 B 29 | 26 | 6 A28 |  | 23 D27 |  |
| Variables: |  |  |  |  |  |  |  |
| B1 |  | 1.40094 |  |  |  |  |  |
| B2 |  | 1.37638 |  |  |  |  |  |
| B3 |  | 1.39024 |  |  |  |  |  |
| B4 |  | 1.3838 |  |  |  |  |  |
| B5 |  | 1.37637 |  |  |  |  |  |
| B6 |  | 1.07191 |  |  |  |  |  |
| B7 |  | 1.0717 |  |  |  |  |  |
| B8 |  | 1.0717 |  |  |  |  |  |
| B9 |  | 1.07192 |  |  |  |  |  |
| B10 |  | 2.0981 |  |  |  |  |  |
| B11 |  | 2.0982 |  |  |  |  |  |
| B12 |  | 1.3994 |  |  |  |  |  |
| B13 |  | 1.3993 |  |  |  |  |  |
| B14 |  | 1.4443 |  |  |  |  |  |
| B15 |  | 1.5551 |  |  |  |  |  |
| B16 |  | 1.3946 |  |  |  |  |  |
| B17 |  | 1.3946 |  |  |  |  |  |
| B18 |  | 1.3810 |  |  |  |  |  |


| B19 | 1.07276 |
| :--- | :---: |
| B20 | 1.38102 |
| B21 | 1.07279 |
| B22 | 1.38187 |
| B23 | 1.07081 |
| B24 | 1.07082 |
| B25 | 1.38727 |
| B26 | 1.45137 |
| B27 | 1.07776 |
| B28 | 1.08256 |
| B29 | 1.08257 |
| A1 | 120.66187 |
| A2 | 118.59955 |
| A3 | 120.73762 |
| A4 | 120.66712 |
| A5 | 120.80201 |
| A6 | 119.44371 |
| A7 | 119.81921 |
| A8 | 120.80454 |
| A9 | 107.10482 |
| A10 | 132.20877 |
| A11 | 131.01493 |
| A12 | 108.32098 |
| A13 | 109.54358 |
| A14 | 127.86459 |
| A15 | 121.20159 |
| A16 | 121.23911 |
| A17 | 121.39301 |
| A18 | 119.65407 |
| A19 | 121.38971 |
| A20 | 119.65334 |
| A21 | 119.8209 |
| A22 | 121.10104 |
| A23 | 121.09524 |
| A24 | 119.97583 |
| A25 | 116.29242 |
| A26 | 105.965 |
| A27 | 110.81494 |
| A28 | 110.82011 |
| D1 | 0.15801 |
| D2 | 0.01188 |
| D3 | -0.24642 |
| D4 | -179.9081 |
| D5 | 179.97903 |
| D6 | 179.95657 |
| D7 | -179.94139 |
|  |  |



## 4. Methyldiazaborole (4.4)

\%chk=T:\CHM\deg013\Janaka\Macrocycles\DAB analogous\methyl DAB\DFT Calculations.
chk
\# opt=maxcycle=500 freq rb3lyp/6-311++g(d,p) geom=connectivity

| Symbolic Z-matrix: |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Charge $=0$ Multiplicity $=1$ |  |  |  |  |  |  |  |
| C |  |  |  |  |  |  |  |
| C |  | B1 |  |  |  |  |  |
| C | 2 | B2 | 1 | A1 |  |  |  |
| C | 3 | B3 | 2 | A2 | 1 | D1 | 0 |
| C | 4 | B4 |  | A3 | 2 | D2 | 0 |
| C | 1 | B5 |  | A4 | 3 | D3 | 0 |
| H | 3 | B6 | 2 | A5 | 1 | D4 | 0 |
| H | 4 | B7 |  |  | 2 | D5 | 0 |
| H | 6 | B8 |  | A7 | 2 | D6 | 0 |
| H | 1 | B9 | 6 | A8 | 5 | D7 | 0 |
| H | 2 | B10 | 1 | A9 |  | D8 | 0 |
| N | 1 | B11 | 6 | A10 |  | 5 D9 | 0 |
| N | 2 | B12 | 1 | A11 |  | 6 D10 | 0 |
| B | 13 | 3 B13 | 2 | A12 |  | 1 D11 | 0 |
| C | 14 | 4 B14 |  | 3 A13 |  | $2 \quad$ D12 |  |
| C | 15 | 5 B15 |  | 4 A14 |  | 13 D13 |  |
| C |  | 5 B16 |  | 4 A15 |  | 13 D14 |  |
| C | 16 | B17 |  | 5 A16 |  | 14 D15 |  |
| H | 16 | 6 B18 |  | 5 A17 |  | 14 D16 |  |
| C | 17 | 7 B19 |  | 5 A18 |  | 14 D17 |  |
| H |  | 7 B 20 |  | 5 A19 |  | 14 D18 |  |
| C | 20 | B21 |  | 7 A20 |  | 15 D19 |  |
| H | 18 | B22 |  | 6 A21 |  | 15 D20 |  |
| H |  | B23 |  | 7 A22 |  | 15 D21 |  |
| H | 22 | B24 |  | 0 A23 |  | 17 D22 |  |
| C | 5 | B25 | 4 | A24 |  | D23 | 0 |
| H |  | B26 | 5 | A25 |  | 4 D24 | 0 |
| H |  | 6 B27 | 5 | A26 |  | 4 D25 | 0 |
| H | 26 | 6 B28 | 5 | A27 |  | 4 D26 | 0 |
| Variables: |  |  |  |  |  |  |  |
| B1 |  | 1.41281 |  |  |  |  |  |
| B2 |  | 1.38756 |  |  |  |  |  |
| B3 |  | 1.39878 |  |  |  |  |  |
| B4 |  | 1.40088 |  |  |  |  |  |
| B5 |  | 1.38871 |  |  |  |  |  |
| B6 |  | 1.08471 |  |  |  |  |  |
| B7 |  | 1.08465 |  |  |  |  |  |
| B8 |  | 1.08598 |  |  |  |  |  |
| B9 |  | 2.10012 |  |  |  |  |  |
| B10 |  | 2.1013 |  |  |  |  |  |
| B11 |  | 1.3947 |  |  |  |  |  |
| B12 |  | 1.3962 |  |  |  |  |  |
| B13 |  | 1.4382 |  |  |  |  |  |


| B14 | 1.55601 |
| :---: | :---: |
| B15 | 1.40612 |
| B16 | 1.40612 |
| B17 | 1.3927 |
| B18 | 1.08577 |
| B19 | 1.39268 |
| B20 | 1.08581 |
| B21 | 1.39433 |
| B22 | 1.08462 |
| B23 | 1.08462 |
| B24 | 1.08441 |
| B25 | 1.51167 |
| B26 | 1.09492 |
| B27 | 1.09487 |
| B28 | 1.09191 |
| A1 | 120.27839 |
| A2 | 118.37931 |
| A3 | 121.9815 |
| A4 | 120.91485 |
| A5 | 121.08564 |
| A6 | 118.94829 |
| A7 | 120.48614 |
| A8 | 106.94209 |
| A9 | 132.21273 |
| A10 | 131.12232 |
| A11 | 108.0648 |
| A12 | 109.6917 |
| A13 | 127.84268 |
| A14 | 121.42934 |
| A15 | 121.31073 |
| A16 | 121.55165 |
| A17 | 119.67086 |
| A18 | 121.56394 |
| A19 | 119.66614 |
| A20 | 120.003 |
| A21 | 119.97177 |
| A22 | 119.97937 |
| A23 | 120.19761 |
| A24 | 120.84092 |
| A25 | 111.46792 |
| A26 | 111.45362 |
| A27 | 111.19317 |
| D1 | 0.31064 |
| D2 | 0.02414 |
| D3 | -0.47554 |
| D4 | -179.82865 |


5. $\boldsymbol{N}$-Methyldiazaborole (4.5)
\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka\Macrocycles\DAB analogous\N-methyl DAB\DFT Calculation
s\DFT CALCULATIONS.chk
\# opt=(maxcycle=500) freq rb3lyp/6-311++g(d,p) geom=conne ctivity

| N-methyl DAB_DFT_Calculations |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |  |  |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |  |  |  |  |  |
| C |  |  |  |  |  |  |  |  |
| C |  | B1 |  |  |  |  |  |  |
| C |  | B2 | 1 | A1 |  |  |  |  |
| C |  | B3 | 2 | A2 | 1 D | D1 0 |  |  |
| C |  | B4 |  | A3 |  | D2 0 |  |  |
| C |  | B5 | 2 | A4 | 3 | D3 0 |  |  |
| H |  | B6 | 2 | A5 | 1 D | D4 |  |  |
| H |  | B7 | 3 | A6 | 2 D | D5 |  |  |
| H |  | B8 |  | A7 | 3 | D6 |  |  |
| H |  | B9 | 1 | A8 | 2 D | D7 |  |  |
| H |  | B10 | 1 | A9 | 6 | D8 | 0 |  |
| N |  | B11 | 6 | A10 | 5 | D9 | 0 |  |
| N |  | B12 | 1 | A11 | 6 | D10 | 0 |  |
| B | 13 | B13 | 2 | A12 | 1 | D11 | 0 | ) |
| C |  | B14 | 13 | A13 | 2 | D12 |  | 0 |
| C |  | B15 | 14 | A14 | 13 | 3 D13 |  | 0 |
| C |  | B16 | 14 | A15 | 13 | 3 D14 |  | 0 |
| C | 16 | B17 | 15 | A16 | 14 | 4 D15 |  | 0 |
| H | 16 | B18 | 15 | A17 |  | 4 D16 |  | 0 |
| C | 17 | B19 | 15 | A18 |  | 4 D17 |  | 0 |
| H | 17 | B20 | 15 | A19 | 14 | 4 D18 |  | 0 |
| C | 20 | B21 | 17 | A20 | 15 | 5 D19 |  | 0 |
| H | 18 | B22 | 16 | A21 |  | 5 D20 |  | 0 |
| H | 20 | B23 | 17 | A22 |  | 5 D21 |  | 0 |
| H | 22 | B24 | 20 | A23 |  | 7 D22 |  | 0 |
| C | 12 | B25 | 1 | A24 | 6 | D23 | 0 | ) |
| H | 26 | B26 | 12 | A25 | 1 | D24 |  | 0 |
| H | 26 | B27 | 12 | A26 | 1 | D25 |  | 0 |
| H | 26 | B28 | 12 | A27 | 1 | D26 |  | 0 |


| B1 | 1.4015 |
| :--- | :--- |
| B2 | 1.3756 |
| B3 | 1.39079 |
| B4 | 1.38307 |
| B5 | 1.37688 |
| B6 | 1.07192 |
| B7 | 1.07175 |
| B8 | 1.07178 |
| B9 | 1.07102 |
| B10 | 2.10198 |
| B11 | 1.39991 |
| B12 | 1.3975 |
| B13 | 1.4425 |
| B14 | 1.56011 |
| B15 | 1.39561 |
| B16 | 1.39465 |
| B17 | 1.38274 |
| B18 | 1.07318 |
| B19 | 1.38387 |
| B20 | 1.07272 |
| B21 | 1.38376 |
| B22 | 1.07228 |
| B23 | 1.07229 |
| B24 | 1.07215 |
| B25 | 1.45827 |
| B26 | 1.07931 |
| B27 | 1.08468 |
| B28 | 1.08518 |
| A1 | 120.79102 |
| A2 | 118.57201 |
| A3 | 120.70941 |
| A4 | 120.53404 |
| A5 | 120.81399 |
| A6 | 119.44755 |
| A7 | 119.81316 |
| A8 | 121.00084 |
| A9 | 131.78528 |
| A10 | 130.51852 |
| A11 | 108.09147 |
| A12 | 109.38835 |
| A13 | 125.92435 |
| A14 | 119.95967 |
| A15 | 122.09391 |
| A16 | 121.15646 |
| A17 | 119.43202 |
| A18 | 121.07811 |
| B1 |  |
| B1 | 10 |



| - Thermochemistry - |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Zero-point correction= |  |  |  |  | 0.236386 (Hartree/Particle) |  |
| Thermal correction to Energy= |  |  |  |  | 0.249329 |  |
| Thermal correction to Enthalpy= |  |  |  |  | 0.250273 |  |
| Thermal correction to Gibbs Free Energy= |  |  |  |  |  | 0.196404 |
| Sum of electronic and zero-point Energies= |  |  |  |  |  | -637.599559 |
| Sum of electronic and thermal Energies= |  |  |  |  |  | -637.586616 |
| Sum of electronic and thermal Enthalpies= |  |  |  |  |  | -637.585672 |
| Sum of electronic and thermal Free Energies= |  |  |  |  |  | -637.639541 |
| 6. $N, N^{\prime}$-Dimethyldiazaborole(4.6) |  |  |  |  |  |  |
| \%chk=T:\CHM\deg013\Janaka\Macrocycles $\backslash \mathrm{DAB}$ analogous\Dimethyl $\mathrm{DAB} \backslash \mathrm{DFT}$ |  |  |  |  |  |  |
| Calculation |  |  |  |  |  |  |
| \# opt=maxcycle=500 freq b3lyp/6-311++g(d,p) geom=connectivity |  |  |  |  |  |  |
| Symbolic Z-matrix: |  |  |  |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |  |  |  |
| C |  |  |  |  |  |  |
| C |  |  |  |  |  |  |
| C |  | B2 | 1 | A1 |  |  |
| C |  | B3 | 2 | A2 1 | 1 D1 0 | 0 |
| C |  | B4 | 3 | A3 2 | 2 D2 0 | 0 |
| C |  | B5 | 2 | A4 3 | 3 D3 0 | 0 |
| H |  | B6 |  | A5 1 | 1 D4 0 | 0 |
| H |  | B7 | 3 | A6 2 | 2 D5 0 | 0 |
| H |  | B8 | 4 | A7 3 | 3 D6 0 | 0 |
| H |  | B9 |  | A8 2 | 2 D7 0 | 0 |
| N | 1 | B10 | 6 | A9 | 5 D8 | 0 |
| N | 2 | B11 | 1 | A10 | 6 D9 | 0 |
| B | 11 | B12 | 1 | A11 | 6 D10 | 0 |
| C | 13 | B13 | 11 | 1 A12 | 1 D11 | 0 |
| C | 14 | B14 | 13 | 3 A13 | 11 D12 | 0 |
| C | 14 | B15 | 13 | 3 A14 | 11 D13 | 0 |
| C | 15 | B16 | 14 | 4 A15 | 13 D14 | 0 |
| H | 15 | B17 | 14 | 4 A16 | 13 D15 | 0 |
| C | 16 | B18 | 14 | 4 A17 | 13 D16 | 0 |
| H | 16 | B19 | 14 | 4 A18 | 13 D17 | 0 |
| C | 17 | B20 | 15 | A19 | 14 D18 | 0 |
| H | 17 | B21 | 15 | 5 A20 | 14 D19 | 0 |
| H | 19 | B22 | 16 | 6 A21 | 14 D20 | 0 |
| H | 21 | B23 | 17 | 7 A22 | 15 D21 | 0 |
| C |  | B24 | 1 | A23 | 6 D22 | 0 |


| H |  | B25 | 11 | A24 | 1 | D23 | 0 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H | 25 | B26 | 11 | A25 | 1 | D24 | 0 |
| H | 25 | B27 | 11 | A26 | 1 | D25 | 0 |
| C | 12 | B28 | 2 | A27 | 1 | D26 | 0 |
| H | 29 | B29 | 12 | A28 | 2 | D27 | 0 |
| H | 29 | B30 | 12 | A29 | 2 | D28 | 0 |
| H | 29 | B31 | 12 | A30 | , | D29 | 0 |
| Variables: |  |  |  |  |  |  |  |
| B1 |  | . 40188 |  |  |  |  |  |
| B2 |  | 1.37601 |  |  |  |  |  |
| B3 |  | 1.39173 |  |  |  |  |  |
| B4 |  | . 38229 |  |  |  |  |  |
| B5 |  | 1.37601 |  |  |  |  |  |
| B6 |  | . 07108 |  |  |  |  |  |
| B7 |  | . 07183 |  |  |  |  |  |
| B8 |  | . 07183 |  |  |  |  |  |
| B9 |  | 1.07108 |  |  |  |  |  |
| B10 |  | 1.39766 |  |  |  |  |  |
| B11 |  | 1.39765 |  |  |  |  |  |
| B12 |  | 1.44452 |  |  |  |  |  |
| B13 |  | 1.56303 |  |  |  |  |  |
| B14 |  | 1.39544 |  |  |  |  |  |
| B15 |  | 1.39545 |  |  |  |  |  |
| B16 |  | 1.38362 |  |  |  |  |  |
| B17 |  | 1.07312 |  |  |  |  |  |
| B18 |  | 1.38361 |  |  |  |  |  |
| B19 |  | 1.07312 |  |  |  |  |  |
| B20 |  | 1.38405 |  |  |  |  |  |
| B21 |  | 1.07231 |  |  |  |  |  |
| B22 |  | 1.07231 |  |  |  |  |  |
| B23 |  | 1.07214 |  |  |  |  |  |
| B24 |  | 1.45777 |  |  |  |  |  |
| B25 |  | 1.07939 |  |  |  |  |  |
| B26 |  | 1.08517 |  |  |  |  |  |
| B27 |  | 1.0849 |  |  |  |  |  |
| B28 |  | 1.45777 |  |  |  |  |  |
| B29 |  | 1.0794 |  |  |  |  |  |
| B30 |  | 1.08518 |  |  |  |  |  |
| B31 |  | 1.0849 |  |  |  |  |  |
| A1 |  | 20.66936 |  |  |  |  |  |
| A2 |  | 18.57569 |  |  |  |  |  |
| A3 |  | 20.75481 |  |  |  |  |  |
| A4 |  | 20.66975 |  |  |  |  |  |
| A5 |  | 21.0085 |  |  |  |  |  |
| A6 |  | 19.40865 |  |  |  |  |  |
| A7 |  | 19.83662 |  |  |  |  |  |


| A8 | 121.00825 |
| :--- | :---: |
| A9 | 130.59758 |
| A10 | 108.73212 |
| A11 | 108.52103 |
| A12 | 127.25416 |
| A13 | 121.05292 |
| A14 | 121.05043 |
| A15 | 121.12532 |
| A16 | 119.55008 |
| A17 | 121.12534 |
| A18 | 119.54975 |
| A19 | 120.03658 |
| A20 | 119.95327 |
| A21 | 119.95343 |
| A22 | 120.11139 |
| A23 | 121.7375 |
| A24 | 109.07755 |
| A25 | 111.17004 |
| A26 | 110.75896 |
| A27 | 121.73972 |
| A28 | 109.07693 |
| A29 | 111.17283 |
| A30 | 110.757 |
| D1 | -0.1079 |
| D2 | -0.01322 |
| D3 | 0.17222 |
| D4 | -179.9556 |
| D5 | -179.9548 |
| D6 | -179.98343 |
| D7 | -179.95968 |
| D8 | -179.95481 |
| D9 | -179.95094 |
| D10 | 179.91655 |
| D11 | 179.97451 |
| D12 | 126.3523 |
| D13 | -53.64768 |
| D14 | -179.77819 |
| D15 | -0.46236 |
| D16 | -179.77698 |
| D17 | -0.46264 |
| D18 | -0.44462 |
| D19 | 179.55259 |
| D20 | 179.55176 |
| D21 | -179.78058 |
| D22 | 2.97303 |
| D23 | 174.79391 |
|  |  |
| D2 |  |
| D2 |  |
| D2 | 103 |



## 7. Dioxaborole (4.7)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB Derivatives\D
OB\DFT Calculations\DFT Calculations.chk
\# opt=(maxcycle=500) freq b3lyp/6-311++g(d,p) geom=connectivity
Symbolic Z-matrix:
Charge $=0$ Multiplicity $=1$

| C | 0. | 0. | 0. |
| :--- | :--- | :--- | :--- |
| C | 0. | 0. | 1.38186 |
| C | 1.15955 | 0. | 2.10411 |
| C | 2.35231 0.00001 1.38341  <br> C 2.3523 0.00001 -0.00157 <br> C 1.15955 0. -0.72226 |  |  |






## 1. Diazaborole (4.1)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB Derivatives $\backslash \mathrm{D}$

AB\DFT_dihedral_0_Calculations\DFT_dihedral_0_CALCULATIONS.chk
\# opt=(modredundant,maxcycle=500,maxstep=30) freq rb3lyp/6-311++g(d,p) geom=connectivity int=grid=ultrafine
dihedral 0

| Symbolic Z-matrix: |  |  |  |
| :--- | :--- | :--- | :--- |
| Charge $=0$ | Multiplicity $=1$ |  |  |
| C | 1.91966 | 0.70617 | -0.02451 |
| C | 1.91965 | -0.70617 | 0.0245 |
| C | 3.11417 | -1.41723 | 0.04556 |
| C | 4.31243 | -0.69866 | 0.02159 |
| C | 4.31243 | 0.69866 | -0.02158 |
| C | 3.11417 | 1.41722 | -0.04556 |
| H | 3.11741 | -2.50128 | 0.08128 |
| H | 5.25447 | -1.23432 | 0.03822 |
| H | 5.25447 | 1.23432 | -0.0382 |
| H | 3.11741 | 2.50127 | -0.08129 |
| H | 0.36428 | 2.11663 | -0.03402 |
| H | 0.36428 | -2.11663 | 0.03399 |
| N | 0.5932 | 1.13674 | -0.0449 |
| N | 0.59319 | -1.13674 | 0.04488 |
| B | -0.28839 | 0. | 0. |
| C | -1.84417 | 0. | 0. |
| C | -2.57599 | -1.1997 | 0.0474 |
| C | -2.57599 | 1.1997 | -0.04739 |
| C | -3.96866 | -1.20419 | 0.04839 |
| H | -2.05039 | -2.14838 | 0.09928 |
| C | -3.96866 | 1.20419 | -0.04838 |
| H | -2.05039 | 2.14838 | -0.09928 |
| C | -4.6699 | 0. | 0. |
| H | -4.50746 | -2.14458 | 0.08988 |
| H | -4.50746 | 2.14458 | -0.08988 |
| H | -5.75429 | 0. | 0. |

Item Value Threshold Converged?
Maximum Force $0.000063 \quad 0.000450$ YES
RMS Force $0.000017 \quad 0.000300$ YES
Maximum Displacement $0.001343 \quad 0.001800$ YES
RMS Displacement $0.000271 \quad 0.001200$ YES
Predicted change in Energy=-2.268439D-07
Optimization completed.
-- Stationary point found.
Full mass-weighted force constant matrix:

| Low frequencies --- | -24.2611 | -6.8117 | -3.2342 | -2.6740 | -0.0009 | -0.0006 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Low frequencies --- | -0.0004 | 56.2676 | 86.9146 |  |  |  |

- Thermochemistry -

Zero-point correction=
Thermal correction to Energy=

$$
\begin{aligned}
& 0.208416 \text { (Hartree/Particle) } \\
& 0.218935
\end{aligned}
$$

| Thermal correction to Enthalpy $=$ | 0.219880 |
| :--- | :---: |
| Thermal correction to Gibbs Free Energy $=$ | 0.171867 |
| Sum of electronic and zero-point Energies $=$ | -598.312160 |
| Sum of electronic and thermal Energies $=$ | -598.301641 |
| Sum of electronic and thermal Enthalpies $=$ | -598.300697 |
| Sum of electronic and thermal Free Energies= | -598.348710 |

## 2. Bromodiazaborole (4.2)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB
Derivatives $\backslash \mathrm{B}$
r.DAB\DFT dihedral 0\DFT CALCULATIONS.chk
\# opt=(modredundant,maxcycle=500, maxstep=30) freq rb3lyp/6-311++g(d,p) geom=connectivity int=grid=ultrafine

| dihedral 0 |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
|  |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | -3.56829 | 0.70593 | 0.02587 |
| C | -3.56827 | -0.70591 | -0.02564 |
| C | -4.76261 | -1.41736 | -0.04752 |
| C | -5.96041 | -0.69876 | -0.0226 |
| C | -5.96043 | 0.69873 | 0.0222 |
| C | -4.76265 | 1.41737 | 0.04742 |
| H | -4.76576 | -2.50132 | -0.08458 |
| H | -6.90253 | -1.23414 | -0.0399 |
| H | -6.90256 | 1.23409 | 0.03926 |
| H | -4.76584 | 2.50132 | 0.08446 |
| H | -2.01339 | 2.11703 | 0.03462 |
| H | -2.01332 | -2.11695 | -0.03441 |
| N | -2.24145 | 1.13689 | 0.04777 |
| N | -2.24142 | -1.13682 | -0.04741 |
| B | -1.36167 | 0.00006 | 0.00006 |
| C | 0.19447 | 0.00007 | 0.00005 |
| C | 0.92835 | -1.19722 | -0.05021 |
| C | 0.9284 | 1.19731 | 0.05027 |
| C | 2.32084 | -1.21033 | -0.05173 |
| H | 0.4082 | -2.14835 | -0.10505 |
| C | 2.32089 | 1.21034 | 0.05177 |
| H | 0.40829 | 2.14845 | 0.10514 |
| C | 3.0053 | 0.0 .0 | 00001 |
| H | 2.86453 | -2.14541 | -0.09608 |



## 3. Methoxydiazaborole (4.3)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB Derivatives $\backslash \mathrm{M}$
ethoxy DAB\Dihedral 0\DFT CALCULATIONS.chk

```
# opt=(modredundant,maxcycle=500,maxstep=30) freq rb3lyp/6-311++g(d,p)
geom=connectivity int=grid=ultrafine
-------------------------------------------------------------------------------
---------------
dihedral 0 freeze
```

-----------------
Charge $=0$ Multiplicity $=1$
C $\quad-2.78022-0.73853-0.01673$
$\begin{array}{llll}\mathrm{C} & -2.83623 & 0.67353 & 0.00807\end{array}$
$\begin{array}{llll}\text { C } & -4.05802 & 1.33651 & 0.00879\end{array}$
$\begin{array}{llll}\mathrm{C} & -5.22738 & 0.57084 & -0.01165\end{array}$
$\begin{array}{llllll}\mathrm{C} & -5.17204 & -0.8255 & -0.03111\end{array}$
$\begin{array}{lllll}C & -3.94557 & -1.49616 & -0.03443\end{array}$


## 4. Methyldiazaborole (4.4)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB
Derivatives $\backslash m$
ethyl DAB\DFT_dihedral_0_Calculations\DFT CALCULATIONS.chk
\# opt=(modredundant, maxcycle=500, maxstep=30) freq rb3lyp/6-311++g(d,p) geom=connectivity int=grid=ultrafine

| dihedral 0 |  |
| :---: | :---: |
| Symbolic Z-matrix: |  |
|  |  |
| Charge $=0$ Multiplicity $=1$ |  |
| C | -1.52988 -0.4907 -0.0631 |
| C | -1.44148 0.917530 .00801 |
| C | -2.59347 1.690690 .02951 |
| C | -3.83127 1.04078-0.01594 |
| C | -3.93462 -0.35477-0.08084 |
| C | -2.76358 -1.12692-0.10487 |
| H | -2.5408 2.772840 .08215 |
| H | -4.73775 1.636150 .00107 |
| H | -2.82346-2.20995 -0.15796 |
| H | -0.06491-1.99513-0.0808 |
| H | 0.199832 .228750 .05121 |
| N | -0.23267-1.00288-0.07987 |
| N | -0.08974 1.26508 0.04622 |
| B | 0.71807 0.07642-0.01004 |
| C | $2.27074-0.024090 .00146$ |
| C | $3.079251 .1241 \quad 0.07321$ |
| C | $2.92303-1.26828-0.05921$ |
| C | 4.469181 .037160 .08453 |
| H | 2.61646 2.10427 0.13643 |
| C | $4.31236-1.36427-0.04985$ |
| H | $2.33685-2.17955-0.12984$ |
| C | $5.09056-0.209550 .02255$ |
| H | 5.068051 .939440 .14478 |
| H | $4.78878-2.33725-0.10205$ |
| H | $6.17261-0.28064-0.03056$ |
| C | -5.28608 -1.03043-0.12747 |
| H | -5.40746-1.62097-1.04147 |
| H | -5.42288-1.71129 0.71896 |
| H | -6.09501 -0.29765-0.09703 |
| Item | Value Threshold Converged? |

Maximum Force $\quad 0.000069 \quad 0.000450$ YES
RMS Force $0.000017 \quad 0.000300$ YES
Maximum Displacement $0.001746 \quad 0.001800$ YES
RMS Displacement $0.000380 \quad 0.001200$ YES
Predicted change in Energy $=-2.508614 \mathrm{D}-07$
Optimization completed.
-- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- $-25.0092-7.8940-2.9531-0.0007-0.0004-0.0003$
Low frequencies --- $2.2422 \quad 2.8911 \quad 48.8509$

| - Thermochemistry - |  |
| :--- | :---: |
| ------------- |  |
| Zero-point correction= | 0.235430 (Hartree/Particle) |
| Thermal correction to Energy= | 0.247021 |
| Thermal correction to Enthalpy $=$ | 0.247965 |
| Thermal correction to Gibbs Free Energy= | 0.197550 |
| Sum of electronic and zero-point Energies= | -637.611581 |
| Sum of electronic and thermal Energies= | -637.599990 |
| Sum of electronic and thermal Enthalpies= | -637.599046 |
| Sum of electronic and thermal Free Energies= | -637.649461 |

## 5. $N$-methyldiazaborole

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB
Derivatives $\backslash \mathrm{N}$
-methyl DAB\DFT_dihedral_0\DFT CALCULATIONS.chk
\# opt=(modredundant, maxcycle=500,maxstep=30) freq rb3lyp/6-311++g(d,p)
geom=connectivity int=grid=ultrafine

| dihedral 0 |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
|  |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | 1.91273 | 0.48256 | -0.16345 |
| C | 1.87545 | -0.89947 | 0.13173 |
| C | 3.04824 | -1.62987 | 0.2779 |
| C | 4.26733 | -0.96146 | 0.13088 |
| C | 4.30654 | 0.40564 | -0.15449 |
| C | 3.12874 | 1.14453 | -0.30475 |
| H | 3.0198 | -2.69062 | 0.50283 |
| H | 5.19365 | -1.51321 | 0.24143 |
| H | 5.26335 | 0.90306 | -0.26351 |



## 6. $N, N^{\prime}$-Dimethyldiazaborole (4.6)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB Derivatives $\backslash \mathrm{D}$
imethyl DAB\DFT_dihedral_0\DFT CALCULATIONS.chk
\# opt=(modredundant, maxcycle=500, maxstep=30) freq rb3lyp/6-311++g(d,p) geom=(redundant,connectivity) int=grid=ultrafine


RMS Force $0.000001 \quad 0.000300$ YES
Maximum Displacement $0.000444 \quad 0.001800$ YES
RMS Displacement $0.000092 \quad 0.001200$ YES
Predicted change in Energy $=-4.309573 D-09$
Optimization completed.
-- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- $-52.5390 \quad-5.2031 \quad-3.3710 ~-0.0009-0.0005 \quad 0.0006$
Low frequencies --- $2.0719 \quad 46.9702 \quad 99.6385$

- Thermochemistry -

| Zero-point correction $=$ | 0.264646 (Hartree/Particle) |
| :--- | :---: |
| Thermal correction to Energy $=$ | 0.278227 |
| Thermal correction to Enthalpy $=$ | 0.279171 |
| Thermal correction to Gibbs Free Energy= $=$ | 0.224625 |
| Sum of electronic and zero-point Energies $=$ | -676.877339 |
| Sum of electronic and thermal Energies $=$ | -676.863758 |
| Sum of electronic and thermal Enthalpies $=$ | -676.862814 |
| Sum of electronic and thermal Free Energies= | -676.917361 |

## 7. $N$-Methyloxazaborole (4.9)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB
Derivatives $\backslash \mathrm{N}$
-methylOAB\DFT_dihedral_0\DFT CALCULATIONS.chk
\# opt=(modredundant, maxcycle=500, maxstep=30) freq rb3lyp/6-311++g(d,p) geom=connectivity int=grid=ultrafine

| dihedral 0 |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | 1.91843 | 0.52173 | -0.08099 |
| C | 1.79671 | -0.86228 | 0.11223 |
| C | 2.89546 | -1.68968 | 0.23666 |
| C | 4.15968 | -1.09098 | 0.16401 |
| C | 4.2938 | 0.28601 | -0.02639 |
| C | 3.17386 | 1.11618 | -0.15251 |
| H | 2.77468 | -2.75567 | 0.38509 |
| H | 5.04582 | -1.70766 | 0.25679 |
| H | 5.2842 | 0.72304 | -0.08036 |
| H | 3.28928 | 2.18266 | -0.30478 |


-- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- -48.2038 $-5.7205-2.7790-0.6229-0.0006$
Low frequencies --- $-0.0005 \quad 51.9453 \quad 78.6754$
--------------------

| Zero-point correction $=$ | 0.223868 (Hartree/Particle) |
| :--- | :---: |
| Thermal correction to Energy $=$ | 0.235813 |
| Thermal correction to Enthalpy $=$ | 0.236757 |
| Thermal correction to Gibbs Free Energy $=$ | 0.185333 |
| Sum of electronic and zero-point Energies $=$ | -657.486359 |
| Sum of electronic and thermal Energies= | -657.474413 |
| Sum of electronic and thermal Enthalpies $=$ | -657.473469 |
| Sum of electronic and thermal Free Energies= | -657.524893 |

a) NICS calculatins of coplanar structures in gas phase

## 1. Diazaborole (4.1)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\NICS dihedral 0\DAB\DFT_dihedral_0_ CALCULATI
ONS.chk
\# nmr=----------------------------------------------

| NICS dihedral 0 |  |  |  |
| :---: | :---: | :---: | :---: |
|  |  |  |  |
| Symbolic Z-matrix: |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | -1.92071 | 0.70648 | -0.00006 |
| C | -1.92071 | -0.70648 | 0.00017 |
| C | -3.11521 | -1.41789 | 0.00001 |
| C | -4.31355 | -0.69895 | -0.00005 |
| C | -4.31355 | 0.69895 | 0.00001 |
| C | -3.11521 | 1.41789 | -0.00001 |
| H | -3.11855 | -2.50254 | -0.00009 |
| H | -5.25552 | -1.23496 | -0.0002 |
| H | -5.25552 | 1.23496 | 0.00005 |
| H | -3.11855 | 2.50254 | -0.0001 |
| H | -0.36989 | 2.11803 | -0.00049 |
| H | -0.36989 | -2.11803 | -0.00077 |
| N | -0.59459 | 1.1373 | -0.00014 |
| N | -0.59459 | -1.1373 | -0.00009 |
| B | 0.28837 | 0.0 | . 00022 |
| C | 1.84436 | 0.0 | . 00039 |
| C | 2.57793 | -1.19954 | 0.00003 |
| C | 2.57793 | 1.19954 | 0.00019 |
| C | 3.97035 | -1.20486 | -0.00008 |
| H | 2.05624 | -2.15173 | 0.00066 |
| C | 3.97035 | 1.20486 | -0.00005 |
| H | 2.05623 | 2.15172 | -0.00027 |
| C | 4.67207 | 0. -0 | . 00015 |
| H | 4.5085 | -2.14648 | -0.00044 |
| H | 4.5085 | 2.14648 | 0.00004 |
| H | 5.75643 | 0. -0. | . 0004 |
| Bq | -3.11713 | 0.00376 | -0.00005 |
| Bq | -0.81617 | 0.14419 | - 0.00014 |
| Bq | 3.25821 |  | 0.00012 |
| Bq | -3.1171 | 0.00374 | 0.99995 |
| Bq | -0.81616 | 0.14447 | 71.00014 |
| Bq | 3.25829 | -0.00012 | 1.00012 |
| Bq | -0.81616 | 0.14475 | 52.00014 |

$\begin{array}{llll}\mathrm{Bq} & -0.81616 & 0.14503 & 3.00014 \\ \mathrm{~Bq} & -0.81615 & 0.14531 & 4.00014\end{array}$
Calculating GIAO nuclear magnetic shielding tensors.
SCF GIAO Magnetic shielding tensor (ppm):
27 Bq Isotropic $=9.5878$ Anisotropy $=4.6201$
$\mathrm{XX}=8.0495 \mathrm{YX}=-0.0065 \mathrm{ZX}=-0.0018$
$\mathrm{XY}=-0.0027 \mathrm{YY}=8.0460 \mathrm{ZY}=0.0010$
$X Z=-0.0026 \quad \mathrm{YZ}=0.0008 \mathrm{ZZ}=12.6679$
Eigenvalues: $8.0429 \quad 8.0527 \quad 12.6679$
28 Bq Isotropic $=$ 9.5018 Anisotropy $=32.1289$
$\mathrm{XX}=5.4494 \mathrm{YX}=2.3041 \mathrm{ZX}=0.0003$
$\mathrm{XY}=2.4776 \mathrm{YY}=30.6966 \mathrm{ZY}=-0.0030$
$X Z=0.0025 \mathrm{YZ}=-0.0064 \mathrm{ZZ}=-7.6408$
Eigenvalues: $-7.6408 \quad 5.2250 \quad 30.9210$
29 Bq Isotropic $=6.7770$ Anisotropy $=4.8747$
$\mathrm{XX}=5.6968 \mathrm{YX}=0.0000 \mathrm{ZX}=0.0022$
$\mathrm{XY}=0.0000 \mathrm{YY}=4.6075 \mathrm{ZY}=-0.0025$
$X Z=0.0008 \mathrm{YZ}=-0.0010 \mathrm{ZZ}=10.0269$
Eigenvalues: $4.6075 \quad 5.6968 \quad 10.0269$
30 Bq Isotropic $=10.1684$ Anisotropy $=25.6143$
$\mathrm{XX}=2.3921 \quad \mathrm{YX}=-0.0023 \quad \mathrm{ZX}=-0.8171$
$\mathrm{XY}=-0.0005 \mathrm{YY}=0.9013 \mathrm{ZY}=-0.0221$
$X Z=-0.9854 \mathrm{YZ}=0.0054 \mathrm{ZZ}=27.2120$
Eigenvalues: $0.9013 \quad 2.3594 \quad 27.2446$
31 Bq Isotropic $=5.8838$ Anisotropy $=13.0159$
$\mathrm{XX}=-0.1088 \quad \mathrm{YX}=0.6934 \mathrm{ZX}=-0.7601$
$\mathrm{XY}=0.7032 \mathrm{YY}=3.4904 \mathrm{ZY}=-2.3384$
$X Z=3.3606 \mathrm{YZ}=-0.5733 \mathrm{ZZ}=14.2698$
Eigenvalues: $-0.4064 \quad 3.4967 \quad 14.5611$
32 Bq Isotropic $=$ 9.4893 Anisotropy $=24.9249$
$\mathrm{XX}=1.6239 \mathrm{YX}=0.0009 \mathrm{ZX}=0.4492$
$\mathrm{XY}=0.0011 \mathrm{YY}=0.7684 \mathrm{ZY}=-0.0010$
$\mathrm{XZ}=1.2745 \mathrm{YZ}=-0.0020 \mathrm{ZZ}=26.0755$
Eigenvalues: $0.7684 \quad 1.5935 \quad 26.1058$
33 Bq Isotropic $=$ 2.2068 Anisotropy $=12.2711$
$\mathrm{XX}=-1.5866 \quad \mathrm{YX}=0.0167 \mathrm{ZX}=-0.0936$
$\mathrm{XY}=0.0094 \mathrm{YY}=-2.0203 \mathrm{ZY}=-0.1136$
$X Z=2.7824 \mathrm{YZ}=0.7878 \mathrm{ZZ}=10.2274$
Eigenvalues: -2.0315 $-1.7356 \quad 10.3876$
34 Bq Isotropic $=1.1532$ Anisotropy $=7.3510$
$\mathrm{XX}=-1.0585 \quad \mathrm{YX}=-0.0083 \quad \mathrm{ZX}=0.0327$
$\mathrm{XY}=-0.0024 \mathrm{YY}=-1.4818 \quad \mathrm{ZY}=0.0830$
$\mathrm{XZ}=1.1092 \mathrm{YZ}=0.4162 \mathrm{ZZ}=5.9997$
Eigenvalues: -1.4917 $-1.1027 \quad 6.0538$
35 Bq Isotropic $=0.7284$ Anisotropy $=4.6740$
$\mathrm{XX}=-0.6920 \mathrm{YX}=-0.0036 \mathrm{ZX}=-0.0024$

```
\(\mathrm{XY}=-0.0020 \mathrm{YY}=-0.9577 \mathrm{ZY}=0.0583\)
\(X Z=0.3224 \mathrm{YZ}=0.2113 \mathrm{ZZ}=3.8350\)
Eigenvalues: -0.9617 -0.6974 3.8444
```


## 2. Bromodiazaborole (4.2)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka Gaussian\NICS dihedral $0 \backslash \mathrm{BrDAB} \backslash \mathrm{DFT}$ CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p) geom=connectivity
$\qquad$
NICS dihedral 0

| Symbolic Z-matrix: |  |  |  |
| :---: | :---: | :---: | :---: |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | -3.57006 | 0.70624 | -0.00004 |
| C | -3.57007 | -0.70624 | 0.00016 |
| C | -4.76434 | -1.4181 | -0.00005 |
| C | -5.96226 | -0.69903 | -0.00014 |
| C | -5.96225 | 0.69905 | -0.00001 |
| C | -4.76433 | 1.41811 | 0.00001 |
| H | -4.7677 | -2.50269 | -0.00021 |
| H | -6.90427 | -1.23485 | -0.00035 |
| H | -6.90426 | 1.23488 | 0.00004 |
| H | -4.76768 | 2.5027 | -0.00002 |
| H | -2.02035 | 2.11863 | -0.00042 |
| H | -2.02037 | -2.11864 | -0.00088 |
| N | -2.24352 | 1.13751 | -0.00008 |
| N | -2.24353 | -1.13751 | -0.00008 |
| B | -1.36227 | -0.00001 | 0.00029 |
| C | 0.19407 | -0.00002 | 0.00053 |
| C | 0.92985 | -1.19718 | 0.0001 |
| C | 0.92984 | 1.19716 | 0.00039 |
| C | 2.32208 | -1.21112 | 0.00012 |
| H | 0.41387 | -2.15206 | 0.00058 |
| C | 2.32207 | 1.21111 | 0.0001 |
| H | 0.41384 | 2.15203 | 0.00004 |
| C | 3.00702 | 0.0 | . 00004 |
| H | 2.86511 | -2.14756 | -0.00016 |
| H | 2.86509 | 2.14755 | 0.00008 |
| Br | 4.92508 | 0.00001 | -0.00047 |
| Bq | -4.76616 | -0.00359 | 0. |
| Bq | 1.60055 | -0.00001 | 0.00041 |
| Bq | -2.46617 | -0.00001 | 10.00018 |


| Bq | -2.46617 | -0.00001 | 1.00018 |  |
| :---: | :---: | :---: | :---: | :---: |
| Bq | -2.46617 | -0.00001 | 2.00018 |  |
| Bq | -2.46617 | -0.00001 | 3.00018 |  |
| Bq | -2.46617 | -0.00001 | 4.00017 |  |
| Bq | -4.76617 | -0.00359 |  |  |
| Bq | 1.60063 | -0.00001 | 1.00041 |  |
| 27 Bq | Isotropic $=9.6$ | 6005 Ani | isotropy $=4.5$ | 673 |
| $\mathrm{XX}=$ | 8.1471 YX= | 0.0061 | $\mathrm{ZX}=-0.0019$ |  |
| XY= | 0.0026 YY= | 8.0091 | $\mathrm{ZY}=0.0010$ |  |
| XZ= | -0.0037 YZ= | 0.0004 | $\mathrm{ZZ}=12.6454$ |  |
| Eigenv | values: 8.0089 | 8.1472 | 12.6454 |  |
| 28 B | Bq Isotropic = | 7.2716 | Anisotropy $=$ | 2.2951 |
| XX= | $8.7842 \mathrm{YX}=$ | 0.0000 | $\mathrm{ZX}=0.0008$ |  |
| XY= | 0.0000 YY= | 4.2290 | $\mathrm{ZY}=-0.0028$ |  |
| XZ= | $0.0001 \mathrm{YZ}=$ | -0.0009 | $\mathrm{ZZ}=8.8017$ |  |
| Eigenv | values: 4.2290 | 8.7842 | 8.8017 |  |
| 29 B | Bq Isotropic = | 8.0346 | Anisotropy $=$ | 32.3621 |
| XX= | $3.8946 \mathrm{YX}=$ | 0.0001 | $\mathrm{ZX}=0.0000$ |  |
| XY= | 0.0001 YY= | 29.6093 | $\mathrm{ZY}=0.0005$ |  |
| XZ= | $0.0012 \mathrm{YZ}=$ | -0.0010 | $\mathrm{ZZ}=-9.4002$ |  |
| Eigenv | values: -9.4002 | 3.8946 | 29.6093 |  |
| 30 B | Bq Isotropic = | 5.7319 | Anisotropy = | 12.2448 |
| XX= | -0.1097 YX= | 0.0007 | $\mathrm{ZX}=-0.7181$ |  |
| XY= | 0.0011 YY= | 3.5376 | $\mathrm{ZY}=0.0007$ |  |
| XZ= | 3.3871 YZ= | 0.0004 | $\mathrm{ZZ}=13.7680$ |  |
| Eigenv | values: -0.2369 | 3.5376 | 613.8951 |  |
| 31 B | Bq Isotropic = | 2.2673 | Anisotropy = | 12.1608 |
| $\mathrm{XX}=$ | -1.3766 YX= | -0.0001 | $\mathrm{ZX}=-0.1876$ |  |
| XY= | 0.0000 YY= | -2.0557 | $\mathrm{ZY}=0.0002$ |  |
| XZ= | 2.7558 YZ= | 0.0000 | $Z Z=10.2342$ |  |
| Eigenv | values: -2.0557 | -1.5169 | 9 10.3745 |  |
| 32 B | Bq Isotropic = | 1.1866 | Anisotropy = | 7.2722 |
| $\mathrm{XX}=$ | -0.8961 YX= | 0.0000 | $\mathrm{ZX}=-0.0790$ |  |
| XY= | 0.0000 YY= | -1.5415 | $\mathrm{ZY}=-0.0001$ |  |
| XZ= | 1.0964 YZ= | 0.0000 | $\mathrm{ZZ}=5.9974$ |  |
| Eigenv | values: -1.5415 | -0.9335 | $5 \quad 6.0348$ |  |
| 33 B | Bq Isotropic = | 0.7450 | Anisotropy = | 4.6122 |
| $\mathrm{XX}=$ | -0.5762 YX= | 0.0001 | $\mathrm{ZX}=-0.1131$ |  |
| XY= | 0.0000 YY= | -1.0065 | $\mathrm{ZY}=-0.0001$ |  |
| XZ= | $0.3002 \mathrm{YZ}=$ | 0.0000 | $\mathrm{ZZ}=3.8178$ |  |
| Eigenv | values: -1.0065 | -0.5782 | 23.8198 |  |
| 34 B | Bq Isotropic = | 10.2065 | Anisotropy = | 25.5793 |
| $\mathrm{XX}=$ | 2.4973 YX= | -0.0004 | $\mathrm{ZX}=-0.8586$ |  |
| XY= | -0.0020 YY= | 0.8980 | $\mathrm{ZY}=0.0215$ |  |
| XZ= | -1.0091 YZ= | -0.0040 | $\mathrm{ZZ}=27.2241$ |  |
| Eigenv | values: 0.8980 | 2.4621 | 27.2593 |  |

```
    35 Bq Isotropic = 9.2006 Anisotropy = 22.0465
XX= 3.7770 YX= -0.0003 ZX= -0.6075
XY= -0.0003 YY= -0.0549 ZY= -0.0020
XZ= 1.8285 YZ= -0.0019 ZZ= 23.8798
Eigenvalues: -0.0549 3.7585 23.8983
```


## 3. Methoxydiazaborole (4.3)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\NICS dihedral 0\MeODAB\DFT CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant,connectivity)
dihedral 0 freeze NICS calculation

| Symbolic Z-matrix: |  |  |  |
| :--- | :---: | :--- | :--- |
| Charge $=0$ | Multiplicity $=1$ |  |  |
| C | 2.7806 | -0.7398 | -0.00003 |
| C | 2.83769 | 0.67224 | -0.00016 |
| C | 4.05991 | 1.3344 | -0.00007 |
| C | 5.22887 | 0.56776 | 0.00014 |
| C | 5.17244 | -0.8286 | 0.00021 |
| C | 3.94542 | -1.49842 | 0.00014 |
| H | 4.10701 | 2.41807 | -0.0001 |
| H | 6.19161 | 1.06559 | 0.0002 |
| H | 6.09187 | -1.40249 | 0.00034 |
| H | 3.905 | -2.58238 | 0.00014 |
| H | 1.17462 | -2.08775 | -0.00004 |
| H | 1.34548 | 2.14534 | -0.00002 |
| N | 1.43823 | -1.11685 | -0.00031 |
| N | 1.53014 | 1.15634 | -0.00014 |
| B | 0.59983 | 0.05565 | -0.0001 |
| C | -0.95059 | 0.12039 | -0.00001 |
| C | -1.64264 | 1.34862 | 0.00004 |
| C | -1.73975 | -1.03816 | -0.00006 |
| C | -3.02602 | 1.4168 | 0.0001 |
| H | -1.08724 | 2.28146 | -0.00001 |
| C | -3.13398 | -0.99741 | -0.00002 |
| H | -1.26543 | -2.01489 | -0.00009 |
| C | -3.78482 | 0.2393 | 0.00007 |
| H | -3.5451 | 2.36792 | 0.0001 |
| H | -3.6936 | -1.92328 | 0.00006 |
| O | -5.13795 | 0.40307 | 0.00013 |
| C | -5.96538 | -0.75308 | 0. |
|  |  |  |  |



Eigenvalues: $0.9033 \quad 2.4510 \quad 27.1004$
38 Bq Isotropic $=$ 7.6663 Anisotropy $=1.0208$
$\mathrm{XX}=7.2770 \mathrm{YX}=0.5068 \mathrm{ZX}=-0.0001$
$\mathrm{XY}=0.2490 \mathrm{YY}=7.3751 \mathrm{ZY}=-0.0006$
$\mathrm{XZ}=-0.0002 \mathrm{YZ}=-0.0001 \mathrm{ZZ}=8.3468$
Eigenvalues: $6.9450 \quad 7.7070 \quad 8.3468$
39 Bq Isotropic $=9.1758$ Anisotropy $=22.2276$
$\mathrm{XX}=2.6872 \mathrm{YX}=0.3128 \quad \mathrm{ZX}=0.1769$
$\mathrm{XY}=0.1787 \mathrm{YY}=0.8845 \mathrm{ZY}=0.1862$
$\mathrm{XZ}=-1.9028 \mathrm{YZ}=0.4017 \mathrm{ZZ}=23.9558$
Eigenvalues: $0.8444 \quad 2.6889 \quad 23.9942$

## 4. Methyldiazaborole (4.4)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\NICS dihedral 0\MeDAB\DFT CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant,connectivity)
--------------------------------------------------------------------------

| Symbolic Z-matrix: |  |  |  |
| :---: | :---: | :---: | :---: |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | -1.52988 | -0.4907 | -0.0631 |
| C | -1.44148 | 0.91753 | 0.00801 |
| C | -2.59347 | 1.69069 | 0.02951 |
| C | -3.83127 | 1.04078 | -0.01594 |
| C | -3.93462 | -0.35477 | -0.08084 |
| C | -2.76358 | -1.12692 | -0.10487 |
| H | -2.5408 | 2.77284 | 0.08215 |
| H | -4.73775 | 1.63615 | 0.00107 |
| H | -2.82346 | -2.20995 | -0.15796 |
| H | -0.06491 | -1.99513 | -0.0808 |
| H | 0.19983 | 2.22875 | 0.05121 |
| N | -0.23267 | -1.00288 | -0.07987 |
| N | -0.08974 | 1.26508 | 0.04622 |
| B | 0.71807 | 0.07642 | -0.01004 |
| C | 2.27074 | -0.02409 | 0.00146 |
| C | 3.07925 | 1.1241 | 0.07321 |
| C | 2.92303 | -1.26828 | -0.05921 |
| C | 4.46918 | 1.03716 | 0.08453 |
| H | 2.61646 | 2.10427 | 0.13643 |
| C | 4.31236 | -1.36427 | -0.04985 |
| H | 2.33685 | -2.17955 | -0.12984 |


| C | 5.09056 | -0.20955 | 0.02255 |  |
| :---: | :---: | :---: | :---: | :---: |
| H | 5.06805 | 1.93944 | 0.14478 |  |
| H | 4.78878 | -2.33725 | -0.10205 |  |
| H | 6.17261 | -0.28064 | 0.03056 |  |
| C | -5.28608 | -1.03043 | -0.12747 |  |
| H | -5.40746 | -1.62097 | -1.04147 |  |
| H | -5.42288 | -1.71129 | 0.71896 |  |
| H | -6.09501 | -0.29765 | -0.09703 |  |
| Bq | -0.38381 | 0.14491 | -0.01879 |  |
| Bq | -0.39335 | 0.08947 | 0.97962 |  |
| Bq | -0.40289 | 0.03403 | 1.97804 |  |
| Bq | -0.41243 | -0.02142 | 2.97646 |  |
| Bq | -0.42197 | -0.07686 | 3.97487 |  |
| Bq | -2.68057 | 0.27504 | -0.03952 |  |
| Bq | -2.69066 | 0.22696 | 0.95927 |  |
| Bq | 3.68065 | -0.11682 | 0.012 |  |
| Bq | 3.67216 | -0.17299 | 1.01039 |  |
| 30 Bq | Isotropic $=7.6$ | 6900 An | nisotropy $=33$ | 260 |
| $\mathrm{XX}=$ | 3.8731 YX= | 1.5807 | $\mathrm{ZX}=0.2159$ |  |
| XY= | 1.5458 YY= | 29.5298 | $\mathrm{ZY}=1.9632$ |  |
| XZ= | 0.2072 YZ= | 1.6577 | $\mathrm{ZZ}=-10.3328$ |  |
| Eigen | values: -10.4162 | 23.778 | 8929.7074 |  |
|  | Bq Isotropic $=$ | 5.5296 | Anisotropy = | 11.5121 |
| XX= | -0.1738 YX= | 0.2850 | ZX= -0.7494 |  |
| XY= | -0.0271 YY= | 3.7003 | $\mathrm{ZY}=-0.3545$ |  |
| XZ= | 3.0911 YZ= | -0.8950 | $\mathrm{ZZ}=13.0622$ |  |
| Eigen | values: -0.2850 | 3.6695 | 513.2043 |  |
| 32 B | Bq Isotropic = | 2.1814 | Anisotropy = | 11.9358 |
| XX= | -1.4564 YX= | 0.0812 | $\mathrm{ZX}=-0.1037$ |  |
| XY= | -0.0254 YY= | -1.9652 | $\mathrm{ZY}=-0.5695$ |  |
| XZ= | $2.5700 \mathrm{YZ}=$ | -0.8579 | $\mathrm{ZZ}=9.9656$ |  |
| Eigen | values: -2.0306 | -1.5639 | 910.1385 |  |
|  | Bq Isotropic $=$ | 1.1464 | Anisotropy = | 7.1924 |
| XX= | -0.9730 YX= | 0.0266 | $\mathrm{ZX}=0.0822$ |  |
| XY= | -0.0117 YY= | -1.4613 | $\mathrm{ZY}=-0.3365$ |  |
| XZ= | 1.0256 YZ= | -0.4983 | $\mathrm{ZZ}=5.8735$ |  |
| Eigen | values: -1.4881 | -1.0140 | 05.9413 |  |
| 34 B | Bq Isotropic $=$ | 0.7222 | Anisotropy = | 4.6000 |
| XX= | -0.6398 YX= | 0.0145 | $\mathrm{ZX}=0.0574$ |  |
| XY= | -0.0009 YY= | -0.9621 | $\mathrm{ZY}=-0.2033$ |  |
| XZ= | 0.3044 YZ= | -0.2947 | $\mathrm{ZZ}=3.7684$ |  |
| Eigen | values: -0.9760 | -0.6464 | 43.7889 |  |
| 35 B | Bq Isotropic $=$ | 9.4158 | Anisotropy = | 2.5871 |
| XX= | 8.6412 YX= | 0.5292 | $\mathrm{ZX}=0.0265$ |  |
| XY= | 0.3663 YY= | 8.4800 | $\mathrm{ZY}=-0.1621$ |  |
| XZ= | 0.0843 YZ= | -0.2250 | $\mathrm{ZZ}=11.1262$ |  |

Eigenvalues: $8.0945 \quad 9.0124 \quad 11.1405$
36 Bq Isotropic $=9.8805$ Anisotropy $=24.0128$
$\mathrm{XX}=2.8944 \mathrm{YX}=0.4103 \mathrm{ZX}=-0.5894$
$\mathrm{XY}=0.5324 \mathrm{YY}=0.9244 \mathrm{ZY}=-0.9147$
$\mathrm{XZ}=-0.8848 \mathrm{YZ}=-1.1193 \mathrm{ZZ}=25.8227$
Eigenvalues: $0.7895 \quad 2.9629 \quad 25.8890$
37 Bq Isotropic $=$ 6.7960 Anisotropy $=4.8065$
$\mathrm{XX}=5.7617 \mathrm{YX}=-0.0598 \mathrm{ZX}=-0.0589$
$\mathrm{XY}=-0.0447 \mathrm{YY}=4.6394 \mathrm{ZY}=-0.2077$
$X Z=-0.0605 \mathrm{YZ}=-0.3120 \mathrm{ZZ}=9.9870$
Eigenvalues: $4.6241 \quad 5.7636 \quad 10.0004$
38 Bq Isotropic $=9.5185$ Anisotropy $=24.8627$
$\mathrm{XX}=1.6583 \mathrm{YX}=-0.0678 \mathrm{ZX}=0.1243$
$\mathrm{XY}=-0.1184 \mathrm{YY}=0.8963 \mathrm{ZY}=-1.4044$
$\mathrm{XZ}=0.9744 \mathrm{YZ}=-1.4383 \mathrm{ZZ}=26.0008$
Eigenvalues: $0.8114 \quad 1.6504 \quad 26.0936$

## 5. N -Methyldiazaborole

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\NICS dihedral 0\N-DAB\DFT CALCULATIONS.chk

| dihedral 0 NICS |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | 1.92936 | 0.50101 | 0.00877 |
| C | 1.8514 | -0.90897 | 0.01279 |
| C | 2.99984 | -1.69084 | -0.0194 |
| C | 4.23897 | -1.04583 | -0.06025 |
| C | 4.32001 | 0.3487 | -0.06814 |
| C | 3.1665 | 1.13853 | -0.0346 |
| H | 2.93656 | -2.77369 | -0.01442 |
| H | 5.14698 | -1.63693 | -0.08826 |
| H | 5.29082 | 0.82924 | -0.10473 |
| H | 3.24427 | 2.21887 | -0.05125 |
| H | 0.22578 | -2.224 | 0.02496 |
| N | 0.63282 | 1.02532 | 0.05227 |
| N | 0.50798 | -1.25893 | 0.05089 |
| B | -0.31201 | -0.07298 | 0.06334 |
| C | -1.87578 | -0.09438 | 0.00422 |
| C | -2.54423 | -1.33398 | 0.06229 |


| C | -2.68941 | 1.05117-0.0764 |
| :---: | :---: | :---: |
| C | -3.93189 | -1.42987 0.03229 |
| H | -1.97253 | -2.25325 0.13672 |
| C | -4.08016 | 0.96599 -0.10639 |
| H | -2.24212 | $2.03396-0.14265$ |
| C | -4.70894 | -0.27535-0.05096 |
| H | -4.40743 | -2.40364 0.07659 |
| H | -4.67264 | $1.8719-0.17509$ |
| H | -5.79088 | -0.3435 -0.07379 |
| C | 0.43438 | 2.463650 .1178 |
| H | -0.52722 | 2.69260 .57097 |
| H | 1.20482 | 2.921010 .74372 |
| H | 0.47788 | 2.92864-0.8737 |
| Bq | 0.78918 | -0.13848 0.03706 |
| Bq | 0.81379 | -0.14823 1.03671 |
| Bq | 0.83839 | -0.15799 2.03636 |
| Bq | 0.86299 | -0.16775 3.03601 |
| Bq | 0.88759 | -0.17751 4.03566 |
| Bq | 3.08416 | -0.27241-0.02574 |
| Bq | 3.11491 | -0.27111 0.97378 |
| Bq | -3.29236 | -0.18487-0.02337 |
| Bq | -3.31813 | -0.12947 0.97476 |
| 30 Bq | Isotropic $=8.02$ | 0292 Anisotropy $=33.0847$ |
| $\mathrm{XX}=$ | 3.9477 YX= | $2.1140 \mathrm{ZX}=0.1356$ |
| XY= | 1.2548 YY= | 29.9769 ZY= -0.1033 |
| XZ= | 0.3796 YZ= | $0.2287 \mathrm{ZZ}=-9.8371$ |
| Eigen | values: -9.8419 | $3.8438 \quad 30.0856$ |
|  | Bq Isotropic $=$ | 5.7702 Anisotropy $=11.1127$ |
| XX= | -0.8076 YX= | $0.3919 \mathrm{ZX}=1.3047$ |
| XY= | -0.2011 YY= | 5.0069 ZY= -0.4733 |
| XZ= | -3.0732 YZ= | -0.1271 ZZ $=13.1113$ |
| Eigen | values: -0.8645 | $4.9965 \quad 13.1787$ |
|  | Bq Isotropic = | 2.3651 Anisotropy = 12.1555 |
| $\mathrm{XX}=$ | -1.9115 YX= | -0.0007 ZX= 0.4507 |
| XY= | -0.0174 YY= | -1.3249 ZY= -0.5923 |
| XZ= | -2.7671 YZ= | $-0.5726 \mathrm{ZZ}=10.3318$ |
| Eigen | values: -2.0260 | -1.3474 10.4688 |
|  | Bq Isotropic $=$ | 1.2351 Anisotropy $=7.5426$ |
| $\mathrm{XX}=$ | -1.2503 YX= | -0.0158 ZX= 0.1540 |
| XY= | 0.0420 YY= | -1.2559 ZY= -0.4319 |
| $\mathrm{XZ}=$ | -1.0917 YZ= | -0.3939 ZZ= 6.2114 |
| Eigen | values: -1.2918 | -1.2664 6.2635 |
|  | Bq Isotropic $=$ | 0.7642 Anisotropy $=4.8789$ |
| XX= | -0.8047 YX= | -0.0043 ZX= 0.1115 |
| XY= | 0.0375 YY= | -0.9056 ZY= -0.2545 |
| $\mathrm{XZ}=$ | -0.2975 YZ= | -0.2324 ZZ= 4.0029 |

```
Eigenvalues: -0.9189 -0.8053 4.0168
    35 Bq Isotropic = 9.5751 Anisotropy = 4.5167
XX= 7.8385 YX= -0.0964 ZX= 0.1218
XY=-0.3592 YY= 8.3008 ZY= 0.0008
XZ= -0.1826 YZ= 0.0278 ZZ= 12.5860
Eigenvalues: 7.7450 8.3940 12.5862
    36 Bq Isotropic = 10.1807 Anisotropy = 25.6526
XX= 2.2191 YX= -0.2009 ZX= 1.6737
XY= -0.5766 YY= 1.1728 ZY= -0.1436
XZ= 1.9001 YZ= -0.5138 ZZ= 27.1502
Eigenvalues: 1.0415 2.2181 27.2824
    37 Bq Isotropic = 6.8322 Anisotropy = 4.9932
XX= 5.6112 YX= 0.1728 ZX= -0.1065
XY= 0.1211 YY= 4.7614 ZY= 0.3900
XZ= 0.0190 YZ= 0.5009 ZZ= 10.1240
Eigenvalues: 4.6999 5.6357 10.1610
    38 Bq Isotropic = 9.5010 Anisotropy = 24.9761
XX=1.5474 YX= 0.0640 ZX= -1.1260
XY=0.0393 YY= 0.9805 ZY= 1.4650
XZ= -1.9030 YZ= 1.4364 ZZ= 25.9753
Eigenvalues: 0.8640 1.4874 26.1518
```


## 6. $N, N^{\prime}$-Dimethyldiazaborole (4.6)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\NICS dihedral 0\DMDAB\DFT CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant, connectivity)

| Dihedral 0 freeze NICS |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | -1.88818 | -0.70786 | 0.0094 |
| C | -1.8897 | 0.70343 | 0.00803 |
| C | -3.08803 | 1.41229 | -0.01893 |
| C | -4.28756 | 0.69507 | -0.03405 |
| C | -4.28677 | -0.70056 | -0.02144 |
| C | -3.08681 | -1.41691 | 0.00197 |
| H | -3.10227 | 2.49509 | -0.03945 |
| H | -5.22825 | 1.23293 | -0.05742 |
| H | -5.22706 | -1.23961 | -0.02837 |
| H | -3.10245 | -2.49966 | 0.02306 |
| N | -0.56584 | -1.15271 | 0.01561 |


| N | -0.56952 | 1.152630 .03505 |
| :---: | :---: | :---: |
| B | 0.31652 | 0.001530 .06416 |
| C | 1.88422 | -0.00536-0.04558 |
| C | 2.63785 | -1.17985 0.16955 |
| C | 2.63416 | 1.1812-0.1926 |
| C | 4.03064 | -1.18278 0.17165 |
| H | 2.1383 | -2.11749 0.3654 |
| C | 4.02675 | 1.18862-0.19285 |
| H | 2.13113 | 2.12207-0.36361 |
| C | 4.73573 | $0.00351-0.01384$ |
| H | 4.56451 | -2.11305 0.33361 |
| H | 4.55765 | $2.12455-0.3299$ |
| H | 5.82008 | 0.00582-0.01055 |
| C | -0.27538 | -2.57049 -0.13973 |
| H | 0.58374 | -2.71522-0.79362 |
| H | -0.07763 | -3.06029 0.82022 |
| H | -1.12338 | -3.07297-0.6066 |
| C | -0.29456 | 2.574460 .18316 |
| H | 0.59673 | 2.729390 .78844 |
| H | -0.15714 | $3.07021-0.78452$ |
| H | -1.12332 | 3.062510 .69934 |
| Bq | -3.08787 | -0.00639 -0.01233 |
| Bq | -3.10113 | 0.001890 .98755 |
| Bq | -0.78621 | -0.00034 0.03644 |
| Bq | -0.81006 | 0.002621 .03615 |
| Bq | -0.8339 | 0.005582 .03586 |
| Bq | -0.85775 | 0.008543 .03557 |
| Bq | -0.8816 | 0.01154 .03528 |
| Bq | 3.30998 | -0.00093-0.02971 |
| Bq | 3.30887 | 0.166370 .9562 |
| 33 Bq Isotropic $=$ 9.5554 Anisotropy $=4.4050$ |  |  |
| $\mathrm{XX}=$ | 7.7026 YX= | 0.0054 ZX= -0.1426 |
| XY= | 0.0006 YY= | 8.4718 ZY= -0.0133 |
| $\mathrm{XZ}=$ | 0.0885 YZ= | $0.0737 \mathrm{ZZ}=12.4917$ |
| Eigenvalues: $\begin{array}{llll}7.7024 & 8.4716 & 12.4921\end{array}$ |  |  |
| 34 Bq Isotropic $=10.2930$ Anisotropy $=26.0514$ |  |  |
| XX= | $2.0705 \mathrm{YX}=$ | 0.0730 ZX= -1.3988 |
| XY= | 0.2576 YY= | $1.2546 \mathrm{ZY}=0.0950$ |
| XZ= | -1.8980 YZ= | 0.1664 ZZ= 27.5539 |
| $35 \mathrm{~Bq} \text { Isotropic }=8.4047 \text { Anisotropy }=33.2758$ |  |  |
|  |  |  |
| XX= | 3.9996 YX= | -0.0392 ZX= -0.3094 |
| XY= | -0.0002 YY= | $30.5761 \mathrm{ZY}=0.2947$ |
| XZ= | -0.1557 YZ= | $1.1133 \mathrm{ZZ}=-9.3617$ |
| Eigen | values: -9.3781 | 4.003730 .5885 |
| 36 Bq Isotropic $=$ 6.1803 Anisotropy $=11.0994$ |  |  |

```
XX= -0.4145 YX= 0.3883 ZX= -1.0183
XY= 0.0984 YY= 5.4772 ZY= -0.5147
XZ= 3.3429 YZ= 0.0609 ZZ= 13.4781
Eigenvalues: -0.5224 5.4833 13.5799
    37 Bq Isotropic = 2.6631 Anisotropy = 12.2114
XX= -1.8324 YX= 0.1313 ZX= -0.3640
XY= -0.1668 YY= -0.8551 ZY= -0.3304
XZ= 2.8168 YZ= -0.2868 ZZ= 10.6767
Eigenvalues: -1.9516 -0.8632 10.8040
    38 Bq Isotropic = 1.4184 Anisotropy = 7.7627
XX= -1.2402 YX= 0.0539 ZX= -0.1506
XY= -0.1575 YY= -1.0657 ZY= -0.1420
XZ= 1.0937 YZ= -0.2067 ZZ= 6.5610
Eigenvalues: -1.2768 -1.0616 6.5935
    39 Bq Isotropic = 0.8720 Anisotropy = 5.1226
XX= -0.8090 YX= 0.0170 ZX= -0.1257
XY= -0.1184 YY= -0.8595 ZY= -0.0375
XZ= 0.2941 YZ= -0.1178 ZZ= 4.2844
Eigenvalues: -0.8910 -0.7801 4.2870
    40 Bq Isotropic = 6.9590 Anisotropy = 5.8778
XX= 5.4232 YX= -0.0785 ZX= -0.3296
XY= -0.0525 YY= 4.8214 ZY= 0.9214
XZ= -0.1716 YZ= 1.4511 ZZ= 10.6325
Eigenvalues: 4.5883 5.4112 10.8776
    41 Bq Isotropic = 9.8059 Anisotropy = 25.8613
XX= 1.3514 YX= -0.0224 ZX= 0.3135
XY=0.0574 YY= 1.6994 ZY= 3.9714
XZ= 1.3063 YZ= 4.1726 ZZ= 26.3669
Eigenvalues: 1.0060 1.3649 27.0468
```


## 7. Dioxaborole (4.7)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka\Macrocycles\NICS Calculations\DOB\DFT CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p)

DOB NICS Calculations
Symbolic Z-matrix:
Charge $=0$ Multiplicity $=1$

| C | 1.76632 | -0.76815 | 0.25409 |
| :--- | :--- | :--- | :--- |
| C | 1.92664 | 0.5315 | -0.22209 |
| C |  | 3.17285 | 1.06807 |


| C | 4.27483 | 0.23699-0.24094 |
| :---: | :---: | :---: |
| C | 4.11407 | -1.06623 0.23655 |
| C | 2.84398 | -1.59798 0.49541 |
| H | 3.28639 | $2.0792-0.8513$ |
| H | 5.27236 | 0.61545-0.43015 |
| H | 4.98908 | -1.681 0.41125 |
| H | 2.70841 | -2.60633 0.86546 |
| O | 0.42227 | -1.02347 0.41741 |
| O | 0.68582 | 1.11301-0.36539 |
| B | -0.23463 | 0.144290 .03212 |
| C | -1.76158 | 0.336990 .04395 |
| C | -2.3371 | $1.553-0.36302$ |
| C | -2.61487 | -0.69871 0.46199 |
| C | -3.71775 | $1.72843-0.35275$ |
| H | -1.69407 | $2.36335-0.68879$ |
| C | -3.99581 | $-0.52564-0.47312$ |
| H | -2.18842 | -1.64403 0.77948 |
| C | -4.54846 | 0.688680 .06555 |
| H | -4.14765 | $2.6722-0.6695$ |
| H | -4.6418 - | $-1.333630 .7982$ |
| H | -5.62449 | 0.824480 .07388 |
| Bq | 0.91282 | -0.00097 0.0234 |
| Bq | 0.96277 | 0.337210 .96316 |
| Bq | 1.01273 | 0.675371 .90292 |
| Bq | 1.06268 | 1.013532 .84268 |
| Bq | 1.11264 | 1.351693 .78244 |
| Bq | 3.01645 | -0.26597 0.00693 |
| Bq | 3.0664 | 0.072190 .94669 |
| Bq | -3.16259 | 0.513790 .05481 |
| Bq | -3.11264 | $0.85195 \quad 0.99457$ |
| 25 Bq Isotropic $=$ 4.1623 Anisotropy $=32.0590$ |  |  |
| $\mathrm{XX}=$ | 5.1283 YX= | $1.8349 \mathrm{ZX}=-1.8478$ |
| XY= | 1.9124 YY= | 20.2303 $\mathrm{ZY}=-13.8696$ |
| XZ= | -1.9144 YZ= | -13.8019 ZZ $=-12.8716$ |
| Eigenvalues: $-17.9485 \quad 4.9005 \quad 25.5350$26 Bq Isotropic $=3.6407$ Anisotropy $=6.1940$ |  |  |
|  |  |  |
| XX= | 1.9671 YX= | $0.2884 \mathrm{ZX}=1.0000$ |
| XY= | -1.1722 YY= | $2.3018 \mathrm{ZY}=1.8317$ |
| XZ= | -3.3134 YZ= | $2.3814 \mathrm{ZZ}=6.6532$ |
| Eigen | values: 1.4469 | $1.7052 \quad 7.7701$ |
| 27 Bq Isotropic $=1.9423$ Anisotropy $=9.7039$ |  |  |
| XX= | -0.6419 YX= | -0.0288 ZX= 0.4041 |
| XY= | -0.9832 YY= | -0.5575 ZY= 3.2241 |
| XZ= | -2.2074 YZ= | $3.4817 \mathrm{ZZ}=7.0264$ |
| 28 Bq Isotropic $=1.1349$ Anisotropy $=6.3327$ |  |  |
|  |  |  |

```
XX= -0.6074 YX= 0.0088 ZX= 0.2801
XY= -0.3187 YY= -0.5267 ZY= 2.1207
XZ= -0.6385 YZ= 2.2414 ZZ= 4.5387
Eigenvalues: -1.3458 -0.6062 5.3566
    29 Bq Isotropic = 0.7396 Anisotropy = 4.1835
XX= -0.4399 YX= 0.0289 ZX= 0.2257
XY= -0.0471 YY= -0.3516 ZY= 1.3934
XZ= 0.0012 YZ= 1.4342 ZZ= 3.0104
Eigenvalues: -0.8724 -0.4374 3.5286
    30 Bq Isotropic = 10.4763 Anisotropy = 5.0365
XX= 8.4203 YX= 0.1779 ZX= 0.2448
XY= 0.2119 YY= 9.7135 ZY= 1.4549
XZ= 0.2216 YZ= 1.4777 ZZ= 13.2952
Eigenvalues: 8.3915 9.2036 13.8340
    31 Bq Isotropic = 10.4090 Anisotropy = 25.2676
XX= 2.6995 YX= 0.3445 ZX= 1.5131
XY=0.2431 YY= 4.3061 ZY= 8.2325
XZ= 0.8677 YZ= 8.2630 ZZ= 24.2213
Eigenvalues: 1.3217 2.6512 27.2540
    32 Bq Isotropic = 6.9500 Anisotropy = 5.7637
XX= 5.8315 YX= -0.0793 ZX= 0.2934
XY= -0.1069 YY= 4.9938 ZY= 2.0951
XZ= 0.2927 YZ= 2.0871 ZZ= 10.0248
Eigenvalues: 4.2164 5.8413 10.7925
    33 Bq Isotropic = 9.7036 Anisotropy = 25.6371
XX= 1.6255 YX= 0.2230 ZX= 0.9450
XY= -0.1657 YY= 3.7507 ZY= 8.3308
XZ= -0.1267 YZ= 8.4460 ZZ= 23.7345
Eigenvalues: 0.6827 1.6330 26.7950
```


## 8. Oxazaborole (4.8)

```
\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka\Macrocycles\NICS Calculations \(\backslash \mathrm{OAB} \backslash \mathrm{DFT}\)
CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p)
OAB NICS Calculations
Symbolic Z-matrix:
Charge \(=0\) Multiplicity \(=1\)
C
\(\begin{array}{llll}\mathrm{C} & 3.16431 & 1.38381 & 0 .\end{array}\)
```



```
    29 Bq Isotropic = 4.2769 Anisotropy = 8.5913
XX= 1.2118 YX= -0.8292 ZX= 0.6927
XY= -0.9384 YY= 1.9305 ZY= -0.7401
XZ= -4.0246 YZ= 0.2843 ZZ= 9.6883
Eigenvalues: 0.3659 2.4604 10.0044
    30 Bq Isotropic = 2.0580 Anisotropy = 10.8961
XX= -0.9501 YX= -0.1565 ZX= -0.0187
XY= -0.1117 YY= -1.9998 ZY= -0.3326
XZ= -2.8317 YZ= 0.1621 ZZ= 9.1240
Eigenvalues: -2.0241 -1.1240 9.3221
    31 Bq Isotropic = 1.1972 Anisotropy = 7.0994
XX= -0.8171 YX= -0.0266 ZX= -0.0304
XY= -0.0305 YY=-1.4694 ZY= -0.0786
XZ= -1.1526 YZ= 0.1275 ZZ= 5.8782
Eigenvalues: -1.4707 -0.8678 5.9302
    32 Bq Isotropic = 0.7539 Anisotropy = 4.5815
XX= -0.5830 YX= -0.0094 ZX= 0.0184
XY= -0.0203 YY= -0.9590 ZY= -0.0120
XZ= -0.2946 YZ= 0.0795 ZZ= 3.8036
Eigenvalues: -0.9598 -0.5868 3.8082
    33 Bq Isotropic = 6.8820 Anisotropy = 5.4493
XX= 5.6651 YX= 0.2082 ZX= -0.0001
XY=0.1142 YY= 4.4660 ZY= 0.0000
XZ= 0.0000 YZ= 0.0000 ZZ= 10.5149
Eigenvalues: 4.4447 5.6864 10.5149
    34 Bq Isotropic = 9.6161 Anisotropy = 25.3810
XX= 1.5802 YX= 0.1508 ZX= -0.3456
XY=0.0259 YY= 0.7599 ZY= -0.1128
XZ= -1.3346 YZ= -0.0071 ZZ= 26.5083
Eigenvalues: 0.7504 1.5612 26.5368
```


## 9. $N$-Methyldiazaborole (4.9)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\NICS dihedral 0\N-DAB\DFT CALCULATIONS.chk
\# nmr=giao rb3lyp/6-311++g(d,p) geom=(connectivity)

NICS dihedral 0
Symbolic Z-matrix:
Charge $=0$ Multiplicity $=1$

| C | -1.93042 | 0.52431 | -0.00948 |
| :--- | :--- | :--- | :--- |
| C | -1.7698 | -0.86798 | -0.01121 |


| C | -2.84409 | -1.73604 | -0.00336 |  |
| :--- | ---: | :--- | :--- | :--- |
| C | -4.12492 | -1.16946 | 0.00914 |  |
| C | -4.29827 | 0.21619 | 0.01356 |  |
| C | -3.20247 | 1.08725 | 0.00473 |  |
| H | -2.69265 | -2.8084 | -0.00608 |  |
| H | -4.99297 | -1.81797 | 0.01686 |  |
| H | -5.3006 | 0.62841 | 0.0257 |  |
| H | -3.34957 | 2.16051 | 0.01234 |  |
| N | -0.65213 | 1.09767 | -0.02603 |  |
| B | 0.29338 | 0.01489 | -0.02314 |  |
| C | 1.84787 | -0.05064 | 0.01323 |  |
| C | 2.44758 | -1.32567 | -0.00866 |  |
| C | 2.70754 | 1.0617 | 0.05452 |  |
| C | 3.83016 | -1.48156 | 0.01145 |  |
| H | 1.81243 | -2.20306 | -0.04161 |  |
| C | 4.09236 | 0.91191 | 0.07449 |  |
| H | 2.30553 | 2.06642 | 0.08528 |  |
| C | 4.65889 | -0.36103 | 0.05202 |  |
| H | 4.26205 | -2.47626 | -0.00499 |  |
| H | 4.72907 | 1.78916 | 0.10922 |  |
| H | 5.73687 | -0.47853 | 0.06752 |  |
| C | -0.50132 | 2.54198 | -0.05492 |  |
| H | -0.77726 | 2.99102 | 0.90528 |  |
| H | 0.52694 | 2.80963 | -0.28074 |  |
| H | -1.13776 | 2.97441 | -0.83281 |  |
| O | -0.43932 | -1.18672 | -0.02089 |  |
| Bq | -3.02755 | -0.32254 | 0.01199 |  |
| Bq | 3.25359 | -0.20601 | 0.01002 |  |
| Bq | -0.77837 | -0.07847 | -0.01674 |  |
| Bq | -0.75613 | -0.08413 | 0.98299 |  |
| Bq | -0.73389 | -0.08979 | 1.98273 |  |
| Bq | -0.71165 | -0.09545 | 2.98247 |  |
| Bq | -0.68941 | -0.10111 | 3.9822 |  |
| Bq | -3.02755 | -0.32254 | 1.01199 |  |
| Bq | 3.25443 | -0.21908 | 1.00994 |  |
| 29 Bq | Isotropic | 9.9408 | Anisotropy $=$ | 4.8426 |
| $\mathrm{XX}=$ | 7.7465 | $\mathrm{YX}=$ | 0.5606 | $\mathrm{ZX}=$ |
| $\mathrm{XY}=$ | 0.8193 | $\mathrm{YY}=$ | 8.90371 | $\mathrm{ZY}=$ |

```
XX= 3.3774 YX= -3.1636 ZX= 0.0873
XY= -2.8080 YY= 29.3872 ZY= 0.0579
XZ= 0.2393 YZ= -0.1191 ZZ= -13.9081
Eigenvalues: -13.9096 3.0405 29.7256
    32 Bq Isotropic = 4.8943 Anisotropy = 8.2730
XX= 0.7636 YX= 0.1400 ZX= -0.3962
XY= 0.9840 YY= 3.8749 ZY= -0.6634
XZ= 4.1422 YZ= 0.2375 ZZ= 10.0442
Eigenvalues: 0.3017 3.9715 10.4096
    33 Bq Isotropic = 2.1405 Anisotropy = 10.3206
XX= -0.9229 YX= 0.0300 ZX= 0.2115
XY= 0.2205 YY=-1.3945 ZY= -0.8013
XZ= 3.0086 YZ= -0.1788 ZZ= 8.7390
Eigenvalues: -1.5323 -1.0671 9.0209
    34 Bq Isotropic = 1.1920 Anisotropy = 6.7270
XX= -0.7914 YX= 0.0182 ZX= 0.1274
XY= 0.0981 YY= -1.2372 ZY= -0.4745
XZ= 1.1092 YZ= -0.1323 ZZ= 5.6047
Eigenvalues: -1.2680 -0.8326 5.6767
    35 Bq Isotropic = 0.7621 Anisotropy = 4.5400
XX= -0.5901 YX= 0.0145 ZX= 0.0297
XY= 0.0593 YY= -0.8994 ZY= -0.2731
XZ= 0.3017 YZ= -0.0825 ZZ= 3.7759
Eigenvalues: -0.9121 -0.5904 3.7888
    36 Bq Isotropic = 10.3245 Anisotropy = 25.6679
XX= 2.2079 YX= 0.3891 ZX= -0.2680
XY=0.7730 YY= 1.3452 ZY= -0.4119
XZ= -0.3895 YZ= -0.6834 ZZ= 27.4203
Eigenvalues: 1.0484 2.4885 27.4364
    37 Bq Isotropic = 9.6934 Anisotropy = 25.1726
XX= 1.5938 YX= -0.2143 ZX= -0.0659
XY= -0.1868 YY= 1.0497 ZY= -0.9268
XZ= 0.9951 YZ= -0.8062 ZZ= 26.4366
Eigenvalues: 0.9652 1.6398 26.4751
```

d) Thermodynamic calculations in gas phase at $100^{\circ} \mathrm{C}$

## 1. Diazaborole (4.1)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka\Macrocycles\Solvation\DMSO\DAB\DFT CALCULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature $=373.15$

DAB OptFrq Calculations in gas phase at 100 C


| Thermal correction to Energy $=$ | 0.226269 |
| :--- | :---: |
| Thermal correction to Enthalpy $=$ | 0.227451 |
| Thermal correction to Gibbs Free Energy $=$ | 0.156492 |
| Sum of electronic and zero-point Energies= | -598.312157 |
| Sum of electronic and thermal Energies= | -598.294429 |
| Sum of electronic and thermal Enthalpies $=$ | -598.293247 |
| Sum of electronic and thermal Free Energies= | -598.364206 |

## 2. Bromodiazaborole (4.2)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
seไBrDAB $\backslash B r D A B \backslash D F T ~ C A L C U L A T I O N S . c h k ~$
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature $=373.15$

| BrDAB_OptFrq_100 C_DFT_GP |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | -3.56829 | 0.69843 | -0.10578 |
| C | -3.56827 | -0.69839 | 0.10603 |
| C | -4.76261 | -1.40151 | 0.21677 |
| C | -5.96041 | -0.6908 | 0.10769 |
| C | -5.96044 | 0.69066 | -0.10805 |
| C | -4.76266 | 1.40147 | -0.21685 |
| H | -4.76575 | -2.47347 | 0.38184 |
| H | -6.90252 | -1.22007 | 0.1902 |
| H | -6.90257 | 1.21986 | -0.1908 |
| H | -4.76584 | 2.47342 | -0.38193 |
| H | -2.0134 | 2.08656 | -0.35948 |
| H | -2.01332 | -2.08647 | 0.35969 |
| N | -2.24146 | 1.12595 | -0.16437 |
| N | -2.24141 | -1.12584 | 0.16474 |
| B | -1.36167 | 0.00006 | 0.00006 |
| C | 0.19447 | 0.00007 | 0.00005 |
| C | 0.92835 | -1.16701 | -0.27188 |
| C | 0.9284 | 1.16711 | 0.27193 |
| C | 2.32084 | -1.17962 | -0.27581 |
| H | 0.40819 | -2.09137 | -0.50255 |
| C | 2.32089 | 1.17964 | 0.27582 |
| H | 0.40829 | 2.09148 | 0.50264 |
| C | 3.0053 | 0 . -0.0 | 00001 |


selMeODAB\MeODAB\DFT CALCULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature=$=373.15$

MeODAB DFT 100 C GP
Symbolic Z-matrix:
Charge $=0$ Multiplicity $=1$
C $\quad-2.78123-0.73259 \quad 0.09049$
$\begin{array}{lllll}\mathrm{C} & -2.83519 & 0.66687 & -0.1\end{array}$
$\begin{array}{llll}\text { C } & -4.05592 & 1.323 & -0.20774\end{array}$
$\begin{array}{lllll}\mathrm{C} & -5.22633 & 0.56384 & -0.11891\end{array}$
$\begin{array}{lllll}\text { C } & -5.17305 & -0.81927 & 0.07447\end{array}$


Sum of electronic and thermal Free Energies= $\quad-712.894614$
4. Methyldiazaborole (4.4)
\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
selMeDAB\MeDAB\DFT CALCULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature=373.15



## 5. $N$-Methyldiazaborole (4.5)

\%nprocshared=4 Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
selMMDAB\MMDAB\DFT CALCULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature $=373.15$
$\qquad$
N-methyl DAB_DFT_Calculations t 100 C GP
Symbolic Z-matrix:
Charge $=0$ Multiplicity $=1$

| C | 1.91262 | 0.48982 | 0.0746 |
| :--- | :---: | :---: | :---: |
| C | 1.87558 | -0.90407 | -0.15823 |
| C | 3.04849 | -1.6369 | -0.29064 |
| C | 4.26747 | -0.96095 | -0.18223 |
| C | 4.30645 | 0.41546 | 0.05423 |
| C |  | 3.12852 | 1.15769 |



## 6. $N, N$ '-Dimethyldiazaborole(4.6)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
seไDMDAB\DMDAB\DFT CALCULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature=373.15

| DMDAB 100C GP |  |
| :---: | :---: |
|  |  |
| Symbolic Z-matrix: |  |
|  | Multiplicity $=1$ |
| C | $\begin{array}{llll}1.88427-0.70225 ~ & 0.08351\end{array}$ |
| C | $1.884270 .70225-0.0835$ |
| C | $3.079421 .40778-0.17217$ |
| C | $4.279090 .69282-0.08542$ |
| C | $4.27909-0.692820 .08545$ |
| C | $3.07942-1.407780 .17219$ |
| H | $3.087332 .48372-0.30103$ |
| H | $5.220971 .22525-0.15077$ |
| H | $5.22097-1.22525-0.15081$ |
| H | $3.08732-2.483720 .30104$ |
| N | $\begin{array}{llll}0.5622 & -1.14336 & 0.13309\end{array}$ |
| N | $0.562211 .14336-0.13312$ |
| B | -0.30558 0.000010 .00002 |
| C | -1.86991 0.000010 .00001 |
| C | -2.60169 0.82220 .87526 |
| C | -2.60168 -0.8222-0.87524 |
| C | $\begin{array}{llll}-3.99547 & 0.82211 & 0.88037\end{array}$ |
| H | $\begin{array}{llll}-2.0742 & 1.46357 & 1.57441\end{array}$ |
| C | -3.99546-0.82211-0.88036 |
| H | -2.07418-1.46357-1.57438 |
| C | -4.69707 0. 0. |
| H | -4.5337 1.46168 1.57166 |
| H | -4.53368-1.46168-1.57165 |
| H | -5.7815 -0.00001 0. |
| C | 0.23546-2.53775 0.3672 |
| H | -0.84474-2.64609 0.45413 |
| H | $0.58441-3.17299-0.45455$ |
| H | $\begin{array}{llll}0.6936 & -2.89689 & 1.29497\end{array}$ |
| C | $0.235462 .53774-0.36727$ |
| H | -0.84473 $2.64607-0.45427$ |



## 7. Dioxaborole (4.7)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
seไDOB\DOB\DFT CALCULATIONS.chk

```
# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo
m=connectivity int=grid=ultrafine temperature=373.15
DOB at 100 C in GP
Symbolic Z-matrix:
Charge \(=0\) Multiplicity \(=1\)
C
C \(\quad 1 \quad\) B1
\(\begin{array}{lllll}\mathrm{C} & 2 & \mathrm{~B} 2 & 1 & \mathrm{~A} 1\end{array}\)
\(\begin{array}{llllllll}\mathrm{C} & 3 & \mathrm{~B} 3 & 2 & \text { A2 } & 1 & \mathrm{D} 1 & 0\end{array}\)
\(\begin{array}{llllllll}\mathrm{C} & 4 & \mathrm{~B} 4 & 3 & \mathrm{~A} 3 & 2 & \mathrm{D} 2 & 0\end{array}\)
\(\begin{array}{llllllll}\mathrm{C} & 1 & \mathrm{~B} 5 & 2 & \text { A4 } & 3 & \text { D3 } & 0\end{array}\)
```

| H | 3 | B6 |  | A5 |  | D4 | 0 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H | 4 | B7 |  | A6 |  | D5 | 0 |
| H | 5 | B8 | 4 | A7 |  | D6 | 0 |
| H | 6 | B9 | 1 | A8 |  | D7 | 0 |
| O | 1 | B10 | 6 | A9 | 5 |  | 0 |
| O | 2 | B11 | 1 | A10 | 11 | 1 D9 | 0 |
| B | 12 | B12 | 2 | A11 | 1 | D10 | 0 |
| C | 13 | B13 | 12 | 2 A12 |  | 2 D11 | 0 |
| C | 14 | B14 | 13 | $3 \mathrm{Al3}$ |  | 12 D12 | 0 |
| C | 14 | B15 | 13 | A14 |  | 12 D13 | 0 |
| C | 15 | B16 | 14 | 4 A15 |  | 13 D14 | 0 |
| H | 15 | B17 | 14 | 4 A16 |  | 13 D15 | 0 |
| C | 16 | B18 | 14 | 4 A17 |  | 13 D16 | 0 |
| H | 16 | B19 | 14 | 4 A18 |  | 13 D17 | 0 |
| C | 19 | B20 | 16 | 6 A19 |  | 14 D18 | 0 |
| H | 17 | B21 | 15 | 5 A20 |  | 14 D19 | 0 |
| H | 19 | B22 | 16 | 6 A21 |  | 14 D20 | 0 |
| H | 21 | 1 B 23 | 19 | 9 A22 |  | 16 D21 | 0 |
| Variables: |  |  |  |  |  |  |  |
| B1 | 1.39339 |  |  |  |  |  |  |
| B2 | 1.38138 |  |  |  |  |  |  |
| B3 | 1.40103 |  |  |  |  |  |  |
| B4 | 1.39722 |  |  |  |  |  |  |
| B5 | 1.38138 |  |  |  |  |  |  |
| B6 | 1.08262 |  |  |  |  |  |  |
| B7 | 1.08356 |  |  |  |  |  |  |
| B8 | 1.08356 |  |  |  |  |  |  |
| B9 | 1.08262 |  |  |  |  |  |  |
| B10 | 1.3778 |  |  |  |  |  |  |
| B11 | 1.3778 |  |  |  |  |  |  |
| B12 | 1.39415 |  |  |  |  |  |  |
| B13 | 1.5391 |  |  |  |  |  |  |
| B14 | 1.40554 |  |  |  |  |  |  |
| B15 | 1.40554 |  |  |  |  |  |  |
| B16 | 1.39179 |  |  |  |  |  |  |
| B17 | 1.08456 |  |  |  |  |  |  |
| B18 | 1.39179 |  |  |  |  |  |  |
| B19 | 1.08456 |  |  |  |  |  |  |
| B20 | 1.39504 |  |  |  |  |  |  |
| B21 | 1.08436 |  |  |  |  |  |  |
| B22 | 1.08436 |  |  |  |  |  |  |
| B23 | 1.0846 |  |  |  |  |  |  |
| A1 | 122.02265 |  |  |  |  |  |  |
| A2 | 116.54768 |  |  |  |  |  |  |
| A3 | 121.42967 |  |  |  |  |  |  |
| A4 | 122.02263 |  |  |  |  |  |  |


-- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- $-7.4847-3.7216-3.0452 ~-0.0006$
Low frequencies --- $46.7604 \quad 54.8864 \quad 79.1531$

- Thermochemistry -

Zero-point correction= 0.183681 (Hartree/Particle)
Thermal correction to Energy $=\quad 0.200535$
Thermal correction to Enthalpy= 0.201717
Thermal correction to Gibbs Free Energy= 0.132564
Sum of electronic and zero-point Energies $=\quad-638.088201$
Sum of electronic and thermal Energies $=\quad-638.071347$
Sum of electronic and thermal Enthalpies $=\quad-638.070165$
Sum of electronic and thermal Free Energies= $\quad-638.139318$

## 8. Oxazaborole (4.8)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
seไOAB\OAB\DFT CALCULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo $\mathrm{m}=$ connectivity int=grid=ultrafine temperature $=373.15$

| OAB 100 C GP |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbolic Z-matrix: |  |  |  |
| Charge $=0$ Multiplicity $=1$ |  |  |  |
| C | 1.84783 | -0.65325 | -0.00001 |
| C | 1.92877 | 0.74765 | 0. |
| C | 3.16431 | 1.38381 | 0. |
| C | 4.30879 | 0.57958 | 0.00001 |
| C | 4.21699 | -0.81459 | 0. |
| C | 2.97251 | -1.45597 | -0.00001 |
| H | 3.24272 | 2.46511 | 0. |
| H | 5.28532 | 1.04973 | 0.00001 |
| H | 5.12188 | -1.41062 | 0. |
| H | 2.88528 | -2.53539 | -0.00001 |
| H | 0.40859 | 2.21052 | -0.00004 |
| C | -1.81126 | 0.04474 | 0.00001 |
| C | -2.59617 | 1.21049 | 0.00001 |
| C | -2.47705 | -1.19357 | 0.00001 |



## 9. $N$-Methyloxazaborole (4.9)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\100 C (373_15) in gas pha
seไN-OAB $\backslash \mathrm{N}-\mathrm{OAB}$ \DFT CALCULATIONS.chk

[^0]

| Zero-point correction $=$ | 0.224022 (Hartree/Particle) |
| :--- | :---: |
| Thermal correction to Energy $=$ | 0.243546 |
| Thermal correction to Enthalpy $=$ | 0.244727 |
| Thermal correction to Gibbs Free Energy= | 0.169891 |
| Sum of electronic and zero-point Energies $=$ | -657.487321 |
| Sum of electronic and thermal Energies $=$ | -657.467798 |
| Sum of electronic and thermal Enthalpies $=$ | -657.466616 |
| Sum of electronic and thermal Free Energies= | -657.541453 |

e) Thermodynamic calculations in DMSO at $100^{\circ} \mathrm{C}$

## 1. Diazaborole (4.1)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka\Macrocycles\Solvation\DMSO\high temperature\DAB\DFT CA
LCULATIONS.chk

```
# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr
f=(solvent=dmso) geom=connectivity int=grid=ultrafine temperature=373.15
```

DAB OptFrq Calculations in DMSO at 100 C

| Symbolic Z-matrix: |  |  |  |
| :--- | :--- | :--- | :--- |
| Charge $=0$ |  |  |  |
| Multiplicity $=1$ |  |  |  |
| C | -1.91966 | 0.69941 | -0.10051 |
| C | -1.91966 | -0.69941 | 0.10051 |
| C | -3.11417 | -1.40302 | 0.20527 |
| C | -4.31243 | -0.6915 | 0.10205 |
| C | -4.31243 | 0.6915 | -0.10206 |
| C | -3.11417 | 1.40302 | -0.20527 |
| H | -3.11741 | -2.47636 | 0.36142 |
| H | -5.25447 | -1.22169 | 0.18022 |
| H | -5.25447 | 1.22169 | -0.18023 |
| H | -3.11741 | 2.47636 | -0.36142 |
| H | -0.36428 | 2.08941 | -0.34006 |
| H | -0.36428 | -2.0894 | 0.34009 |
| N | -0.5932 | 1.12682 | -0.15641 |
| N | -0.5932 | -1.12682 | 0.15643 |
| B | 0.28839 | 0. | 0. |
| C | 1.84417 | 0. | 0. |
| C | 2.57599 | -1.17251 | -0.25838 |
| C | 2.57599 | 1.17251 | 0.25838 |
| C | 3.96866 | -1.17675 | -0.26014 |
| H | 2.05039 | -2.09714 | -0.47688 |

```
C 
H
C 4.6699 0. 0.
H 4.50746 -2.09505 -0.46695
H 4.50746 2.09505 0.46694
H 5.75429 0. 0.
    Item Value Threshold Converged?
Maximum Force 0.000217 0.000450 YES
RMS Force 0.000057 0.000300 YES
Maximum Displacement 0.001375 0.001800 YES
RMS Displacement 0.000346 0.001200 YES
Predicted change in Energy=-2.696698D-07
Optimization completed.
    -- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- -4.8650 -0.0007 -0.0005 -0.0003 1.5202 
Low frequencies --- 33.1230 56.3973 89.9136
- Thermochemistry -
Zero-point correction= 0.208589 (Hartree/Particle)
Thermal correction to Energy= 0.226255
Thermal correction to Enthalpy=}0.22743
Thermal correction to Gibbs Free Energy= 0.156840
Sum of electronic and zero-point Energies= -598.321340
Sum of electronic and thermal Energies= -598.303674
Sum of electronic and thermal Enthalpies= -598.302492
Sum of electronic and thermal Free Energies= -598.373089
```


## 2. Bromodiazaborole (4.2)

```
\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\Br.DAB \(\backslash \mathrm{DMSO} \backslash \mathrm{BrDAB} \backslash\) DFT CAL CULATIONS.chk
```

```
# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr
```


# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr

f=(solvent=dmso) geom=connectivity int=grid=ultrafine temperature=373.15
f=(solvent=dmso) geom=connectivity int=grid=ultrafine temperature=373.15
BrDAB_OptFrq_100 C_DFT_DMSO
BrDAB_OptFrq_100 C_DFT_DMSO
Symbolic Z-matrix:
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

```
Charge = 0 Multiplicity = 1
```



Sum of electronic and thermal Enthalpies $=\quad-3171.854135$
Sum of electronic and thermal Free Energies $=\quad-3171.931320$

## 3. Methoxydiazaborole (4.3)

| \%nprocshared=4 |  |
| :---: | :---: |
|  | - 4 processors via shared men |
| \%chk=T:\CHM $\backslash$ deg013\Janaka_Gaussian\Solvation\Solvation\MeO.DAB\DMSO\MeOD |  |
| AB\DFT C |  |
| ALCULATIONS.chk |  |
| \# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr $\mathrm{f}=($ solvent $=\mathrm{dmso})$ geom=connectivity int=grid=ultrafine temperature=373.15 |  |
| MeODAB DFT 100 C DMSO |  |
| Symbolic Z-matrix: |  |
| Charge $=0$ Multiplicity $=1$ |  |
| C | $2.78092-0.73303-0.08882$ |
| C | 2.83556 |
| C | 4.056581 .323230 .20086 |
| C | 5.226710 .563430 .11419 |
| C | $5.17276-0.82037-0.07365$ |
| C | $3.94706-1.48452-0.17677$ |
| H | 4.101792 .397410 .34448 |
| H | 6.188521 .056860 .19266 |
| H | $6.09316-1.38893-0.13925$ |
| H | $3.90853-2.55899-0.32041$ |
| H | 1.17476 -2.06306 -0.32294 |
| H | 1.337352 .121480 .30666 |
| N | $1.43902-1.1077-0.15004$ |
| N | 1.527141 .147590 .13918 |
| B | $0.599710 .05534-0.01129$ |
| C | -0.95069 $0.1189-0.0212$ |
| C | -1.64201 1.32995-0.22819 |
| C | -1.73821-1.02385 0.176 |
| C | -3.02566 1.39625-0.23851 |
| H | -1.08438 $2.24565-0.39944$ |
| C | -3.13266 -0.98333 0.17138 |
| H | -1.26082-1.98273 0.35408 |
| C | -3.78361 $0.2355-0.03755$ |
| H | -3.54556 $2.33254-0.40344$ |
| H | -3.69233-1.89484 0.33379 |
| O | -5.1371 $0.39668-0.06342$ |
| C | -5.96379 -0.74331 0.13169 |

$\mathrm{H} \quad-6.98857-0.38112 \quad 0.06899$
$\mathrm{H} \quad-5.79707-1.49577 \quad-0.64659$
$\mathrm{H} \quad-5.79807-1.19336 \quad 1.11642$
Item Value Threshold Converged?
Maximum Force $\quad 0.000025 \quad 0.000450$ YES
RMS Force $0.000007 \quad 0.000300$ YES
Maximum Displacement $0.001002 \quad 0.001800$ YES
RMS Displacement $0.000396 \quad 0.001200$ YES
Predicted change in Energy=-9.660343D-09
Optimization completed.
-- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- $-3.4108 \quad-0.0004 \quad 0.0004 \quad 0.0005 \quad 0.9966$
Low frequencies --- $31.9011 \quad 39.3802 \quad 68.7954$

- Thermochemistry -

Zero-point correction $=\quad 0.240678$ (Hartree/Particle)
Thermal correction to Energy $=\quad 0.262219$
Thermal correction to Enthalpy= 0.263401
Thermal correction to Gibbs Free Energy= 0.183677
Sum of electronic and zero-point Energies $=\quad-712.848650$
Sum of electronic and thermal Energies $=\quad-712.827108$
Sum of electronic and thermal Enthalpies= $\quad-712.825926$
Sum of electronic and thermal Free Energies= $\quad-712.905650$

## 4. Methyldiazaborole (4.4)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\Me.DAB\DMSO\MeDAB \DFT CAL
CULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr
$\mathrm{f}=($ solvent $=\mathrm{dmso})$ geom=connectivity int=grid=ultrafine temperature $=373.15$

| N-methyl DAB_DFT_ Calculations t 100 C DMSO |
| :---: |
| Symbolic Z-matrix: |
| Charge $=0$ Multiplicity $=1$ |
| $\begin{array}{lllll}\text { C } & 1.91231 & 0.48943 & 0.07563\end{array}$ |
| C $\quad 1.87613-0.90419-0.15913$ |
| $\begin{array}{llllllll}\text { C } & 3.04961 & -1.63584 & -0.29282\end{array}$ |


$\begin{array}{lc}\text { Sum of electronic and thermal Enthalpies }= & -637.586003 \\ \text { Sum of electronic and thermal Free Energies }= & -637.661347\end{array}$

## 5. $N$-Methyldiazaborole (4.5)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\NMe DAB\DMSO\NDAB $\backslash \mathrm{DFT}$ CA
LCULATIONS.chk


```
H 0.84129 2.65176 1.39774
H
    Item Value Threshold Converged?
Maximum Force 0.000023 0.000450 YES
RMS Force 0.000005 0.000300 YES
Maximum Displacement 0.001723 0.001800 YES
RMS Displacement 0.000570 0.001200 YES
Predicted change in Energy=-9.541761D-09
Optimization completed.
    -- Stationary point found.
Full mass-weighted force constant matrix:
    Low frequencies --- -0.0009 -0.0003 0.0007 1.7057
    Low frequencies --- 45.6547 53.5218 77.5965
    - Thermochemistry -
    --------------------
Zero-point correction= 0.236306 (Hartree/Particle)
Thermal correction to Energy= 0.256244
Thermal correction to Enthalpy=}0.25742
Thermal correction to Gibbs Free Energy= 0.182082
Sum of electronic and zero-point Energies= -637.607123
Sum of electronic and thermal Energies= -637.587184
Sum of electronic and thermal Enthalpies= -637.586002
Sum of electronic and thermal Free Energies= -637.661346
```


## 6. $N, N^{\prime}$-Dimethyldiazaborole (4.6)

```
\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\DMDAB\DMSO\DMDA B\DFT CALC
ULATIONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr \(\mathrm{f}=(\) solvent \(=\mathrm{dmso})\) geom=connectivity int \(=\) grid \(=\) ultrafine temperature \(=373\). 15
```

$\qquad$

```
DMDAB 100C DMSO
Symbolic Z-matrix:
Charge \(=0\) Multiplicity \(=1\)
\(\begin{array}{lllll}\text { C } & -1.88424 & 0.70228 & 0.08345\end{array}\)
\(\begin{array}{lllll}\text { C } & -1.88424 & -0.70228 & -0.08346\end{array}\)
```



[^1]Zero-point correction $=\quad 0.263922$ (Hartree/Particle)

| Thermal correction to Energy $=$ | 0.286205 |
| :--- | :---: |
| Thermal correction to Enthalpy $=$ | 0.287386 |
| Thermal correction to Gibbs Free Energy= | 0.206891 |
| Sum of electronic and zero-point Energies= | -676.894107 |
| Sum of electronic and thermal Energies= | -676.871824 |
| Sum of electronic and thermal Enthalpies $=$ | -676.870642 |
| Sum of electronic and thermal Free Energies= | -676.951137 |

## 7. Dioxaborole (4.7)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\DOB\DMSO\DOB\DFT CALCULAT
IONS.chk

```
# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr
f=(solvent=dmso) geom=connectivity int=grid=ultrafine temperature= = 373.
15
```

-------------------------------------------------------------------------------

DOB at 100 C in DMSO
Symbolic Z-matrix:

| Charge $=0$ Multiplicity $=1$ |
| :--- |

C
C
C

| H | 17 | B21 | 15 | A20 | 14 | D19 |
| :--- | :---: | :--- | :--- | :--- | :--- | :--- | 000



## 8. Oxazaborole (4.8)

\%nprocshared=4
Will use up to 4 processors via shared memory.
\%chk=T:\CHM\deg013\Janaka_Gaussian\Solvation\Solvation\OAB\DMSO\OAB\DFT CALCULAT
IONS.chk
\# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) scr $\mathrm{f}=($ solvent $=\mathrm{dmso})$ geom=connectivity int=grid=ultrafine temperature $=373.15$

OAB 100 C DMSO

| Symbolic Z-matrix: |  |  |  |
| :--- | :--- | :--- | :--- |
| Charge $=0$ | Multiplicity $=1$ |  |  |
| C | -1.84783 | -0.65325 | 0.00001 |
| C | -1.92877 | 0.74765 | 0. |
| C | -3.16431 | 1.38381 | 0. |
| C | -4.30879 | 0.57958 | -0.00001 |
| C | -4.21699 | -0.81459 | 0. |
| C | -2.97251 | -1.45597 | 0.00001 |
| H | -3.24272 | 2.46511 | 0. |
| H | -5.28532 | 1.04973 | -0.00001 |
| H | -5.12188 | -1.41062 | 0. |
| H | -2.88528 | -2.53539 | 0.00001 |
| H | -0.40859 | 2.21052 | 0.00004 |
| C | 1.81126 | 0.04474 | -0.00001 |
| C | 2.59617 | 1.21049 | -0.00001 |
| C | 2.47705 | -1.19357 | -0.00001 |
| C | 3.98677 | 1.14677 | 0. |
| H | 2.11879 | 2.18593 | -0.00001 |
| C | 3.86753 | -1.26367 | 0. |
| H | 1.8929 | -2.10714 | -0.00002 |
| C | 4.62566 | -0.0931 | 0.00001 |
| H | 4.57238 | 2.05951 | 0.00001 |
| H | 4.36132 | -2.22922 | 0. |
| H | 5.70885 | -0.1461 | 0.00001 |
| N | -0.61542 | 1.22583 | 0.00002 |
| O | -0.53456 | -1.05557 | 0.00002 |
| B | 0.26453 | 0.09762 | -0.00003 |

RMS Displacement $0.000335 \quad 0.001200$ YES
Predicted change in Energy=-7.468133D-09
Optimization completed.
-- Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies --- -13.1152 $-9.2685-4.5806-0.0005-0.0004 \quad 0.0007$
Low frequencies --- $\begin{array}{lllll}17.0728 & 54.9876 & 84.1848\end{array}$

- Thermochemistry -

Zero-point correction $=\quad 0.195938$ (Hartree/Particle)
Thermal correction to Energy= 0.213267
Thermal correction to Enthalpy= 0.214448
Thermal correction to Gibbs Free Energy= 0.143435
Sum of electronic and zero-point Energies $=\quad-618.208389$
Sum of electronic and thermal Energies $=\quad-618.191061$
Sum of electronic and thermal Enthalpies $=\quad-618.189879$
Sum of electronic and thermal Free Energies $=\quad-618.260893$

## EDUCATION

Master of Science in Chemistry
Aug 2015-Aug 2017
Sam Houston State University
Thesis title DIAZABOROLES: EXPERIMENTAL INVESTIGATIONS OF THEIR DYNAMIC COVALENT NATURE AND COMPUTATIONAL CHEMISTRY
GPA $\quad 4.00 / 4.00$
Bachelor of Science (Joint Major) in Chemistry and Physics
Sep 2007-June 2012
Rajarata University of Sri Lanka
GPA $\quad 3.62$ (First Class)

## ACADEMIC RESEARCH EXPERIENCE

## Presentations

Abeysinghe, J. P.; Gross, D. E. Experimental and Computational studies of Diazaborole. Texas Academy of Science, $120^{\text {th }}$ Annual Meeting, University of Mary Hardin-Baylor, Belton, TX, March 3, 2017.

Abeysinghe, J. P.; Gross, D. E. Efficient formation and interchange of diazaborole under mild conditions. SWRM of the American Chemical Society, Galveston, TX, November 10-12, 2016.

## Sam Houston State University

Aug 2015-Aug 2017
Diazaboroles: Experimental Investigations of their Dynamic Covalent Nature and
Computational Chemistry- The diazaborole, two B-N moieties included heterocycle which is isoelectronic and isosteric with its carbon derivative. Since the B-N moiety brings dynamic nature to the molecule, diazaborole shows error checking and proofreading characters. Diazaborole undergoes self-assembly reactions with deriving more thermodynamically stable macrocycles.

- Studied solvent effect for the diazaborole formation reaction
- Dynamic nature of the diazaborole reaction has been observing
- Computational calculations of diazaborole derivatives have been studying
- XRD structure recognition and comparison of substituents of diazaborole have been following

Rajarata University of Sri Lanka.
July 2011-July 2012

- Designed a mobile temperature measurement station by using PIC16F877 with LM35 temperature sensor
- Converted Receiving analog signals from LM35 to the digital PC readable codes and then it was supplied to the computer
- Measured elapsed temperature and it was displayed graphically and attractively with the time in LabVIEW interface


## Rajarata University of Sri Lanka

Mar 2012-May 2012

- Designed a Dye Sensitized Solar Cell by using mesoscopic $\mathrm{TiO}_{2}$ semiconductor oxide film (highly porous structure with an extremely high surface area) and it was deposited upon two transparent conducting oxide coating glass sheets
- Immersed $\mathrm{TiO}_{2}$ thin film in HEMATOXYLINE dye and it was kept some time to form covalent bonds with the dye
- Tested efficiency of HEMATOXYLINE as an electrolyte in the Dye-Sensitized Solar cell


## TEACHING EXPERIENCE

## Graduate Teaching Assistant

Sep 2015 -Apr 2017
Department of Chemistry, Sam Houston State University

- Conducted General Chemistry laboratory classes and tutoring classes
- Conducting-Instrumental Analytical chemistry laboratory classes (AAS, ICP/AES, UV/Vis, GC/MS, Fluorescence spectroscopy) for 4th-year students.


## INDUSTRY EXPERIENCE

## Research and Development Chemist

Aug 2012-Aug 2014
Haycarb PLC, Madampe, Sri Lanka.
Haycarb PLC is the world's leading manufacturer and marketer of coconut shell based activated carbon solutions over 35 years. Innovation, implementation, and review form a constant cycle, as Haycarb PLC strives to improve product quality, process efficiency, energy conservation, reliability and usefulness for the customers. Haycarb manufactures a complete range of standard and tailor-made activated carbon granules, powders, and pellets for a full spectrum of applications across diverse industries.

- Collaborated with other departments from variety of large scale manufacturing processes
- Developed new activated carbon samples to fulfill the customer requirements
- Improved available activated carbon properties to cure diverse customer requirements


## Manufacturing Executive

Aug 2014-Aug 2015
Ultracarb, Haycarb PLC, Madampe, Sri Lanka.
Ultracarb is a very special and separate section in Haycarb. Ultracarb is produced very pure ( $\mathrm{Na}, \mathrm{K}, \mathrm{Fe}<20 \mathrm{ppm}$ ), small size ( $\mu \mathrm{m}$ range) powder carbon which adapts to Electrical Double Layer Capacitors as carbon electrodes.

- Continued the process with extreme attention and the utmost caution to produce contamination free product
- Administrated the workers towards fulfilling the targets in expected time intervals and it improved my management skills
- Handled ISO Documents and maintain calibrations in instruments in the production plant


## AWARDS

- Sam Houston State University Graduate Scholarship in 2015 and 2016
- Sam Houston State University College of Science Summer stipend for Thesis Research in 2016
- College of Sciences Special Graduate Scholarship 2016


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[^1]:    - Thermochemistry -

