# 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.

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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.<sup>1</sup>

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.<sup>2</sup> 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 non-covalent interactions so as to form supramolecular entities, supramolecules possessing features as well defined as those of molecules themselves."<sup>3</sup>

In supramolecular chemistry, non-covalent interactions occur between molecular components in order to make larger molecular architectures through intermolecular interactions such as hydrogen bonding,<sup>4</sup> metal-ligands coordination bonds,<sup>5</sup> van der Waals forces,<sup>6</sup> pi-pi interactions,<sup>7</sup> and electrostatic interactions.<sup>8</sup> The non-covalent interactions are weak but dynamic by nature.<sup>9</sup> Molecular self-assembly, molecular recognition,<sup>10</sup> mechanically interlocked molecular architectures,<sup>11</sup> host-guest chemistry<sup>12</sup> and dynamic covalent chemistry<sup>13–20</sup> 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 self-assemble 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,<sup>21,22</sup> gas purification, molecular recognition,<sup>23</sup> and heterogeneous catalysis.<sup>24</sup> 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,<sup>4</sup> van der Waals forces,<sup>6</sup> pi-pi interactions,<sup>7</sup> and electrostatic interactions.<sup>10</sup> 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,<sup>25</sup> and drug delivery.<sup>26,27</sup>

**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 (C, N, O, S etc.) and high thermal stability from covalent bonding.<sup>28,29</sup> 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 B<sub>3</sub>O<sub>3</sub> (boroxine) ring (Figure 1).<sup>30</sup> COF-8 (Figure 2) has been reported as the least dense crystalline material.<sup>30</sup>



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,<sup>30–32</sup> catalysis,<sup>33,34</sup> optoelectronics,<sup>35–37</sup> and charge storage.<sup>38</sup> 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.<sup>39,40</sup> 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.<sup>41</sup> 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,<sup>17</sup> and the presence of stabilization sources (templates, metal ions, protons, etc.).<sup>14</sup>

**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 C-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,<sup>41</sup> aldol, and metathesis reactions<sup>42,43</sup> are well-known C-C dynamic covalent bond forming reactions.

*Carbon–heteroatom dynamic covalent reactions*. Replacing a carbon atom with a heteroatom such as O, 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)<sup>20</sup> are well-known examples for this category.

$$\begin{array}{c} O \\ H \\ R_1 \end{array} + R_2 - NH_2 \longrightarrow R_1 \\ R_1 \\ R_2 \end{array}$$

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.<sup>44</sup> Boroncontaining molecular systems have received attention in the field of supramolecular chemistry because of the superior structure-directing property of boron based interactions.<sup>45</sup> 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 sp<sup>2</sup> 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,<sup>46</sup> blue emissive materials,<sup>47</sup> sensors,<sup>48</sup> and covalent organic frameworks.<sup>30,49,50</sup>

**1.4.3 B-N Bond.** Recently, the substitution of C=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 C=C, B-N containing organic compounds have different reactivity and photo physical properties.<sup>51</sup> The B-N bond strength strongly depends on the steric effects of the bulky substituents on boron or nitrogen.<sup>52</sup> Thus, B-N bonds can be used to tune the structural properties of large molecular architectures via the changes of substituents on the nitrogen.<sup>53</sup> Höpfl and his group have shown that the capability of dative B-N bonds to provide rigidity to boronate ester-based structures.<sup>54,55</sup>

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

Diazaborole **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 **1.3** exhibits exceptional stability to hydrolysis due to the stable B-N bonds.<sup>56,57</sup>



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,<sup>58</sup> Letsinger's,<sup>59–61</sup> Snyder's,<sup>62</sup> and Soloway's groups.<sup>63</sup> In 1962, Marvel reported the first diazaborole polymer.<sup>64</sup> The synthesis of diazaborole based materials has been ongoing since the 1970s.<sup>65,66,67</sup> During this time,

researchers have studied the potential applications of diazaborole.<sup>48,58–62</sup> Recently, rapid and waste-free methods for diazaborole formation in solvent free conditions were introduced.<sup>68,69</sup> In addition to the study of diazaborole monomers, the applications, and properties of diazaborole containing oligomers<sup>61,70,45</sup> and polymers<sup>64,71,72,73,74</sup> 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,<sup>70,74</sup> benzene,<sup>59</sup> ether,<sup>75</sup> and N-methyl-2pyrrolidone<sup>72</sup> are common solvents for diazaborole synthesis. Further, reflux of starting materials in dimethylacetamide,<sup>64</sup> and toluene,<sup>76</sup> 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).<sup>77</sup> 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. <sup>61</sup> They formed bis-phenylboradiazole **1.6** by boiling 2,2'-tolanediboronic acid (**1.7**) and diamine **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.<sup>58</sup> Various diazaborole analogues (dioxaborole **1.9**, oxazaborole **1.10**, dithiaborole **1.11**, and thiazaborole **1.12**) have been synthesized using this method (Figure 8).<sup>58</sup>



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 **1.5** and ethyl tartrate ester of benzeneboronic acid **1.13** 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).<sup>60</sup>



Figure 9. Synthesis of diazaborole from a tartrate ester.

Brotherton and group introduced diazaborole preparation from the condensation reaction of boroxine **1.16** and diamine **1.5** (Figure 10).<sup>78</sup>



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 °C under vacuum for 1 h to remove the water that forms in this reaction.<sup>69</sup>



Figure 11. The formation of diazaborole 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).<sup>68</sup>



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 **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 **1.3** is lowered, and **1.3** shows a blue luminescence when it is irradiated with UV light.<sup>79</sup> Furthermore, diazaborole **1.3** can act as an electron transporting material because of the extended  $\pi$ -electron conjugation.<sup>80</sup>



*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 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.<sup>45</sup>



*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).<sup>80</sup> Compounds **1.18a-c** and **1.19a-b** show good p-type semiconducting behavior with hole
mobilities ranging from 10<sup>-7</sup> to 10<sup>-2</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.



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  $10^{-2}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Further, they have shown ambipolar FET characteristic of biphenyl diazaborole derivative, 1.22b to have  $2.3 \times 10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (n-type) and  $1.5 \times 10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (p-type) electron and hole mobilities, respectively (Figure 16).<sup>81</sup>



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.<sup>74</sup>



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.<sup>82</sup>

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 **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<sup>60,62,68,70,74,80,81,83</sup> as the solvent. The use of xylene,<sup>78</sup> benzene,<sup>58,59</sup> and ether<sup>75</sup> 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,<sup>77</sup> heating in toluene at 80 °C for 8 h,<sup>76</sup> heating in dry dimethylacetamide at 230 °C bath temperature,<sup>64</sup> or heating in dimethylformamide under nitrogen atmosphere at 130 °C for three days.<sup>84</sup>

Our research group has qualitatively examined the kinetics of diazaborole formation through the condensation of starting materials in CDCl<sub>3</sub> and DMSO-d<sub>6</sub>. The formation reaction was carried out in CDCl<sub>3</sub> at 50 °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 **2.3a**, 72% for **2.3b**, and 41% for **2.3c** (Figure 19).<sup>85</sup>



Figure 18. The formation of diazaboroles 2.3a-c in CDCl<sub>3</sub> at 50 °C.



Figure 19. The formation of diazaborole derivatives in CDCl<sub>3</sub> at 50 °C.<sup>85</sup>

The relatively slow formation of **2.3c** 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 (61 °C). So, the reaction was then repeated in DMSO-d<sub>6</sub> at  $100 \ ^{\circ}$ C (Figure 20).<sup>85</sup>



*Figure 20*. The formation of diazaborole **2.3a** in DMSO-d<sub>6</sub> at 100 °C.<sup>85</sup>

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<sub>6</sub> at 100  $^{\circ}$ C.<sup>85</sup>



Figure 21. The reaction kinetic of diazaborole formation in DMSO-d<sub>6</sub> at 100 °C.<sup>85</sup>

# 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 **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.


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.

<sup>1</sup>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 **2.1** as the starting materials under reflux reaction conditions in toluene.



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  $\stackrel{\phantom{1}}{\delta}(ppm)$ 

*Figure 26.* <sup>1</sup>H-NMR of diazaborole formation under reflux conditions. <sup>1</sup>H NMR were taken in CDCl<sub>3</sub>.

The <sup>1</sup>H-NMR spectra showed a boroxine peak shift at  $\approx$  8.2 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 CDCl<sub>3</sub> is relatively slow.<sup>76</sup> 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 °C.

#### Table 1

Solvent	Polar or non-polar	Boiling Point* (°C)	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

### Solvents and their polar/non-polar characteristics

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

After two weeks, <sup>1</sup>H-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 1,4-dioxane (Figure 30).



*Figure 27.* <sup>1</sup>H-NMR of diazaborole prepared by two-week reaction in different solvents: tetrahydrofuran, ethyl acetate, acetonitrile, and 1,4-dioxane. <sup>1</sup>H-NMR was taken in CDCl<sub>3</sub>.

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 °C. <sup>1</sup>H NMR were taken in CDCl<sub>3</sub>.

A similar time dependent study was carried out with tetrahydrofuran at room temperature (Figure 30). The reaction progress was monitored from <sup>1</sup>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.



*Figure 31.* <sup>1</sup>H-NMR spectra of the reaction of benzenediamine **2.1** and phenylboronic acid (**2.2a**) in THF. <sup>1</sup>H NMR were taken in CDCl<sub>3</sub>.

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 <sup>1</sup>H-NMR signals reveal that the addition of molecular sieves resulted in the formation of more boroxine **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* **2.3***a and boroxine* **2.4** *in THF with varying amounts of molecular sieves* 

Molecular sieves (equiv)	% diazaborole 2.3a	% boroxine <b>2.4</b>
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 **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.



Figure 33. The solvents used to study diazaborole formation.

# Table 3

Solvent	Boiling Point* °C	Evaporation temperature °C	Evaporation time (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

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

\*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 <sup>1</sup>H-NMR spectra of boroxine and diazaborole (Figure 34, Figure 35, and Figure 36)



*Figure 34.* <sup>1</sup>H-NMR spectra of diazaborole formation in low boiling solvents. <sup>1</sup>H NMR were taken in CDCl<sub>3</sub>.



*Figure 35.* <sup>1</sup>H-NMR spectra of diazaborole formation in high boiling solvents. <sup>1</sup>H NMR were taken in CDCl<sub>3</sub>.



Percent diazabborole formation

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 *N*,*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 (>100 °C) 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

Solute	"Good" solvent	"Bad" solvent	Crystal formation	Color	X-ray quality
diazaborole <b>2.3a</b>	1,4-dioxane	hexane	yes	colorless	yes
	1,4-dioxane	hexane	no	-	No
	DCM	hexane	yes	colorless	yes
	CHCl <sub>3</sub>	hexane	yes	colorless	no
	ethyl acetate	hexane	yes	yellow	no
bromodiazaborole <b>2.3b</b>	1,4-dioxane	hexane	no	-	no
methoxydiazaborole <b>2.3c</b>	1,4-dioxane	hexane	no	-	no
boroxine <b>2.4</b>	1,4-dioxane	hexane	no	-	no
methyldiazaborole <b>2.5</b>	1,4-dioxane	hexane	no	-	no
	CHCl <sub>3</sub>	hexane	no	-	no
	DCM	hexane	no	-	no
	ethyl acetate	hexane	no	-	no

Crystal formation from vapor diffusion

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 1,4-dioxane 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 (-20 °C) 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" solvent	"Bad" solvent	Crystal formation	Color _	X-ray quality
					Yes/No
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 <b>2.4</b>	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 8h reaction time. Boroxine is always present below the 8 h reaction time. The reaction of phenylboronic acid and benzene-1,2-diamine in 1,4-dioxane 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 CHCl<sub>3</sub>-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 CDCl<sub>3</sub> was stored over activated 4 Å molecular sieves.

*NMR spectroscopy*. The <sup>1</sup>H-NMR spectra were collected on a JEOL Eclipse 300<sup>+</sup> spectrometer. Chemical shifts were reported in  $\delta$  (ppm) relative to residual solvent protons (CHCl<sub>3</sub>: 7.26) or (DMSO-d<sub>6</sub>: 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 mmol, 1 equiv) and phenylboronic acid **2.2a** (61.1 mg, 0.5 mmol, 1 equiv) were mixed in toluene (20 mL) in a round bottom flask. The reaction mixture was refluxed (20 min, 1 h, 2 h, 3 h, and 8 h). Then, the solvent was removed under reduced pressure (27 in Hg) at 45 °C and <sup>1</sup>H NMR was obtained. 100% diazaborole formation was observed for 8 h reaction (A tan color solid (67.9 mg, 78%)). The 20 min, 1h, 2h, 3h refluxed reactions resulted in 13.8%, 54.3%, 74.2%, 87.3% conversion of diazaborole, respectively, compare to boroxine.<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) δ: 7.74 (d, 2H), 7.43 (t, 3H), 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 mmol, 1 equiv) and phenylboronic acid **2.2a** (121 mg, 1 mmol, 1 equiv) were mixed in the solvent (5 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 <sup>1</sup>H NMR was obtained.

*Reaction in 1,4-dioxane.* An equimolar amount of benzene-1,2-diamine **2.1** (108 mg, 1 mmol, 1 equiv) and phenylboronic acid **2.2a** (121 mg, 1 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 °C for 10 min and <sup>1</sup>H NMR was obtained.

*Reaction in tetrahydrofuran.* An equimolar amount of benzene-1,2-diamine **2.1** (108 mg, 1 mmol, 1 equiv) and phenylboronic acid **2.2a** (121 mg, 1 mmol, 1 equiv) were mixed in tetrahydrofuran (5 mL) in a vial. The reaction mixture was kept at room temperature (30 min, 1 h, and 5 h). Then, vial was connected to the rotary evaporator. Aspirator vacuum was applied (27 in Hg) and heated at 45 °C for 10 min and <sup>1</sup>H NMR was obtained. <sup>1</sup>H-NMR spectra of the reaction time 30 min, 1 h and 5h 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 mg, 1 mmol, 1 equiv) and phenylboronic acid **2.2a** (121 mg, 1 mmol, 1 equiv), were mixed in tetrahydrofuran (5 mL) in a vial. Then, molecular sieves (3 Å: 200 mg, 403 mg, 601 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 <sup>1</sup>H NMR was obtained. <sup>1</sup>H-NMR spectra of the reaction with 200 mg, 403 mg, 601 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 **2.1** (108 mg, 1 mmol, 1 equiv) and phenylboronic acid **2.2a** (121 mg, 1 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 <sup>1</sup>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 Mo 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.<sup>86</sup> 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.<sup>17</sup> 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.<sup>14</sup> DCRs give thermodynamically stable products and ensure the capability of designing rational large-scale molecular architectures.<sup>87</sup> Even though dynamic covalent chemistry resembles supramolecular chemistry in the sense of reaction reversibility,<sup>13</sup> the equilibrium process can be very slow due to the associated slow reaction kinetics.<sup>14</sup> 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.<sup>88</sup> In that study, diazaborole was shown to readily hydrolyze under acidic or basic reaction conditions (Figure 39).



*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.<sup>85</sup>



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 CDCl<sub>3</sub> at 50 °C to give diazaborole **3.6** and **3.7**, respectively (Figure 41).<sup>85</sup>



*Figure 41*. The exchange reaction of diazaborole **3.1** with bromo and methoxy-substituted boronic acids **3.4** and **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 **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 **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 **3.1** in solution was examined by monitoring the changes in its <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) at 100 °C (Figure 42). The <sup>1</sup>H-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 **3.2** and benzenediamine **3.3** discloses the stability of **3.1** to hydrolysis even under these harsh conditions.



Figure 42. Heating diazaborole **3.1** in DMSO at 100 °C.



*Figure 43*. Partial <sup>1</sup>H NMR spectra of diazaborole **3.1** in DMSO-d<sub>6</sub> at 100 °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.<sup>64</sup> 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 °C. Peaks assignable to all four boroxines were observed in the <sup>1</sup>H NMR spectrum (Figure 45).



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



#### 3.3.2 Exchange reactions of diazaborole.

First, the exchange diazaborole **3.1** with bromophenylboronic acid **3.4** (1 mmol each) was examined in 1,4-dioxane (5 mL) at 50 °C (Figure 46).



*Figure 46*. The reaction of diazaborole **3.1** and bromophenylboronic acid **3.4** in 1,4-dioxane at 50 °C.

The reaction was monitored by observing the signals for 3.1 (H<sub>a</sub>) and 3.6 (H<sub>d</sub>, H<sub>e</sub>). However, due to the peak overlap of boroxines (7.5 ppm) 3.8-3.11 and bromodiazaborole

3.6, the exchange reaction of 3.1 with 3.4 could not be examined quantitatively (Figure 47). A clear decrease in intensity for 3.1 and an increase in the signals for 3.6 was observed.



*Figure 47.* <sup>1</sup>H NMR spectra of the reaction of diazaborole **3.1** and bromophenylboronic acid **3.4** in 1,4-dioxane at 50 °C. <sup>1</sup>H NMR spectra were obtained in CDCl<sub>3</sub>.

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 <sup>1</sup>H-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).



*Figure 48.* <sup>1</sup>H-NMR spectra of the reaction of diazaborole **3.1** and bromophenylboronic acid **3.4** in 1-butanol at 50 °C and 70 °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 °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).



*Figure 49.* <sup>1</sup>H-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 **3.12** 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 **3.1** and **3.12** was first studied in CDCl<sub>3</sub> at room temperature (Figure 51). The reaction progress was monitored by integrating the <sup>1</sup>H-NMR signals associated with the methyl protons of **3.12** (2.21 ppm) and **3.13** (2.39 ppm).



*Figure 51*. The reaction of diazaborole **3.1** and methylbenzenediamine **3.12** in CDCl<sub>3</sub> 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.* <sup>1</sup>H-NMR spectra of the reaction of diazaborole **3.1** and methylbenzenediamine **3.15** in CDCl<sub>3</sub> at room temperature.

Due to the slow equilibration of the reaction in CDCl3 at room temperature, the

transamidation reaction of **3.1** and **3.12** was studied in DMSO-d<sub>6</sub> at 100 °C (Figure 53).



*Figure 53*. The reaction of diazaborole **3.1** and methylbenzenediamine **3.12** in DMSO-d<sub>6</sub> at 100 °C.



*Figure 54.* <sup>1</sup>H-NMR spectra of the reaction of diazaborole **3.1** and methylbenzenediamine **3.12** in DMSO-d<sub>6</sub> at 100 °C.

The initial equilibration rate was slow. However, the increase of **3.13** (H<sub>a</sub>) and decrease of **3.12** (H<sub>b</sub>) in the <sup>1</sup>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 **3.1** to methyldiazaborole **3.13** in DMSO-d<sub>6</sub> at 100 °C.

Concurrent with the above, the reverse reaction of 3.13 and 3.3 was investigated

in DMSO-d<sub>6</sub> at 100 °C (Figure 56).



*Figure 56*. The reaction of methyldiazaborole **3.13** and benzenediamine **3.3** in DMSO-d<sub>6</sub> at 100 °C.

The reaction was monitored by following the consumption and formation of **3.13** (H<sub>b</sub>) and **3.12** (H<sub>a</sub>), respectively. The <sup>1</sup>H-NMR spectra revealed that methylbenzenediamine **3.12** began forming within 5 h and increased with time, whereas peaks associated to methyldiazaborole **3.13** 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 **3.1** with **3.12** where 56% conversion was observed, but the equilibration time was significantly shorter.



benzenediamine **3.3** in DMSO-d<sub>6</sub> at 100 °C.



*Figure 58.* Percent conversion of methyldiazaborole **3.13** to methylbenzenediamine **3.12** in DMSO-d<sub>6</sub> at 100 °C..

While heating in DMSO at 100 °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 **3.12** were mixed in dioxane and heated to 50 °C (Figure 59). Aliquots were taken from the reaction and most of the dioxane was removed. <sup>1</sup>H NMR analysis provided qualitative evidence of the conversion of diazaborole **3.1** to diazaborole **3.13** (Figure 60).


*Figure 59.* The reaction of diazaborole **3.1** and methylbenzenediamine **3.12** in 1,4-dioxane at 50 °C.



*Figure 60.* <sup>1</sup>H-NMR spectra of the transamidation of diazaborole **3.1** and methylbenzenediamine **3.12** in 1,4-dioxane at 50 °C. <sup>1</sup>H-NMR were taken in CDCl<sub>3</sub>.

The reverse reaction was carried out under the same conditions (Figure 61). Aliquots were taken from the reaction of methyldiazaborole **3.13** and benzenediamine **3.3**  in 1,4-dioxane at 50 °C over a 278 h period and most of the solvent was removed under reduced pressure.



*Figure 61*. The reaction of methyldiazaborole **3.16** and benzenediamine **3.3** in 1,4-dioxane at 50  $^{\circ}$ C.

The <sup>1</sup>H-NMR spectra (Figure 62) illustrate the formation of

methylbenzenediamine **3.12** (H<sub>a</sub>) and consumption of methyldiazaborole **3.13** (H<sub>b</sub>) 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.* <sup>1</sup>H-NMR spectra of aliquots taken from the reaction of methyldiazaborole **3.13** and benzenediamine **3.3** in 1,4-dioxane at 50 °C over a 278 h period. <sup>1</sup>H NMR were taken in CDCl<sub>3</sub>.



*Figure 63.* Percent conversion of methyldiazaborole **3.13** in the reaction of methyldiazaborole **3.13** and benzenediamine **3.3** in 1,4-dioxane at 50 °C.

# **3.4 Conclusions**

Diazaborole showed high stability in solvent phase, at 100 °C in DMSO-d<sub>6</sub>, for more than 15 days without significant changes. Therefore, it is determined that diazaborole **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 **3.1** and **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 **3.1** to **3.5** in reflux conditions.

The transamidation reaction of diazaborole **3.1** and methylbenzenediamine **3.12** in CDCl<sub>3</sub> was slow and reaction reached 22 % conversion of methyldiazaborole **3.13** after 168 h. However, in DMSO-d<sub>6</sub> at 100 °C the transamidation of diazaborole **3.1** and methylbenzenediamine **3.12** revealed that the reaction reached equilibrium within 220 h, while reaching nearly 55 % conversion of methyldiazaborole **3.13**. Further, the reverse reaction of **3.13** and **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 °C reached equilibrium within 45 h with 70 % conversion. The reverse reaction of **3.13** and **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 CDCl<sub>3</sub> was stored over activated 4 Å molecular sieves.

NMR spectroscopy. The <sup>1</sup>H-NMR spectra were collected from JEOL Eclipse 300+ spectrometer. Chemical shifts were reported in  $\delta$  (ppm) relative to the <sup>1</sup>H (CHCl<sub>3</sub>: 7.26) or (DMSO-d<sub>6</sub>: 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 g, 15.00 mmol) and methylbenzenediamine **3.9** (1.83 g, 15.00 mmol) was dissolved in toluene (50 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 mL), then cold hexane (10 mL). The crude product was recrystallized from toluene and white color crystals (2.50 g) were obtained in 80% yield. The <sup>1</sup>H-NMR analysis of the product was consistent with expectations. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 7.71 (m, 2H), 7.42 (m, 3H), 6.99 (d, 1H), 6.93 (s, 1H), 6.77 (d, 1H).

*Exchange reaction of diazaborole with bromophenylboronic acid.* Diazaborole **3.1** (38.8 mg, 0.2 mmol, 1 equiv) and bromophenylboronic acid **3.4** (40.3 mg, 0.2 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 °C. Then, the solvent was removed under reduced pressure at 50 °C and <sup>1</sup>H NMR was obtained.

Diazaborole **3.1** (38.8 mg, 0.2 mmol, 1 equiv) and bromophenylboronic acid **3.4** (40.3 mg, 0.2 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 °C. Then, the solvent was removed under reduced pressure at 50 °C and <sup>1</sup>H NMR was obtained.

Diazaborole **3.1** (9.8 mg, 0.05 mmol, 1 equiv) and bromophenylboronic acid **3.4** (10.2 mg, 0.05 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  $^{\circ}$ C and <sup>1</sup>H NMR was obtained.

Diazaborole **3.1** (9.8 mg, 0.05 mmol, 1 equiv) and bromophenylboronic acid **3.4** (10.2 mg, 0.05 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 °C and <sup>1</sup>H NMR was obtained.

Diazaborole **3.1** (0.194 g, 1 mmol, 1 equiv) and bromophenylboronic acid **3.4** (0.201 g, 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 °C. <sup>1</sup>H NMR was obtained periodically for 101.5 h.

# *Reaction of diazaborole with methylbenzenediamine.* An equimolar amount of diazaborole **3.1** (9.7 mg, 0.05 mmol, 1 equiv) and methylbenzenediamine **3.12** (6.1 mg, 0.05 mmol, 1 equiv) were mixed in NMR tube in CDCl<sub>3</sub> (0.6 mL). Reaction progress was monitored by <sup>1</sup>H NMR spectroscopy.

An equimolar amount of diazaborole **3.1** (0.194 g, 1 mmol, 1 equiv) and methylbenzenediamine **3.12** (0.122 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  $^{\circ}$ C. <sup>1</sup>H NMR was obtained periodically for 119.5 h

An equimolar amount of diazaborole **3.1** (9.7 mg, 0.05 mmol, 1 equiv) and methylbenzenediamine **3.12** (6.1 mg, 0.05 mmol, 1 equiv) were mixed in an NMR tube in DMSO-d<sub>6</sub> (0.75 mL). Reaction mixture was heated at 100 °C in an oil bath. Reaction progress was monitored by <sup>1</sup>H NMR spectroscopy.

*Reaction of methyldiazaborole with benzenediamine.* An equimolar amount of benzenediamine **3.3** (0.208 g, 1 mmol, 1 equiv) and methyldiazaborole **3.13** (0.108 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 °C. <sup>1</sup>H NMR was obtained periodically for 278 h.

An equimolar amount of benzenediamine **3.3** (5.4 mg, 0.05 mmol, 1 equiv) and methyldiazaborole **3.13** (10.4 mg, 0.05 mmol, 1 equiv) were mixed in NMR tube in DMSO (0.75 mL). Reaction mixture was heated at 100 °C in an oil bath. Reaction progress was monitored by <sup>1</sup>H NMR spectroscopy.

### Table 6

Reaction	starting material	product
3.1 + 3.4	δ 7.74 ppm ( <b>3.1</b> )	δ 7.57 ppm ( <b>3.5</b> )
3.1 + 3.12	δ 2.02 ppm ( <b>3.12</b> )	δ 2.26 ppm ( <b>3.13</b> )
3.3 + 3.13	δ 7.26 ppm ( <b>3.13</b> )	δ 2.02 ppm ( <b>3.12</b> )

<sup>1</sup> H-NMR signal	s used to a	letermine th	ne percent	conversion
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### **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.<sup>76,81,89–98</sup> Furthermore, Weber et al.,<sup>90,93</sup> and Lu-Yi Zou et al.,<sup>92</sup> 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,<sup>76,94,99</sup> dipole moments,<sup>94</sup> and ring currents in the diazaborole system as indicated by nucleus-independent chemical shift values.<sup>96,99</sup> Most recently, Northrop and Goldberg used computational calculations to determine thermodynamics of diazaborole and some of its analogues alongside experimental information.<sup>76</sup>

# 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.





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 6-311G 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 p-characteristics 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 Å) 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 Å and the N-B bond length is relatively longer (1.44 Å). The other diazaborole derivatives possess similar bond lengths (1.44 Å for the B-N bond). The calculated B-N bond length (1.44 Å) 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 Å B-N bond).<sup>76</sup>



Figure 65. The isostructural framework of diazaborole.

Table 7

Bond lengths of diazaborole analogues

Molecule	1-6	4-6	Bonds 5-6	2-4	3-5
	1.56	1.44	1.44	1.39	1.39
	С-В	N-B	N-B	N-C	N-C
	1.56	1.44	1.44	1.40	1.40
	C-B	N-B	N-B	N-C	N-C
	1.55	1.44	1.44	1.39	1.39
	С-В	N-B	N-B	N-C	N-C
	1.56	1.44	1.44	1.39	1.40
	С-В	N-B	N-B	N-C	N-C
	1.56	1.44	1.44	1.39	1.39
	C-B	N-B	N-B	N-C	N-C

Molecule	1-6	4-6	Bonds 5-6	2-4	3-5
	1.56	1.44	1.44	1.40	1.39
	C-B	N-B	N-B	N-C	N-C
	1.54	1.39	1.39	1.38	1.38
	С-В	O-B	О-В	O-C	O-C
	1.55	1.43	1.40	1.40	1.37
	С-В	N-B	О-В	N-C	O-C
	1.55	1.43	1.40	1.40	1.37
	C-B	N-B	O-B	N-C	O-C

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° 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° dihedral angle between the A and C rings. As expected, the A and B ring substituents (Br, OCH<sub>3</sub>, CH<sub>3</sub>) have little effect on the dihedral angle (bromodiazaborole **4.2**=21°, methoxydiazaborole **4.3**=18° and methyldiazaborole **4.4**=21°). As the steric repulsion increases with larger methyl groups, the dihedral angle between the A and C rings increases (N,N'-dimethyldiazaborole **4.5**=53° and N-methyldiazaborole **4.6**=43°).

# Table 8

Molecule -	Dihedral angle	G <sub>Actual</sub>	GPlanar	$\Delta G_{Difference}$	$\Delta G_{\text{Difference}}$
	α	(Hartrees)	(Hartrees)	(Hartrees)	(kJ/mol)
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
4.4	21	-637.651	-637.649	0.002	5
4.5	53	-676.930	-676.918	0.012	32
4.6	43	-637.640	-637.635	0.005	13
4.7	0	-638.126	-638.126	0.000	0
4.8	0	-618.238	-618.238	0.000	0
4.9	29	-657.527	-657.525	0.002	6

Rotational barriers of diazaborole analogues

The energy differences between the optimized geometry and the coplanar geometry of diazaborole analogues are very low (5-32 kJ/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 **4.1**-**4.9** (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

Molecule	A ring - Center	B ring - center	C ring - Center
4.1	-0.02180	-0.02976	-0.01529
4.2	-0.01328	-0.02631	-0.01051
4.3	-0.02238	-0.03165	-0.01852
4.4	-0.02249	-0.02958	-0.01629
4.5	-0.02163	-0.03017	-0.01522
4.6	-0.02239	-0.03072	-0.01546
4.7	-0.01921	-0.01599	-0.07162
4.8	-0.02108	-0.02358	-0.00432
4.9	-0.02211	-0.02355	-0.00448

Estimated charge densities/surface mapped values of diazaborole analogues

# 4.3.3 NICS value.

The Hückel 4n+2 rule for  $\pi$ -conjugated molecules indicates aromaticity and the 4n rule indicates antiaromaticity.<sup>100</sup> 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 (Bq)" to probe the electron shielding at that position using modern quantum chemical methods.<sup>99</sup> 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).<sup>99,100</sup> 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.<sup>101</sup> 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.<sup>100,101</sup> 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.<sup>99</sup>



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

Table 10

Reported NICS values for diazaborole 4.199

Diazaborole 4.1	NICS (0) B Ring ppm	NICS (1) B Ring ppm	NICS (0) C Ring ppm	NICS (1) C Ring ppm
B C B	-9.34	-9.96	-6.32	-5.30

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 Å increments (Figure 67 and Table 11).

# Table 11

Molecule	NICS (0C) ppm	NICS (1C) ppm	NICS (2C) ppm	NICS (3C) ppm	NICS (4C) ppm
4.1	-9.50	-5.88	-2.21	-1.25	-0.73
4.2	-8.03	-5.73	-2.27	-1.29	-0.74
4.3	-7.92	-5.61	-2.20	-1.25	-0.73
4.4	-7.69	-5.53	-2.18	-1.25	-0.72
4.5	-8.40	-6.18	-2.66	-1.42	-0.87
4.6	-8.03	-5.77	-2.37	-1.24	-0.76
4.7	-4.16	-3.64	-1.94	-1.23	-0.74
4.8	-5.31	-4.28	-2.06	-1.2	-0.75
4.9	-5.54	-4.37	-2.37	-1.25	-0.76

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

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 ppm) on the A ring as well as by electron donating group substitution to the A ring (methoxydiazaborole **4.3** (NICS (1) = -5.61 ppm) and B ring (methyldiazaborole **4.4** (NICS (1) = -5.53 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'-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 Å and 1.0 Å (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

		Ring A		Ring B		
Molecule —	NICS (0) ppm	NICS (1) ppm	NICS (0) ppm	NICS (1) ppm		
4.1	-6.78	-9.49	-9.59	-10.17		
4.2	-7.27	-9.20	-9.60	-10.21		
4.3	-7.67	-9.18	-9.56	-10.15		
4.4	-6.80	-9.52	-9.41	-9.88		
4.5	-6.96	-9.81	-9.56	-10.29		
4.6	-6.83	-9.50	-9.58	-10.18		
4.7	-6.95	-9.70	-10.48	-10.41		

Molecule —		Ring A	Ring B		
	NICS (0) ppm	NICS (1) ppm	NICS (0) ppm	NICS (1) ppm	
4.8	-6.88	-9.62	-9.94	-10.25	
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 (NICS (1) = -9.18 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 (NICS (1) = -9.20 ppm and 9.18 ppm, respectively) compared to diazaborole 4.1 (NICS (1) = -9.49 ppm). However, methyl substitution on the B ring (methyldiazaborole 4.4) (NICS (1) = -9.52 ppm) does not have any impact on the A ring aromaticity whereas the aromaticity on the B ring decreased (NICS (1) = -9.88ppm). The highest NICS values on the B ring were found on dioxaborole 4.5 (-10.41 ppm). While the lowest value is obtained with methyldiazaborole 4.4 (NICS (1) = -9.88ppm). 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 ppm and -9.96 ppm) and this study (NICS (1) = -9.59 ppm and -10.17 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 ( $\Delta$ G<sub>formation</sub>) of diazaborole in the gas phase at room temperature (298 K) were calculated using the equation of  $\Delta$ G<sub>formation</sub> = G products-G starting materials. (Table 13 shows the  $\Delta$ 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

	Produc	ets (P)	Starting Materials (SM)		
	DAB isostructure (Hartrees)	2 H <sub>2</sub> O (Hartrees)	PBA derivative (Hartrees)	BDA derivative (Hartrees)	$\Delta$ G (P-SM) (Hartrees)
4.1	-598.35	-152.91	-408.30	-342.96	-0.002
4.2	-3171.91	-152.91	-2981.86	-342.96	0.001

	Produc	ets (P)	Starting Ma	aterials (SM)	
4.3	-712.88	-152.91	-522.83	-342.96	-0.001
4.4	-637.65	-152.91	-408.30	-382.26	-0.001
4.5	-637.64	-152.91	-408.30	-382.25	0.001
4.6	-676.93	-152.91	-408.30	-421.53	-0.003
4.7	-638.13	-152.91	-408.30	-382.73	-0.004
4.8	-618.24	-152.91	-408.30	-362.84	-0.001
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 °C (kJ/mol)	50 °C (kJ/mol)	100 °C (kJ/mol)			
4.1	-5.16	-8.94	-16.58			
4.2	1.77	-9.00	-16.63			
4.3	-3.31	-7.70	-15.39			
4.4	-2.78	-6.80	-14.44			
4.5	-7.45	-10.88	-17.69			
4.6	3.67	0.56	-6.30			
4.7	-10.31	-13.40	-20.16			
4.8	-3.25	-6.50	-12.98			

The Gibbs free energies ( $\Delta$ 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 °C and lowest at 25 °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

	Solvent phase							
	CH <sub>3</sub> CN 25 °C	THF 25 °C	methanol 25 °C	dioxane 50 °C	butanol 50 °C	CHCl <sub>3</sub> 50 °C	DMSO 100 °C	
	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	
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	
4.3	-7.84	-4.94	-7.70	-14.38	-9.90	-3.41	23.60	
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	
4.6	-9.04	-6.53	-9.00	-2.54	-11.16	1.96	-3.84	
4.7	-17.77	-16.63	-17.76	-14.74	-20.23	-8.83	-12.44	
4.8	-23.87	-22.74	-23.85	-15.08	-26.91	-13.71	-20.01	

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

The  $\Delta$ 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 CHCl<sub>3</sub> and DMSO. In DMSO, all diazaborole analogues had lower  $\Delta$ G of formation values than in the gas phase at 100 °C except methyldiazaborole **4.4**. A similar trend was observed in CHCl<sub>3</sub> where methyldiazaborole **4.4** and oxazaborole **4.8** obtained high  $\Delta$ 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  $\Delta$ G values in all solvent phases.

# 4.4 Conclusions

Bond length comparisons showed that dioxaborole **4.7** comprises the lowest C-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 kJ/mol-32 kJ/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'-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 CHCl<sub>3</sub> at 50 °C and DMSO at 100 °C have lower values except methyldiazaborole **4.4** in both solvents and oxazaborole **4.8** in CDCl<sub>3</sub>.

# 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 (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 Å above and two NICS indices along the center of two phenyl rings in every 1 Å distance were calculated. For the thermodynamic calculations, first, the  $\Delta G$  values of optimized structures of **4.1-4.9**, its starting materials and byproduct (H<sub>2</sub>O) were obtained using DFT/6-311G++(d,p) method and basis sets in gas phase at room temperature. The change in Gibbs free energies at room temperature was calculated using  $\Delta G=G_{\text{products}}-G_{\text{starting materials}}$ equation. Then, the optimized structures were exposed to re-optimization and frequency calculations at reaction corresponding temperatures to obtain the  $\Delta G$  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



 $^1\!\mathrm{H}\text{-}\mathrm{NMR}$  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



<sup>&</sup>lt;sup>1</sup>H-NMR spectra of the products in the exchange reaction of diazaborole with bromophenylboronic acid at 50 °C in 1,4-dioxane. <sup>1</sup>H-NMR spectra were taken in CDCl<sub>3</sub>.


<sup>&</sup>lt;sup>1</sup>H-NMR spectra of the products in the exchange reaction of diazaborole with methylbenzenediamine at room temperature in CDCl<sub>3</sub>.



<sup>&</sup>lt;sup>4</sup>H-NMR spectra of the products in the exchange reaction of diazaborole with methylbenzenediamine at 100 °C in DMSO-d<sub>6</sub>.



10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0  $\delta$  (ppm) <sup>1</sup>H-NMR spectra of the products in the exchange reaction of diazaborole with methylbenzenediamine at 100 °C in DMSO-d<sub>6</sub>.



<sup>&</sup>lt;sup>1</sup>H-NMR spectra of the products in the exchange reaction of methyldiazaborole 3.13 with benzenediamine 3.3 at 100 °C in DMSO-d<sub>6</sub>.

98



^1H-NMR spectra of the products in the exchange reaction of diazaborole with methylbenzenediamine at 100  $^{\rm o}{\rm C}$  in DMSO-d\_6.



8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0  $\delta$  (ppm) <sup>1</sup>H-NMR spectra of the products in the exchange reaction of methyldiazaborole **3.13** with benzenediamine **3.3** at 50 °C in 1,4-dioxane. <sup>1</sup>H-NMR were taken in CDCl<sub>3</sub>.

# **APPENDIX B** – The output data for the computational studies

a) Computational data of optimized structures in gas phase

## 1. Diazaborole (4.1)

 $\c hk=T:\CHM\deg 013\Janaka\Macrocycles\DAB\ analogous\DAB\DFT$ Calculations\DFT cal culations.chk

\_\_\_\_\_

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

\_\_\_\_\_

Symbolic	Z-mat	rix:					
Charge =	0 Mult	iplicity	y = 1				
С							
С	1	B1					
С	2	B2	1	A1			
С	3	B3	2	A2	1	D1	0
С	4	B4	3	A3	2	D2	0
С	1	B5	2	A4	3	D3	0
Η	3	B6	2	A5	1	D4	0
Η	4	<b>B</b> 7	3	A6	2	D5	0
Η	5	<b>B</b> 8	4	A7	3	D6	0
Η	6	B9	1	A8	2	D7	0
Η	1	B10	6	A9	5	D8	0
Η	2	B11	1	A10	6	D9	0
Ν	1	B12	6	A11	5	D10	0
Ν	2	B13	1	A12	6	D11	0
В	14	B14	2	A13	1	D12	2 0
С	15	B15	14	4 A14	2	D1	3 0
С	16	B16	15	5 A15	1	4 D1	14 C
С	16	B17	15	5 A16	1	4 D]	15 0
С	17	B18	16	5 A17	1	5 D1	16 0
Н	17	B19	10	5 A18	1	5 D	17 (
С	18	B20	16	5 A19	1	5 DI	18 0
Η	18	B21	10	5 A20	1	5 D	19 (
С	19	B22	17	7 A21	1	6 D2	20 0
Η	19	B23	11	7 A22	1	6 D2	21 (
Н	21	B24	18	8 A23	1	6 D2	22 (
Н	23	B25	19	9 A24	1	7 D2	23 (

Item Value Threshold Converged? Maximum Force 0.000011 0.000450 YES 0.000003 0.000300 YES RMS Force Maximum Displacement 0.001037 0.001800 YES Displacement 0.000164 RMS 0.001200 YES Predicted change in Energy=-1.163935D-08

Optimization completed.

-- Stationary point found.

-----

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure	1.00000 Atm.
Zero-point correction= 0.2	208582 (Hartree/Particle)
Thermal correction to Energy=	0.219963
Thermal correction to Enthalpy=	0.220907
Thermal correction to Gibbs Free Energy=	= 0.170112
Sum of electronic and zero-point Energies	-598.312132
Sum of electronic and thermal Energies=	-598.300751
Sum of electronic and thermal Enthalpies=	-598.299806
Sum of electronic and thermal Free Energ	ies= -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\DAB Derivatives\B

 $r.DAB \verb|DFT Calculations\verb|Recalc\verb|DFT CALCULATIONS.chk|$ 

\_\_\_\_\_

# opt=(maxcycle=500,z-matrix,maxstep=30) freq b3lyp/6-311++g(d,p) geom =connectivity int=grid=ultrafine

BrDAB\_OptFrq\_RT\_DFT\_GP

Symbolic Z-r	natrix:		
Charge = $0 \text{ M}$	Aultiplic	ity = 1	
С	0.	0. 0.	
С	0.	0. 1.4	1278
С	1.1943	6 O. 2	2.12454
С	2.3921	4 0.0053	7 1.40549
С	2.39212	2 0.0115	6 0.0073
С	1.1943	3 0.0084′	7 -0.71176
Н	1.1975	3 -0.0024	8 3.20913
Н	3.3342	6 0.00634	4 1.94113
Н	3.3342	2 0.0172	3 -0.52835
Н	1.1974	9 0.0109	9 -1.79635
Н	-1.5550	6 0.0374	2 -1.41045
Н	-1.5547	8 -0.0479	7 2.82323
Ν	-1.3268	2 -0.0106	8 -0.43145
Ν	-1.3268	6 0.0015	3 1.84423
В	-2.2066	-0.00746	5 0.70638
С	-3.7627	3 -0.0127	4 0.7064
С	-4.4980	9 0.4285	9 1.81953

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

Item Value Threshold Converged? Maximum Force 0.000214 0.000450 YES RMS Force 0.000045 0.000300 YES Maximum Displacement 0.001277 0.001800 YES RMS Displacement 0.000260 0.001200 YES Predicted change in Energy=-1.842696D-07 Optimization completed.

-- Stationary point found.

-----

- Thermochemistry -

-----

Temperature 298.150 Kelvin. Pressure	1.00000 Atm.
Zero-point correction= 0.1	198333 (Hartree/Particle)
Thermal correction to Energy=	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=	-3171.852438
Sum of electronic and thermal Enthalpies=	-3171.851494
Sum of electronic and thermal Free Energie	es= -3171.907121

# 3. Methoxydiazaborole (4.3)

.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

С	3	B3	2	A2	1 I	D1	0
С	4	B4	3	A3	2 I	D2	0
С	1	B5	2	A4	3 I	)3	0
Η	3	B6	2	A5	1 I	D4	0
Η	4	B7	3	A6	2 I	D5	0
Н	5	B8	4	A7	3 I	D6	0
Η	6	B9	1	A8	2 I	D7	0
Η	1	B10	6	A9	5	D8	0
Η	2	B11	1	A10	6	D9	0
Ν	1	B12	6	A11	5	D10	0
Ν	2	B13	1	A12	6	D11	0
В	14	B14	2	A13	1	D12	0
С	15	B15	14	A14	2	D13	0
С	16	B16	15	A15	14	D14	0
С	16	B17	15	A16	14	D15	5 O
С	17	B18	16	A17	15	5 D16	5 0
Н	17	B19	16	A18	15	5 D17	0
С	18	B20	16	A19	15	5 D18	<b>3</b> 0
Η	18	B21	16	A20	15	5 D19	) 0
С	19	B22	17	A21	16	5 D20	0 (
Н	19	B23	17	A22	16	5 D21	. 0
Н	21	B24	18	A23	16	5 D22	2 0
0	23	B25	19	A24	17	7 D23	3 0
С	26	B26	23	A25	19	) D24	0
Н	27	B27	26	A26	23	3 D25	5 0
Н	27	B28	26	A27	23	3 D26	5 0
Н	27	B29	26	A28	23	B D27	7 O
Variables	:						
B1	1.	40094					
B2	1.	37638					
B3	1.	39024					
B4	1.	3838					
B5	1.	37637					
B6	1.	07191					
B7	1.	0717					
<b>B</b> 8	1.	0717					
B9	1.	07192					
B10	2	.09817	,				
B11	2	.09822					
B12	1	.39943					
B13	1	.39939	)				
B14	1	.44433					
B15	1	.55511					
B16	1	.39468					
B17	1	.39468					
B18	1	.38101					

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

D8	178.97863							
D9	-178.57852							
D10	-179.937							
D11	179.81798							
D12	0.14863							
D13	-179.7293							
D14	20.22274							
D15	-159.82641							
D16	179.63487							
D17	0.27508							
D18	-179.83226							
D19	1.05164							
D20	0.38895							
D21	179.45269							
D22	-178.86549							
D23	179.24958							
D24	90.48898							
D25	179.82592							
D26	-60.86327							
D27	60.52918							
Ite	tem Value Threshold Converg	ed?						
Maxim	mum Force 0.000097 0.000450	YES						
RMS	Force 0.000016 0.000300 Y	(ES						
Maxim	mum Displacement 0.0011/2 0.0018	00 YES						
RMS	Displacement 0.000259 0.001200	YES						
Predict	cted change in Energy=-3.498638D-08							
Optimi	nization completed.							
Sta	tationary point found.							
- Therr	rmochemistry -							
Zoro po	$\sim 0.24072$	8 (Hartras/Partials)						
Therm	nal correction to Energy=	3/786						
Therm	nal correction to Entral $v = 0.2$	55730						
Therm	nal correction to Gibbs Free Energy=	0 198640						
Sum of	of electronic and zero-point Energies=	-712 837181						
Sum of	of electronic and thermal Energies=	-712.037101						
Sum of	of electronic and thermal Entralnies-	_712.025155						
Sum of	of electronic and thermal Free Energies=	-712 879279						
Sull U	Sum of electronic and mermai rice Energies/12.8/92/9							

# 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-m	natri	x:					
Charge = 0 N	Ault	iplicity	= 1				
С							
С	1	B1					
С	2	B2	1	A1			
С	3	B3	2	A2	1	D1	0
С	4	B4	3	A3	2	D2	0
С	1	B5	2	A4	3	D3	0
Н	3	B6	2	A5	1	D4	0
Н	4	B7	3	A6	2	D5	0
Н	6	B8	1	A7	2	D6	0
Н	1	B9	6	A8	5	D7	0
Н	2	B10	1	A9	6	D8	0
Ν	1	B11	6	A10	5	D9	0
Ν	2	B12	1	A11	6	D10	0
В	13	B13	2	A12	1	D11	0
С	14	B14	13	3 A13	2	D12	2 0
С	15	B15	14	4 A14	1.	3 D1	3 0
С	15	B16	14	4 A15	1.	3 D14	4 0
С	16	B17	15	5 A16	14	4 D1:	5 0
Н	16	B18	1.	5 A17	14	4 D1	6 0
С	17	B19	15	5 A18	14	4 D1'	7 0
Н	17	B20	1.	5 A19	14	4 D1	8 0
С	20	B21	17	7 A20	1:	5 D1	9 0
Н	18	B22	10	5 A21	1	5 D2	0 0
Н	20	B23	1′	7 A22	1	5 D2	1 0
Н	22	B24	20	) A23	1	7 D2	2 0
С	5	B25	4	A24	3	D23	0
Н	26	B26	5	A25	4	D24	0
H	26	B27	5	A26	4	D25	0
H	26	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	4	2.10134					
B11	]	1.39477					
B12	1	1.39621					
B13	]	1.43825					

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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	111.10792
A27	111 19317
D1	0 31064
D2	0 02414
D3	-0 47554
D4	-179,82865
<i>-</i> ·	1, , , 02000

D5	179.92948
D6	-179.85846
D7	178.97144
D8	-178.72994
D9	-179.68804
D10	179.56141
D11	0.39736
D12	179.72993
D13	30.
D14	-149.9775
D15	-179.99916
D16	0.91098
D17	179.93338
D18	0.84304
D19	0.07079
D20	-179.7519
D21	-179.73384
D22	179.97572
D23	179.89754
D24	119.79964
D25	-120.43914
D26	-0.32186
-0.00394	0.00000 -0.00010 0.00008 -0.00002 -0.00396
Item	Value Threshold Converged?
Maximum	Force 0.000017 0.000450 YES
RMS Fo	rce 0.000005 0.000300 YES
Maximum	Displacement 0.001633 0.001800 YES
RMS Di	splacement 0.000280 0.001200 YES
Predicted c	hange in Energy=-3.400403D-08
Optimizati	on completed.
Station	ary point found.
Full mass-v	veighted force constant matrix:
Low freque	encies $-13.9056 - 0.0009 - 0.0005 0.0003 3.6665 7.4082$
Low freque	encies 12.5338 31.7862 49.5058
- Thermoci	iemistry -
Zero-point	correction= 0.235575 (Hartree/Particle)
Thermal co	0.255575 (Harrice's arrents)
Thermal co	prrection to Entralpy 0.248024
Thermal co	prection to Gibbs Free Energy $0.195829$
Sum of ele	ctronic and zero-point Energies= -637 611589
Sum of ele	ctronic and thermal Energies= -637 599140
Sum of ele	ctronic and thermal Enthalpies -637,598196
Sum of ele	ctronic and thermal Free Energies $= -637.651335$

## 5. *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

\_\_\_\_\_

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N-methyl DAB\_DFT\_ Calculations

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

С									
С	1	B1							
С	2	B2	1	A	<b>A</b> 1				
С	3	B3	2	A	42	1	D	1	0
С	4	B4	3	A	43	2	Dź	2	0
С	1	B5	2	A	<b>\</b> 4	3	D.	3	0
Н	3	B6	2	A	15	1	D	4	0
Н	4	B7	3	A	46	2	D	5	0
Н	5	B8	4	A	<b>\</b> 7	3	D	6	0
Η	6	B9	1	A	48	2	Ď	7	0
Η	2	B10	1	,	A9	6	D	8	0
Ν	1	B11	6	,	A10	5	Ι	)9	0
Ν	2	B12	1	,	A11	6	Ι	D10	0
В	13	B13	2		A12	1	]	D11	0
С	14	B14	1	3	A13	4	2	D12	0
С	15	B15	1	4	A14	]	13	D13	<b>6</b> 0
С	15	B16	1	4	A15	]	13	D14	0
С	16	B17	1	5	A16	]	4	D15	5 0
Η	16	B18	1	5	A17	•	14	D16	<b>5</b> 0
С	17	B19	1	5	A18	]	4	D17	0
Н	17	B20	1	5	A19		14	D18	3 0
С	20	B21	1	7	A20	1	15	D19	) 0
Н	18	B22	1	6	A21		15	D20	) 0
Н	20	B23	1	7	A22		15	D21	0
Η	22	B24	2	0	A23		17	D22	2 0
С	12	B25	1		A24	6	]	D23	0
Η	26	B26	1	2	A25		1	D24	0
Η	26	B27	1	2	A26		1	D25	0
Η	26	B28	1	2	A27		1	D26	0

Variables:

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

A19	119.66772		
A20	120.04567		
A21	120.0135		
A22	119.95143		
A23	120.1037		
A24	121.45037		
A25	109.17961		
A26	110.59288		
A27	111.29902		
D1	0.14204		
D2	0.00081		
D3	-0.19541		
D4	-179.91673		
D5	179.98091		
D6	-179.99389		
D7	179.88299		
D8	-178.4511		
D9	179.87761		
D10	179.82404		
D11	0.4253		
D12	179.8986		
D13	42.20049		
D14	-136.53602		
D15	-179.42424		
D16	1.24235		
D17	178.96973		
D18	-0.01279		
D19	0.29789		
D20	-179.49576		
D21	-179.58297		
D22	179.76233		
D23	-3.81132		
D24	-171.03673		
D25	-51.85416		
D26	68.71989		
Item	Value Threshold Converged?		
Maxim	um Force 0.000048 0.000450 YES		
RMS	Force 0.000009 0.000300 YES		
Maxim	um Displacement 0.001777 0.001800 YES		
RMS	Displacement 0.000431 0.001200 YES		
Predict	ted change in Energy=-2.804780D-08		
Optimi	zation completed.		
Stationary point found.			
Full mass-weighted force constant matrix:			
Low frequencies8.5968 -6.6029 -0.0011 -0.0006 -0.0003 4.4695			
Low fr	equencies 42.7728 52.7357 74.4794		

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- Thermochemistry -

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Zero-point correction=	0.236386 (Hartree/Particle)
Thermal correction to Energy=	0.249329
Thermal correction to Enthalpy=	0.250273
Thermal correction to Gibbs Free Ene	rgy= 0.196404
Sum of electronic and zero-point Ener	-637.599559
Sum of electronic and thermal Energie	es= -637.586616
Sum of electronic and thermal Enthalp	bies= -637.585672
Sum of electronic and thermal Free En	nergies= -637.639541

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

%chk=T:\CHM\deg013\Janaka\Macrocycles\DAB analogous\Dimethyl DAB\DFT Calculation

s.chk

\_\_\_\_\_

\_\_\_\_\_

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

Charge =	0 Mult	iplicity	v = 1				
С							
С	1	B1					
С	2	B2	1	A1			
С	3	B3	2	A2	1	D1	0
С	4	B4	3	A3	2	D2	0
С	1	B5	2	A4	3	D3	0
Н	3	B6	2	A5	1	D4	0
Н	4	B7	3	A6	2	D5	0
Н	5	<b>B</b> 8	4	A7	3	D6	0
Н	6	B9	1	A8	2	D7	0
Ν	1	B10	6	A9	5	D8	0
Ν	2	B11	1	A10	6	D9	0
В	11	B12	1	A11	6	D10	0 0
С	13	B13	1	1 A12	1	D1	1 0
С	14	B14	1.	3 A13	1	1 D1	2 0
С	14	B15	1.	3 A14	1	1 D1	3 0
С	15	B16	14	4 A15	1	3 D1	4 0
Н	15	B17	14	4 A16	1	3 D1	5 0
С	16	B18	14	4 A17	1	3 D1	6 0
Н	16	B19	14	4 A18	1	3 D1	7 0
С	17	B20	1:	5 A19	1-	4 D1	8 0
Н	17	B21	1:	5 A20	1	4 D1	9 0
Н	19	B22	1	6 A21	1	4 D2	20 0
Н	21	B23	1	7 A22	1	5 D2	21 0
С	11	B24	1	A23	6	D22	2 0

Н	25 B25	11 A24	1 D23	0
Н	25 B26	11 A25	1 D24	0
Η	25 B27	11 A26	1 D25	0
С	12 B28	2 A27	1 D26	0
Н	29 B29	12 A28	2 D27	0
Н	29 B30	12 A29	2 D28	0
Н	29 B31	12 A30	2 D29	0
Variab	les:			
B1	1.40188			
B2	1.37601			
В3	1.39173			
B4	1.38229			
B5	1.37601			
B6	1.07108			
B7	1.07183			
B8	1.07183			
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	120.66936	5		
A2	118.57569	)		
A3	120.75481	l		
A4	120.66975	5		
A5	121.0085			
A6	119.40865	5		
A7	119.83662	2		

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	0.01322
D4	-179 9556
D5	-179 9548
D6	-179 98343
D7	-179 95968
D8	-179 95481
D9	-179 95094
D10	179 91655
D10	179 97451
D12	126 3523
D12	-53 64768
D13	-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
	- · · · / / / / 1

D24 -65.19768 D25 55.41807 D26 -176.89837 D27 174.72686 D28 -65.26254D29 55.35355 Item Value Threshold Converged? Maximum Force 0.000032 0.000450 YES RMS 0.000006 YES Force 0.000300 Maximum Displacement 0.001547 0.001800 YES RMS Displacement 0.000276 0.001200 YES Predicted change in Energy=-1.314857D-08 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -4.8036 -4.3893 -0.0007 0.0003 0.0015 4.9126 Low frequencies --- 47.2538 50.0449 68.8369 ------ Thermochemistry ------Zero-point correction= 0.264081 (Hartree/Particle) Thermal correction to Energy= 0.278667 0.279611 Thermal correction to Enthalpy= Thermal correction to Gibbs Free Energy= 0.222321 Sum of electronic and zero-point Energies= -676.887799 Sum of electronic and thermal Energies= -676.873213 Sum of electronic and thermal Enthalpies= -676.872269 Sum of electronic and thermal Free Energies= -676.929558 7. Dioxaborole (4.7) %nprocshared=4 Will use up to 4 processors via shared memory. %chk=T:\CHM\deg013\Janaka Gaussian\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 = 1С 0. 0. 0. С 0. 0. 1.38186 С 1.15955 0. 2.10411 С 2.35231 0.00001 1.38341 С 2.3523 0.00001 -0.00157 С 1.15955 0. -0.72226

1.14472 -0.00001 3.17312 Η Η 3.28371 0.00002 1.91238 Η 3.2837 0.00002 -0.53054 Η 1.14472 0. -1.79127 0.00001 -0.4487 0 -1.3191 Ο -1.3191 -0.00002 1.83055 В -2.14753 0. 0.69093 С -3.6802 -0.00001 0.69094 С -4.38715 -0.00006 1.89196 С -4.38719 0.00004 -0.51001 С -5.76909 -0.00006 1.89264 Η -3.84713 -0.00011 2.81822 С -5.76916 0.00003 -0.51064 Η -3.84723 0.00008 -1.43631 С -6.4584 -0.00003 0.691 Η -6.30682 -0.00011 2.8198 Η -6.3069 0.00006 -1.43779 Η -7.53073 -0.00004 0.69104 Item Value Threshold Converged? Maximum Force 0.000110 0.000450 YES 0.000021 0.000300 RMS Force YES 0.000386 0.001800 Maximum Displacement YES RMS Displacement 0.000101 0.001200 YES Predicted change in Energy=-7.696988D-08 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -0.0011 -0.0007 0.0008 1.5485 1.7844 1.9107 Low frequencies --- 47.4286 55.8555 79.6399 ------- Thermochemistry -\_\_\_\_\_ Zero-point correction= 0.183783 (Hartree/Particle) 0.194658 Thermal correction to Energy= Thermal correction to Enthalpy= 0.195602 Thermal correction to Gibbs Free Energy= 0.145911 Sum of electronic and zero-point Energies= -638.088072 Sum of electronic and thermal Energies= -638.077198 Sum of electronic and thermal Enthalpies= -638.076253 Sum of electronic and thermal Free Energies= -638.125945 8. Oxazaborole (4.8) %nprocshared=4

Will use up to 4 processors via shared memory. %chk=T:\CHM\deg013\Janaka\_Gaussian\DAB analogous\DAB analogous\DAB Derivatives\O AB\DFT Calculations\DFT Calculations.chk

\_\_\_\_\_ # opt=maxcycle=500 freq rb3lyp/6-311++g(d,p) geom=connectivity \_\_\_\_\_ OAB ---Symbolic Z-matrix: Charge = 0 Multiplicity = 11.84783 -0.65325 -0.00001 С С 1.92877 0.74765 0. С 3.16431 1.38381 0. С 4.30879 0.57958 0.00001 С 4.21699 -0.81459 0. С 2.97251 -1.45597 -0.00001 Η 3.24272 2.46511 0. Η 5.28532 1.04973 0.00001 Η 5.12188 -1.41062 0. Η 2.88528 -2.53539 -0.00001 Η 0.40859 2.21052 -0.00004 С -1.81126 0.04474 0.00001 С -2.59617 1.21049 0.00001 С -2.47705 -1.19357 0.00001 С -3.98677 1.14677 0. Η -2.11879 2.18593 0.00001 С -3.86753 -1.26367 0. Η -1.8929 -2.10714 0.00002 С -4.62566 -0.0931 -0.00001 Η -4.57238 2.05951 -0.00001 Η -4.36132 -2.22922 0. Η -5.70885 -0.1461 -0.00001 Ν 0.61542 1.22583 -0.00002 0 0.53456 -1.05557 -0.00002 В -0.26453 0.09762 0.00003 0.00006 0.00000 0.00000 -0.00012 -0.00012 -0.00006 Item Value Threshold Converged? Maximum Force 0.000069 0.000450 YES RMS Force 0.000013 0.000300 YES Maximum Displacement 0.000830 0.001800 YES Displacement 0.000251 0.001200 YES RMS Predicted change in Energy=-3.474686D-08 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -11.2931 -0.0012 -0.0011 0.0003 1.4285 5.1485 Low frequencies --- 31.5389 56.1411 83.1363

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- Thermochemistry -

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Zero-point correction=	0.196130 (Hartree/Particle)
Thermal correction to Energy=	0.207270
Thermal correction to Enthalpy=	0.208214
Thermal correction to Gibbs Free Ene	argy = 0.157828
Sum of electronic and zero-point Ener	rgies= -618.200268
Sum of electronic and thermal Energie	es= -618.189128
Sum of electronic and thermal Enthal	pies= -618.188183
Sum of electronic and thermal Free En	nergies= -618.238570

### 9. *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\N

-methylOAB\DFT Calculations\DFT\_New\_Recal\DFT Calculations.chk

# opt=maxcycle=500 freq rb3lyp/6-311++g(d,p) geom=connectivity

\_\_\_\_\_

-----

N-OAB\_DFT\_RT\_GP\_Recal

Charge = $0$ Multiplicity = $1$			
С	0. 0. 0.		
С	0. 0. 1.40274		
С	1.16724 0. 2.1409		
С	2.37442 0.00378 1.43051		
С	2.38743 0.00681 0.03403		
С	1.19881 0.00457 -0.70528		
Н	1.14027 -0.00136 3.22359		
Н	3.31135 0.00381 1.97486		
Н	3.33592 0.00828 -0.49053		
Н	1.22032 0.00168 -1.78852		
Ν	-1.33574 0.00223 -0.41962		
В	-2.14543 -0.01249 0.76368		
С	-3.68757 -0.01576 0.94689		
С	-4.23792 0.54849 2.11277		
С	-4.57653 -0.57988 0.01509		
С	-5.61303 0.5679 2.32786		
Н	-3.57424 0.97547 2.8565		
С	-5.95318 -0.57058 0.22983		
Н	-4.1938 -1.05741 -0.88021		
С	-6.47534 0.00943 1.38466		

Η -6.01318 1.01422 3.23169 Η -6.6176 -1.01993 -0.50017 Η -7.54682 0.02024 1.55179 С -1.68702 0.09235 -1.82557 Η -1.46957 -0.84171 -2.35502 Η -2.74816 0.31285 -1.92439 Η -1.1263 0.89911 -2.30743 -1.28664 -0.00308 1.87528 0 -0.00913 0.00000 0.00001 -0.00001 -0.00001 -0.00914 Value Threshold Converged? Item 0.000450 Maximum Force 0.000010 YES RMS Force 0.000003 0.000300 YES 0.001800 Maximum Displacement 0.000907 YES RMS Displacement 0.000165 0.001200 YES Predicted change in Energy=-9.971152D-09 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -10.0088 -3.8851 -0.0016 -0.0008 -0.0004 3.0610 Low frequencies --- 37.1107 54.1890 83.0698 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ 0.223995 (Hartree/Particle) Zero-point correction= Thermal correction to Energy= 0.236715 Thermal correction to Enthalpy= 0.237659 Thermal correction to Gibbs Free Energy= 0.184052 Sum of electronic and zero-point Energies= -657.487341 Sum of electronic and thermal Energies= -657.474622 Sum of electronic and thermal Enthalpies= -657.473678

Sum of electronic and thermal Free Energies= -657.527285

b) Computational data of coplanar structures in gas phase

# 1. Diazaborole (4.1)

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
Н 3.11741 -2.50128 0.08128
Н 5.25447 -1.23432 0.03822
Н 5.25447 1.23432 -0.0382
Н 3.11741 2.50127 -0.08129
Н 0.36428 2.11663 -0.03402
Н 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
Н -2.05039 -2.14838 0.09928
C -3.96866 1.20419 -0.04838
Н -2.05039 2.14838 -0.09928
C -4.6699 0. 0.
Н -4.50746 -2.14458 0.08988
Н -4.50746 2.14458 -0.08988
Н -5.75429 0. 0.
Item Value Threshold Converged?
Maximum Force 0.000063 0.000450 YES
RMS Force 0.000017 0.000300 YES
Maximum Displacement 0.001343 0.001800 YES
RMS Displacement 0.000271 0.001200 YES
Predicted change in Energy=-2.268439D-07
Optimization completed.
Stationary point found.
Full mass-weighted force constant matrix:
Low frequencies24.2611 -6.8117 -3.2342 -2.6740 -0.0009 -0.0006
Low frequencies0.0004 56.2676 86.9146
- Thermochemistry -
Zero-point correction= 0.208416 (Hartree/Particle)
Thermal correction to Energy= 0.218935

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 Energie	s= -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\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

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

Η 2.86463 2.1454 0.09609 Br 4.92322 -0.00004 -0.00003 Item Value Threshold Converged? Maximum Force 0.000072 0.000450 YES RMS Force 0.000018 0.000300 YES Maximum Displacement 0.001465 0.001800 YES Displacement 0.000276 RMS 0.001200 YES Predicted change in Energy=-2.472232D-07 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -25.3836 -6.0372 -1.8883 -1.4183 0.0060 0.0076 Low frequencies --- 0.0104 34.3280 60.9143 ------ Thermochemistry -Zero-point correction= 0.198195 (Hartree/Particle) Thermal correction to Energy= 0.210223 Thermal correction to Enthalpy= 0.211168 Thermal correction to Gibbs Free Energy= 0.158358 Sum of electronic and zero-point Energies= -3171.865318 Sum of electronic and thermal Energies= -3171.853290 Sum of electronic and thermal Enthalpies= -3171.852346 Sum of electronic and thermal Free Energies= -3171.905156

### 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\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

#### ------Symbolic Z-matrix:

, j			
Charge =	0 Multiplicity	y = 1	
С	-2.78022	-0.73853	-0.01673
С	-2.83623	0.67353	0.00807
С	-4.05802	1.33651	0.00879
С	-5.22738	0.57084	-0.01165
С	-5.17204	-0.8255	-0.03111
С	-3.94557	-1.49616	-0.03443

Н -4.10445 2.42006 0.0266			
Н -6.18975 1.06941 -0.01085			
Н -6.09194 -1.39847 -0.04525			
Н -3.90576 -2.58001 -0.05158			
Н -1.17271 -2.08703 0.01215			
Н -1.33906 2.14434 0.00666			
N -1.43793 -1.11688 -0.01789			
N -1.52812 1.15632 0.03071			
B -0.59972 0.05472 0.01358			
C 0.95066 0.118 0.02465			
C 1.64236 1.34599 0.0546			
C 1.73767 -1.04176 0.00304			
C 3.02602 1.41233 0.06281			
Н 1.08487 2.27715 0.08573			
C 3.13211 -1.00171 0.00915			
Н 1.25979 -2.01611 -0.03418			
C 3.78358 0.23426 0.03896			
Н 3.54631 2.36243 0.0906			
Н 3.69103 -1.92771 -0.01383			
O 5.13711 0.39685 0.04681			
C 5.96356 -0.75965 0.02445			
Н 6.98841 -0.39233 0.03318			
Н 5.79627 -1.38771 0.90613			
Н 5.79842 -1.35156 -0.88224			
Item Value Threshold Converged?			
Maximum Force 0.000017 0.000450 YES			
RMS Force 0.000004 0.000300 YES			
Maximum Displacement 0.000519 0.001800 YES			
RMS Displacement 0.000098 0.001200 YES			
Predicted change in Energy=-1.421127D-08			
Optimization completed.			
Stationary point found.			
Full mass-weighted force constant matrix:			
Low frequencies20.4617 -6.7285 -2.0387 -0.5657 -0.0003 0.0006			
Low frequencies 0.0008 38.6524 67.1415			
- Thermochemistry -			
Zero-point correction= 0.240583 (Hartree/Particle)			
Thermal correction to Energy= 0.253769			
Thermal correction to Enthalpy= 0.254713			
Thermal correction to Gibbs Free Energy= 0.200503			
Sum of electronic and zero-point Energies= -712.837254			
Sum of electronic and thermal Energies= -712.824069			
Sum of electronic and thermal Enthalpies= -712.823125			
Sum of electronic and thermal Free Energies= -712.877335			

# 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\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

\_\_\_\_\_

Charge =	0 Multiplicity $= 1$	
С	-1.52988 -0.4907 -0.0631	
С	-1.44148 0.91753 0.00801	
С	-2.59347 1.69069 0.02951	
С	-3.83127 1.04078 -0.01594	
С	-3.93462 -0.35477 -0.08084	
С	-2.76358 -1.12692 -0.10487	
Н	-2.5408 2.77284 0.08215	
Н	-4.73775 1.63615 0.00107	
Н	-2.82346 -2.20995 -0.15796	
Н	-0.06491 -1.99513 -0.0808	
Н	0.19983 2.22875 0.05121	
Ν	-0.23267 -1.00288 -0.07987	
Ν	-0.08974 1.26508 0.04622	
В	0.71807 0.07642 -0.01004	
С	2.27074 -0.02409 0.00146	
С	3.07925 1.1241 0.07321	
С	2.92303 -1.26828 -0.05921	
С	4.46918 1.03716 0.08453	
Н	2.61646 2.10427 0.13643	
С	4.31236 -1.36427 -0.04985	
Н	2.33685 -2.17955 -0.12984	
С	5.09056 -0.20955 0.02255	
Н	5.06805 1.93944 0.14478	
Н	4.78878 -2.33725 -0.10205	
Н	6.17261 -0.28064 0.03056	
С	-5.28608 -1.03043 -0.12747	
Н	-5.40746 -1.62097 -1.04147	
Н	-5.42288 -1.71129 0.71896	
Н	-6.09501 -0.29765 -0.09703	
Item	Value Threshold Converged	?

Maximum Force 0.000069 0.000450 YES RMS Force 0.000017 0.000300 YES Maximum Displacement 0.001746 0.001800 YES RMS Displacement 0.000380 0.001200 YES Predicted change in Energy=-2.508614D-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 2.8911 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 En	ergies= -637.599990
Sum of electronic and thermal En	thalpies= -637.599046
Sum of electronic and thermal Fre	ee 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\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

С	1.91273	0.48256	-0.16345
С	1.87545	-0.89947	0.13173
С	3.04824	-1.62987	0.2779
С	4.26733	-0.96146	0.13088
С	4.30654	0.40564	-0.15449
С	3.12874	1.14453	-0.30475
Н	3.0198	-2.69062	0.50283
Н	5.19365	-1.51321	0.24143
Н	5.26335	0.90306	-0.26351

Η 3.16816 2.20372 -0.52993 Η 0.27265 -2.2384 0.37146 Ν 0.60175 0.95678 -0.26062 Ν 0.5391 -1.27871 0.2263 В -0.30399 -0.14087 -0.02629 С -1.86457 -0.1418 -0.02696 С -2.57512 -1.33529 0.19656 С -2.61713 1.01983 -0.2759 С -3.96782 -1.36792 0.18107 Η -2.0294 -2.25146 0.40042 С -4.01028 0.99306 -0.29855 Η -2.1086 1.95722 -0.47626 С -4.69025 -0.20156 -0.06669 Η -4.48954 -2.30118 0.36371 Η -4.56537 1.90277 -0.50065 Η -5.77436 -0.22385 -0.08113 С 0.32596 2.36587 -0.47322 Η -0.74314 2.54596 -0.37277 Η 0.8472 2.97992 0.26861 Η 0.64347 2.69133 -1.47027 Item Value Threshold Converged? Maximum Force 0.000011 0.000450 YES 0.000002 YES RMS Force 0.000300 Maximum Displacement 0.001293 0.001800 YES Displacement 0.000192 0.001200 YES RMS Predicted change in Energy=-5.921139D-09 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -44.6563 -3.8061 -0.0005 -0.0002 0.0002 1.4891 Low frequencies --- 3.1666 54.3413 76.8550 - Thermochemistry -\_\_\_\_\_ Zero-point correction= 0.236346 (Hartree/Particle) Thermal correction to Energy= 0.248487 Thermal correction to Enthalpy= 0.249431 Thermal correction to Gibbs Free Energy= 0.197843 Sum of electronic and zero-point Energies= -637.596194 Sum of electronic and thermal Energies= -637.584053Sum of electronic and thermal Enthalpies= -637.583109 Sum of electronic and thermal Free Energies= -637.634697

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

%nprocshared=4 Will use up to 4 processors via shared memory.

Domisso	%chk=T:\C	HM\deg013\Janaka_Gaussian\DAB analogous\DAB analogous\DAB			
Deriva	imethyl DAB\DFT_dihedral_0\DFT CALCULATIONS.chk				
	# opt=(mod geom=(red	redundant,maxcycle=500,maxstep=30) freq rb3lyp/6-311++g(d,p) undant,connectivity) int=grid=ultrafine			
	Dihedral 0	freeze			
	Symbolic Z				
	Charge = $0$	Multiplicity $= 1$			
	С	1.88427 - 0.24114 - 0.66484			
	С	1.88428 0.2411 -0.6648			
	С	3.07943 0.47907 -1.33487			
	С	4.27909 0.23514 -0.65723			
	С	4.27908 -0.23517 0.6573			
	С	3.07941 -0.47911 1.33493			
	Н	3.08734 0.84768 -2.35388			
	Н	5.22098 0.41612 -1.16221			
	Н	5.22097 -0.41616 1.16228			
	Н	3.08732 -0.84772 2.35393			
	Ν	0.5622 -0.39515 1.08115			
	Ν	0.56221 0.39509 -1.08113			
	В	-0.30558 0.00001 0.00002			
	С	-1.86991 0.00001 0.00001			
	С	-2.60169 -0.41218 1.12792			
	С	-2.60168 0.41218 -1.1279			
	С	-3.99547 -0.41679 1.13013			
	Н	-2.0742 -0.74834 2.01514			
	С	-3.99546 0.41679 -1.13013			
	Н	-2.07418 0.74835 -2.01512			
	С	-4.69707 0. 0.			
	Н	-4.5337 -0.74675 2.0122			
	Н	-4.53368 0.74675 -2.01221			
	Н	-5.7815 00.00001			
	С	0.23545 -0.8129 2.43193			
	Н	-0.84475 -0.78396 2.56778			
	Н	0.5844 -1.83251 2.62993			
	Н	0.69359 -0.14564 3.16983			
	С	0.23547 0.81281 -2.43192			
	Н	-0.84472 0.7838 -2.56781			
	Н	0.58436 1.83244 -2.62992			
	Н	0.69367 0.14557 -3.16981			
	Item	Value Threshold Converged?			
	Maximum I	Force 0.000007 0.000450 YES			

RMS 0.000001 0.000300 YES Force Maximum Displacement 0.000444 0.001800 YES RMS Displacement 0.000092 0.001200 YES Predicted change in Energy=-4.309573D-09 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -52.5390 -5.2031 -3.3710 -0.0009 -0.0005 0.0006 Low frequencies --- 2.0719 46.9702 99.6385 ------ Thermochemistry ------0.264646 (Hartree/Particle) Zero-point correction= 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

-676.862814

-676.917361

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

%nprocshared=4

Will use up to 4 processors via shared memory.

Sum of electronic and thermal Enthalpies=

Sum of electronic and thermal Free Energies=

%chk=T:\CHM\deg013\Janaka\_Gaussian\DAB analogous\DAB analogous\DAB Derivatives\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

e	· ·	
С	1.91843	0.52173 -0.08099
С	1.79671	-0.86228 0.11223
С	2.89546	-1.68968 0.23666
С	4.15968	-1.09098 0.16401
С	4.2938	0.28601 -0.02639
С	3.17386	1.11618 -0.15251
Н	2.77468	-2.75567 0.38509
Н	5.04582	-1.70766 0.25679
Н	5.2842	0.72304 -0.08036
Н	3.28928	2.18266 -0.30478

Ν 0.62413 1.04973 -0.16049 В -0.28509 -0.05083 -0.02543 С -1.83728 -0.10073 -0.02879 С -2.48047 -1.34582 0.09997 С -2.64825 1.03784 -0.17951 С -3.86878 -1.44669 0.10017 Η -1.87915 -2.2426 0.20062 С -4.03819 0.9411 -0.18863 Η -2.19464 2.01312 -0.31787 С -4.65213 -0.30164 -0.0423 Η -4.34088 -2.4172 0.20727 Η -4.64176 1.83328 -0.315 Η -5.73391 -0.3782 -0.04596 С 0.39575 2.4793 -0.27193 Η 0.66404 2.85294 -1.26615 Η -0.6541 2.69791 -0.08644 Η 0.99133 3.01931 0.47045 Ο 0.47396 -1.21937 0.15197 -0.00175 -0.00001 0.00002 0.00002 0.00004 -0.00170 Item Value Threshold Converged? 0.000046 0.000450 Maximum Force YES 0.000006 0.000300 YES RMS Force Maximum Displacement 0.001142 0.001800 YES 0.000213 RMS Displacement 0.001200 YES Predicted change in Energy=-5.489547D-11 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -48.2038 -5.7205 -2.7790 -0.6229 -0.0006 -0.0006 Low frequencies --- -0.0005 51.9453 78.6754 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ Zero-point correction= 0.223868 (Hartree/Particle) 0.235813 Thermal correction to Energy= 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= -657.473469Sum 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=giao rb3lyp/6-311++g(d,p) geom=(connectivity) \_\_\_\_\_ -----NICS dihedral 0 -----Symbolic Z-matrix: Charge = 0 Multiplicity = 1С -1.92071 0.70648 -0.00006 С -1.92071 -0.70648 0.00017 С -3.11521 -1.41789 0.00001 С -4.31355 -0.69895 -0.00005 С -4.31355 0.69895 0.00001 С -3.11521 1.41789 -0.00001 Η -3.11855 -2.50254 -0.00009 Η -5.25552 -1.23496 -0.0002 Η -5.25552 1.23496 0.00005 Η -3.11855 2.50254 -0.0001 -0.36989 2.11803 -0.00049 Η Η -0.36989 -2.11803 -0.00077 Ν -0.59459 1.1373 -0.00014 -0.59459 -1.1373 -0.00009 Ν В 0.28837 0. 0.00022 С 1.84436 0. 0.00039 С 2.57793 -1.19954 0.00003 С 2.57793 1.19954 0.00019 С 3.97035 -1.20486 -0.00008 Η 2.05624 -2.15173 0.00066 С 3.97035 1.20486 -0.00005 Η 2.05623 2.15172 -0.00027 С 4.67207 0. -0.00015Η 4.5085 -2.14648 -0.00044 Η 2.14648 0.00004 4.5085 Η 5.75643 0. -0.0004Bq -3.11713 0.00376 -0.00005 Bq -0.81617 0.14419 0.00014 Bq 3.25821 0. 0.00012 Bq -3.1171 0.00374 0.99995 Bq -0.81616 0.14447 1.00014Bq 3.25829 -0.00012 1.00012 Bq -0.81616 0.14475 2.00014

-0.81616 0.14503 3.00014 Bq -0.81615 0.14531 4.00014 Bq Calculating GIAO nuclear magnetic shielding tensors. SCF GIAO Magnetic shielding tensor (ppm): 27 Bq Isotropic = 9.5878 Anisotropy = 4.62018.0495 YX= -0.0065 ZX= -0.0018 XX= XY= -0.0027 YY= 8.0460 ZY= 0.0010 XZ= -0.0026 YZ= 0.0008 ZZ= 12.6679 Eigenvalues: 8.0429 8.0527 12.6679 28 Bq Isotropic = 9.5018 Anisotropy = 32.1289XX= 5.4494 YX= 2.3041 ZX= 0.0003 XY =2.4776 YY= 30.6966 ZY= -0.0030 XZ= 0.0025 YZ= -0.0064 ZZ= -7.6408Eigenvalues: -7.6408 5.2250 30.9210 29 Bq Isotropic = 6.7770 Anisotropy = 4.87475.6968 YX= 0.0000 ZX= 0.0022 XX= XY =0.0000 YY = 4.6075 ZY = -0.0025XZ=0.0008 YZ= -0.0010 ZZ= 10.0269 Eigenvalues: 4.6075 5.6968 10.0269 30 Bq Isotropic = 10.1684 Anisotropy = 25.6143XX= 2.3921 YX= -0.0023 ZX= -0.8171 XY= -0.0005 YY= 0.9013 ZY= -0.0221 XZ= -0.9854 YZ= 0.0054 ZZ= 27.2120 Eigenvalues: 0.9013 2.3594 27.2446 31 Bq Isotropic = 5.8838 Anisotropy = 13.0159XX= -0.1088 YX= 0.6934 ZX= -0.7601 0.7032 YY= 3.4904 ZY= -2.3384 XY =XZ= 3.3606 YZ= -0.5733 ZZ= 14.2698 Eigenvalues: -0.4064 3.4967 14.5611 32 Bg Isotropic = 9.4893 Anisotropy = 24.9249XX =1.6239 YX = 0.0009 ZX = 0.4492XY =0.0011 YY= 0.7684 ZY= -0.0010 XZ=1.2745 YZ= -0.0020 ZZ= 26.0755 0.7684 1.5935 26.1058 Eigenvalues: 33 Bq Isotropic = 2.2068 Anisotropy = 12.2711XX = -1.5866 YX = 0.0167 ZX = -0.0936XY= 0.0094 YY= -2.0203 ZY= -0.1136XZ= 2.7824 YZ= 0.7878 ZZ= 10.2274 Eigenvalues: -2.0315 -1.7356 10.3876 34 Bq Isotropic = 1.1532 Anisotropy = 7.3510XX= -1.0585 YX= -0.0083 ZX= 0.0327 XY= -0.0024 YY= -1.4818 ZY= 0.0830 XZ= 1.1092 YZ= 0.4162 ZZ= 5.9997 Eigenvalues: -1.4917 -1.1027 6.0538 35 Bq Isotropic = 0.7284 Anisotropy = 4.6740XX = -0.6920 YX = -0.0036 ZX = -0.0024

XY= -0.0020 YY= -0.9577 ZY= 0.0583 XZ= 0.3224 YZ= 0.2113 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\BrDAB\DFT CALCULATIONS.chk

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# nmr=giao rb3lyp/6-311++g(d,p) geom=connectivity

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NICS dihedral 0

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Charge =	0 Multiplicity = $1$
С	-3.57006 0.70624 -0.00004
С	-3.57007 -0.70624 0.00016
С	-4.76434 -1.4181 -0.00005
С	-5.96226 -0.69903 -0.00014
С	-5.96225 0.69905 -0.00001
С	-4.76433 1.41811 0.00001
Н	-4.7677 -2.50269 -0.00021
Н	-6.90427 -1.23485 -0.00035
Н	-6.90426 1.23488 0.00004
Н	-4.76768 2.5027 -0.00002
Н	-2.02035 2.11863 -0.00042
Н	-2.02037 -2.11864 -0.00088
Ν	-2.24352 1.13751 -0.00008
Ν	-2.24353 -1.13751 -0.00008
В	-1.36227 -0.00001 0.00029
С	0.19407 -0.00002 0.00053
С	0.92985 -1.19718 0.0001
С	0.92984 1.19716 0.00039
С	2.32208 -1.21112 0.00012
Н	0.41387 -2.15206 0.00058
С	2.32207 1.21111 0.0001
Н	0.41384 2.15203 0.00004
С	3.00702 0. 0.00004
Н	2.86511 -2.14756 -0.00016
Н	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 0.00018

Bq -2.46617 -0.00001 1.00018 Bq -2.46617 -0.00001 2.00018 Bq -2.46617 -0.00001 3.00018 -2.46617 -0.00001 4.00017 Bq Bq -4.76617 -0.00359 1. 1.60063 -0.00001 1.00041 Bq 27 Bq Isotropic = 9.6005 Anisotropy = 4.56730.0061 ZX= -0.0019XX= 8.1471 YX= XY =0.0026 YY= 8.0091 ZY= 0.0010XZ= -0.0037 YZ= 0.0004 ZZ= 12.6454 Eigenvalues: 8.0089 8.1472 12.6454 28 Bq Isotropic = 7.2716 Anisotropy = 2.29518.7842 YX= 0.0000 ZX= 0.0008 XX =0.0000 YY= 4.2290 ZY= -0.0028 XY =XZ=0.0001 YZ= -0.0009 ZZ= 8.8017 4.2290 8.7842 8.8017 Eigenvalues: 29 Bq Isotropic = 8.0346 Anisotropy = 32.36210.0001 ZX= 0.0000 XX= 3.8946 YX= 0.0001 YY= 29.6093 ZY= 0.0005 XY =XZ=0.0012 YZ= -0.0010 ZZ= -9.4002 Eigenvalues: -9.4002 3.8946 29.6093 30 Bq Isotropic = 5.7319 Anisotropy = 12.2448 $XX = -0.1097 \quad YX = 0.0007 \quad ZX = -0.7181$ XY= 0.0011 YY= 3.5376 ZY= 0.0007 XZ= 3.3871 YZ= 0.0004 ZZ= 13.7680 Eigenvalues: -0.2369 3.5376 13.8951 2.2673 Anisotropy = 12.160831 Bq Isotropic = XX= -1.3766 YX= -0.0001 ZX= -0.1876 0.0000 YY = -2.0557 ZY = 0.0002XY= XZ= 2.7558 YZ= 0.0000 ZZ= 10.2342 Eigenvalues: -2.0557 -1.5169 10.3745 32 Bq Isotropic = 1.1866 Anisotropy = 7.2722XX= -0.8961 YX= 0.0000 ZX= -0.0790 XY= 0.0000 YY = -1.5415 ZY = -0.0001XZ= 1.0964 YZ = 0.0000 ZZ =5.9974 Eigenvalues: -1.5415 -0.9335 6.0348 33 Bq Isotropic = 0.7450 Anisotropy = 4.6122XX= -0.5762 YX= 0.0001 ZX= -0.1131XY =0.0000 YY= -1.0065 ZY= -0.0001 XZ=0.3002 YZ= 0.0000 ZZ= 3.8178 Eigenvalues: -1.0065 -0.5782 3.8198 34 Bq Isotropic = 10.2065 Anisotropy = 25.5793XX= 2.4973 YX= -0.0004 ZX= -0.8586 XY= -0.0020 YY= 0.8980 ZY= 0.0215 XZ= -1.0091 YZ= -0.0040 ZZ= 27.2241 Eigenvalues: 0.8980 2.4621 27.2593

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

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# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant,connectivity)

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dihedral 0 freeze NICS calculation

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

Η -6.98992 -0.38485 -0.0001 Η -5.79938 -1.3631 -0.89441 Η -5.79958 -1.36318 0.8944 1.70449 0.01094 -0.0001 Bq Bq 1.70449 0.01094 0.99991 1.70449 0.01094 1.99991 Bq 1.70449 0.01094 2.99991 Bq 1.70449 0.01094 3.99991 Bq 4.00474 -0.08602 0.00006 Bq 4.00474 -0.08602 1.00005 Bq Bq -2.36771 0.17985 0.00003 -2.36771 0.17985 1.00003 Bq 31 Bq Isotropic = 7.9241 Anisotropy = 32.9997XX= 3.7435 YX= 1.0321 ZX= -0.0004XY =0.9762 YY= 29.8854 ZY= 0.0014 XZ= -0.0004 YZ= -0.0013 ZZ= -9.8566 Eigenvalues: -9.8566 3.7050 29.9239 32 Bq Isotropic = 5.6115 Anisotropy = 11.8602XX= -0.2101 YX= 0.2054 ZX= 0.7418 XY= 0.0357 YY=  $3.6610 \ ZY = 0.0274$ XZ= -3.4596 YZ= 0.0794 ZZ= 13.3836 Eigenvalues: -0.3486 3.6647 13.5182 33 Bq Isotropic = 2.1999 Anisotropy = 12.0316XX= -1.4472 YX= 0.0172 ZX= 0.1747 XY = -0.0012 YY = -2.0272 ZY = 0.0057XZ= -2.7908 YZ= 0.1083 ZZ= 10.0740 Eigenvalues: -2.0280 -1.5934 10.2210 34 Bq Isotropic = 1.1517 Anisotropy = 7.2417XX= -0.9628 YX= 0.0010 ZX= 0.0527 XY= -0.0050 YY= -1.5215 ZY= 0.0093 XZ= -1.1063 YZ= 0.0445 ZZ= 5.9394 Eigenvalues: -1.5216 -1.0028 5.9795 35 Bq Isotropic = 0.7284 Anisotropy = 4.6099XX= -0.6270 YX= 0.0023 ZX= 0.0802 XY= -0.0041 YY= -0.9865 ZY= 0.0093 XZ= -0.3112 YZ= 0.0146 ZZ= 3.7986 Eigenvalues: -0.9865 -0.6300 3.8016 36 Bq Isotropic = 9.5642 Anisotropy = 4.3579XX= 8.1336 YX= 0.0088 ZX= -0.00058.0895 ZY= 0.0004 -0.0593 YY= XY= 0.0009 YZ= XZ =0.0012 ZZ= 12.4695 Eigenvalues: 8.0780 8.1451 12.4695 37 Bq Isotropic = 10.1516 Anisotropy = 25.4232XX= 2.4765 YX= -0.0475 ZX= 0.8284 XY= -0.1512 YY= 0.9097 ZY= -0.0019XZ= 0.9429 YZ= -0.0437 ZZ= 27.0685

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

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# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant,connectivity)

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dihedral 0 NICS

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

С 5.09056 -0.20955 0.02255 Η 5.06805 1.93944 0.14478 Η 4.78878 -2.33725 -0.10205 Η 6.17261 -0.28064 0.03056 С -5.28608 -1.03043 -0.12747 Η -5.40746 -1.62097 -1.04147 Η -5.42288 -1.71129 0.71896 Η -6.09501 -0.29765 -0.09703 Bq -0.38381 0.14491 -0.01879 -0.39335 0.08947 0.97962Bq Bq -0.40289 0.03403 1.97804 -0.41243 -0.02142 2.97646 Bq -0.42197 -0.07686 3.97487 Bq Bq -2.68057 0.27504 -0.03952 -2.69066 0.22696 0.95927 Bq 3.68065 -0.11682 0.012 Bq 3.67216 -0.17299 1.01039 Bq 30 Bq Isotropic = 7.6900 Anisotropy = 33.0260XX= 3.8731 YX=  $1.5807 \ ZX = 0.2159$ XY= 1.5458 YY= 29.5298 ZY= 1.9632 1.6577 ZZ= -10.3328 XZ= 0.2072 YZ= Eigenvalues: -10.4162 3.7789 29.7074 31 Bq Isotropic = 5.5296 Anisotropy = 11.5121XX= -0.1738 YX= 0.2850 ZX= -0.7494 XY= -0.0271 YY= 3.7003 ZY= -0.3545 XZ= 3.0911 YZ= -0.8950 ZZ= 13.0622 Eigenvalues: -0.2850 3.6695 13.2043 32 Bq Isotropic = 2.1814 Anisotropy = 11.9358 $XX = -1.4564 \ YX = 0.0812 \ ZX = -0.1037$ XY= -0.0254 YY= -1.9652 ZY= -0.5695 2.5700 YZ= -0.8579 ZZ= XZ= 9.9656 Eigenvalues: -2.0306 -1.5639 10.1385 33 Bq Isotropic = 1.1464 Anisotropy = 7.1924XX= -0.9730 YX= 0.0266 ZX= 0.0822 XY= -0.0117 YY= -1.4613 ZY= -0.3365 XZ= 1.0256 YZ = -0.4983 ZZ = 5.8735Eigenvalues: -1.4881 -1.0140 5.9413 34 Bq Isotropic = 0.7222 Anisotropy = 4.6000XX= -0.6398 YX= 0.0145 ZX= 0.0574 XY= -0.0009 YY= -0.9621 ZY= -0.2033 XZ=0.3044 YZ= -0.2947 ZZ= 3.7684 Eigenvalues: -0.9760 -0.6464 3.7889 35 Bq Isotropic = 9.4158 Anisotropy = 2.58718.6412 YX= 0.5292 ZX= XX= 0.0265 XY =0.3663 YY= 8.4800 ZY= -0.1621 XZ= 0.0843 YZ= -0.2250 ZZ= 11.1262

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

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# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant,connectivity)

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dihedral 0 NICS

Charge =	0 Multiplicity = $1$
С	1.92936 0.50101 0.00877
С	1.8514 -0.90897 0.01279
С	2.99984 -1.69084 -0.0194
С	4.23897 -1.04583 -0.06025
С	4.32001 0.3487 -0.06814
С	3.1665 1.13853 -0.0346
Н	2.93656 -2.77369 -0.01442
Н	5.14698 -1.63693 -0.08826
Н	5.29082 0.82924 -0.10473
Н	3.24427 2.21887 -0.05125
Н	0.22578 -2.224 0.02496
Ν	0.63282 1.02532 0.05227
Ν	0.50798 -1.25893 0.05089
В	-0.31201 -0.07298 0.06334
С	-1.87578 -0.09438 0.00422
С	-2.54423 -1.33398 0.06229

С -2.68941 1.05117 -0.0764 С -3.93189 -1.42987 0.03229 Η -1.97253 -2.25325 0.13672 С -4.08016 0.96599 -0.10639 Η -2.24212 2.03396 -0.14265 С -4.70894 -0.27535 -0.05096 Η -4.40743 -2.40364 0.07659 Η -4.67264 1.8719 -0.17509 Η -5.79088 -0.3435 -0.07379 С 0.43438 2.46365 0.1178 Η -0.52722 2.6926 0.57097 Η 1.20482 2.92101 0.74372 Η 0.47788 2.92864 -0.8737 Bq 0.78918 -0.13848 0.03706 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 Bq 3.08416 -0.27241 -0.02574 Bq 3.11491 -0.27111 0.97378 Bq -3.29236 -0.18487 -0.02337 -3.31813 -0.12947 0.97476 Bq 30 Bq Isotropic = 8.0292 Anisotropy = 33.0847XX= 3.9477 YX= 2.1140 ZX= 0.1356 XY=1.2548 YY= 29.9769 ZY= -0.1033 XZ= 0.3796 YZ= 0.2287 ZZ= -9.8371 Eigenvalues: -9.8419 3.8438 30.0856 31 Bq Isotropic = 5.7702 Anisotropy = 11.1127XX= -0.8076 YX= 0.3919 ZX= 1.3047 XY= -0.2011 YY= 5.0069 ZY= -0.4733 XZ= -3.0732 YZ= -0.1271 ZZ= 13.1113 Eigenvalues: -0.8645 4.9965 13.1787 32 Bq Isotropic = 2.3651 Anisotropy = 12.1555XX= -1.9115 YX= -0.0007 ZX= 0.4507 XY= -0.0174 YY= -1.3249 ZY= -0.5923 XZ= -2.7671 YZ= -0.5726 ZZ= 10.3318 Eigenvalues: -2.0260 -1.3474 10.4688 33 Bq Isotropic = 1.2351 Anisotropy = 7.5426XX= -1.2503 YX= -0.0158 ZX= 0.1540 0.0420 YY= -1.2559 ZY= -0.4319 XY= XZ= -1.0917 YZ= -0.3939 ZZ= 6.2114 Eigenvalues: -1.2918 -1.2664 6.2635 34 Bq Isotropic = 0.7642 Anisotropy = 4.8789XX = -0.8047 YX = -0.0043 ZX =0.1115 XY= 0.0375 YY= -0.9056 ZY= -0.2545 XZ= -0.2975 YZ= -0.2324 ZZ= 4.0029

Eigenvalues: -0.9189 -0.8053 4.0168 35 Bq Isotropic = 9.5751 Anisotropy = 4.5167XX= 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 = 25.65262.2191 YX= -0.2009 ZX= 1.6737 XX= 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 = 4.99325.6112 YX= 0.1728 ZX= -0.1065XX =0.1211 YY= 4.7614 ZY= 0.3900 XY =XZ=0.0190 YZ= 0.5009 ZZ= 10.1240 4.6999 5.6357 10.1610 Eigenvalues: 38 Bq Isotropic = 9.5010 Anisotropy = 24.9761XX= 1.5474 YX= 0.0640 ZX= -1.1260XY =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*'-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

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# nmr=giao rb3lyp/6-311++g(d,p) geom=(modredundant,connectivity)

\_\_\_\_\_

#### Dihedral 0 freeze NICS

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Charge =	0 Multiplicity	y = 1	
С	-1.88818	-0.70786	0.0094
С	-1.8897	0.70343	0.00803
С	-3.08803	1.41229	-0.01893
С	-4.28756	0.69507	-0.03405
С	-4.28677	-0.70056	-0.02144
С	-3.08681	-1.41691	0.00197
Н	-3.10227	2.49509	-0.03945
Н	-5.22825	1.23293	-0.05742
Н	-5.22706	-1.23961	-0.02837
Н	-3.10245	-2.49966	0.02306
Ν	-0.56584	-1.15271	0.01561

Ν	-0.56952 1.15263 0.03505
В	0.31652 0.00153 0.06416
С	1.88422 -0.00536 -0.04558
С	2.63785 -1.17985 0.16955
С	2.63416 1.1812 -0.1926
С	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
Н	4.55765 2.12455 -0.3299
Н	5.82008 0.00582 -0.01055
C	-0.27538 -2.57049 -0.13973
H	0.58374 -2.71522 -0.79362
Н	-0.07763 - 3.06029 - 0.82022
Н	-1.12338 -3.07297 -0.6066
C	-0.29456 2.57446 0.18316
Н	0.59673 2.72939 0.78844
Н	-0.15714 3.07021 -0.78452
Н	-1.12332 3.06251 0.69934
Bq	-3.08787 -0.00639 -0.01233
Bq	-3.10113 0.00189 0.98755
Bq	-0.78621 -0.00034 0.03644
Bq	-0.81006 0.00262 1.03615
Bq	-0.8339 0.00558 2.03586
Bq	-0.85775 0.00854 3.03557
Bq	-0.8816 0.0115 4.03528
Bq	3.30998 -0.00093 -0.02971
Bq	3.30887 0.16637 0.9562
33 <sup>Bq</sup>	Isotropic = $9.5554$ Anisotropy = $4.4050$
XX=	7.7026 YX= 0.0054 ZX= -0.1426
XY=	0.0006 YY= 8.4718 ZY= -0.0133
XZ=	0.0885 YZ= 0.0737 ZZ= 12.4917
Eigenv	values: 7.7024 8.4716 12.4921
34 B	q Isotropic = $10.2930$ Anisotropy = $26.0514$
XX=	2.0705 YX= 0.0730 ZX= -1.3988
XY=	0.2576 YY= 1.2546 ZY= 0.0950
XZ=	-1.8980 YZ= 0.1664 ZZ= 27.5539
Eigenv	values: 1.2140 2.0044 27.6606
35 B	q Isotropic = 8.4047 Anisotropy = 33.2758
XX=	3.9996 YX= -0.0392 ZX= -0.3094
XY=	-0.0002 YY= 30.5761 ZY= 0.2947
XZ=	-0.1557 YZ= 1.1133 ZZ= -9.3617
Eigenv	values: -9.3781 4.0037 30.5885
36 B	q Isotropic = $6.1803$ Anisotropy = $11.0994$

 $XX = -0.4145 \quad YX = 0.3883 \quad ZX = -1.0183$ 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 = 12.2114XX= -1.8324 YX= 0.1313 ZX= -0.3640 XY = -0.1668 YY = -0.8551 ZY = -0.3304XZ= 2.8168 YZ= -0.2868 ZZ= 10.6767 Eigenvalues: -1.9516 -0.8632 10.8040 38 Bq Isotropic = 1.4184 Anisotropy = 7.7627 $XX = -1.2402 \quad YX = 0.0539 \quad ZX = -0.1506$ XY= -0.1575 YY= -1.0657 ZY= -0.1420XZ= 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 = 5.8778XX= 5.4232 YX= -0.0785 ZX= -0.3296XY= -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 = 25.8613XX= 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

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# nmr=giao rb3lyp/6-311++g(d,p)

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**DOB NICS Calculations** 

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 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 -0.48142

С	4.27483 0.23699 -0.24094
С	4.11407 -1.06623 0.23655
С	2.84398 -1.59798 0.49541
Н	3.28639 2.0792 -0.8513
Н	5.27236 0.61545 -0.43015
Н	4.98908 -1.681 0.41125
Н	2.70841 -2.60633 0.86546
0	0.42227 - 1.02347 - 0.41741
Õ	0.68582 1.11301 -0.36539
B	-0 23463 0 14429 0 03212
C	-1 76158 0 33699 0 04395
C	-2 3371 1 553 -0 36302
C C	-2 61487 -0 69871 0 46199
C C	-3 71775 1 72843 -0 35275
н	-1 69407 2 36335 -0 68879
n C	-3.09581 -0.52564 -0.47312
Ч	-2.18842 $-1.64403$ 0.77948
n C	-1 54846 0 68868 0 06555
ч	A 14765 2 6722 0 6605
и П	A 6418 1 23363 0 7082
н Ц	5 62440 0 82448 0 07388
II Da	-5.02449 $0.02448$ $0.075880.01282 0.00007 0.0224$
Dq Da	0.91282 - 0.00097 - 0.0234 0.06277 - 0.22721 - 0.06216
Dq Da	$0.90277 \ 0.33721 \ 0.90310$ 1 01272 0 67527 1 00202
Бq Da	1.012/5 $0.07557$ $1.902921.06268$ $1.01252$ $2.84268$
Bq	1.00208 $1.01555$ $2.842081.11264$ $1.25160$ $2.78244$
Бq Da	1.11204 1.55109 5.78244
Bq	3.01043 - 0.20397 - 0.00093
Bq	3.0004  0.07219  0.94009
Вq	-3.16259 0.51379 0.05481
Bq	-3.11264 0.85195 0.99457
25 Bq	150tropic = 4.1623 Anisotropy = $32.0590$
XX=	5.1283 YX= $1.8349$ ZX= $-1.84/8$
XY = XZ	1.9124 Y Y = 20.2303 Z Y = -13.8696
XZ=	-1.9144 YZ= $-13.8019$ ZZ= $-12.8/16$
Eigenv	values: $-1/.9485 + 4.9005 + 25.5350$
20 E VV-	10671 VV $- 0.2884$ 7V $- 1.0000$
$\Lambda\Lambda^-$ VV-	1.90/1 $1X = 0.2004$ $ZX = 1.00001.1722$ $XX = 2.2019$ $7X = 1.9217$
ΛI- V7-	-1.1/22 $II = 2.3016$ $ZI = 1.651/$
$\Lambda L^{=}$	-5.5134 $IZ = 2.5814$ $ZZ = 0.0552$
	values: $1.4409  1.7032  7.7701$
2/B VV-	0.6410 VV $-$ 0.0200 7V $-$ 0.4041
$\Lambda\Lambda^{-}$ VV_	-0.0417 1A $-0.0200$ ZA $-0.40410.022 VV -0.5575 7V -2.2241$
$\Lambda I = $ V7-	-0.7052 II $ -0.5575$ $LI =$ $5.22412 2074 VZ = 2 4817 ZZ = 7 0264$
AL=	-2.20/4 I $L$ $ 3.481/$ $LL$ $ 1.0204$
Eigen	values: $-1.848 / -0./300 - 8.4110$
28 B	Sq isotropic = $1.1349$ Anisotropy = $6.332/$

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 = 4.1835XX= -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 = 25.2676XX= 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 = 5.7637XX= 5.8315 YX= -0.0793 ZX= 0.2934 XY= -0.1069 YY= 4.9938 ZY= 2.0951 XZ= 0.2927 YZ= 2.0871 ZZ= 10.0248Eigenvalues: 4.2164 5.8413 10.7925 33 Bq Isotropic = 9.7036 Anisotropy = 25.6371XX= 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\OAB\DFT CALCULATIONS.chk

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# nmr=giao rb3lyp/6-311++g(d,p)

**OAB NICS Calculations** 

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 Symbolic Z-matrix:

 Charge = 0 Multiplicity = 1

 C
 1.84783 -0.65325 0.

 C
 1.92877 0.74764 0.

 C
 3.16431 1.38381 0.

С	4.30879 0.57958 0.00001
С	4.21699 -0.81459 0.
С	2.97251 -1.45597 -0.00001
Н	3.24272 2.46511 0.
Н	5.28532 1.04973 0.00001
Н	5.12188 -1.41062 0.
Н	2.88528 -2.53539 -0.00001
Н	0.40859 2.21052 -0.00004
C	-1 81126 0.04474 0.00001
C	-2 59617 1 21049 0 00001
C C	-2 47705 -1 19357 0 00001
C	-3 98677 1 14677 0
н	-2 11879 2 18593 0 00001
C C	-3 86753 -1 26367 0
н	-1 8929 -2 10714 0 00002
C C	-4 62566 -0 0931 -0 00001
н	-4.57238 2.05951 -0.00001
Н	-4 36132 -2 22922 0
H	-5.70885 -0.1461 -0.00001
N	0.61542 + 1.22583 = 0.00001
0	0.53456 -1.05558 -0.00002
B	-0.26453 0.09762 0.00003
Ba	3 0732 -0 03546 0
Ba	3.0732 - 0.03548 - 0.03548 - 1
Ba	0.07321 - 0.03348 1.
Ba	$0.93241 \ 0.07240 \ 0.07244 \ 1$
Ba	$0.93242 \ 0.07244 \ 1.$
Ba	0.93242 $0.07243$ 2. 0.93243 0.07241 2.92203
Ba	$0.93243 \ 0.07241 \ 2.92203 \ 0.93244 \ 0.0724 \ 3.92203$
Ba	-3 22741 -0.02472 -0
Ba	-3.22741 -0.02472 = 0.
26 Ba	5.22741 + 0.02472 + 1. Isotronic = 9.9387 Anisotrony = 4.8177
XX =	8.0467 VX= $-0.5158$ ZX= $0.0001$
XV=	-0.5047 VV= 8.6188 ZV= 0.0000
XT = XT	0.0002 YZ= $-0.0001$ ZZ= $13.1505$
Eigenv	values: 7.7480 8.9175 13.1505
27 B	a Isotropic = $10.2498$ Anisotropy = $25.3255$
XX =	25152 YX= $-0.2520$ ZX= $0.5620$
XY=	-0.3252 YY= $1.1092$ ZY= $-0.2241$
XZ =	0.2496 YZ= -0.1911 ZZ= 27.1250
Eigenv	values: 1.0516 2.5643 27.1335
28 B	a  Isotropic = 53073  Anisotropy = 30.9921
XX =	5.4305 YX= 0.9433 ZX= 0.0001
XY=	1.3317 YY= 25.9057 ZY= 0.0000
X7 =	0.0000  YZ = 0.0000  ZZ = -15.4143
Eigen	values: -15 4143 5 3675 25 9687
Ligen	alaoo, 15,7175 5,5075 45,7007

29 Bq Isotropic = 4.2769 Anisotropy = 8.5913XX= 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 = 10.8961XX= -0.9501 YX= -0.1565 ZX= -0.0187 XY= -0.1117 YY= -1.9998 ZY= -0.3326 XZ = -2.8317 YZ = 0.1621 ZZ = 9.1240Eigenvalues: -2.0241 -1.1240 9.3221 31 Bq Isotropic = 1.1972 Anisotropy = 7.0994XX= -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 = 4.5815XX= -0.5830 YX= -0.0094 ZX= 0.0184 XY = -0.0203 YY = -0.9590 ZY = -0.0120XZ= -0.2946 YZ= 0.0795 ZZ= 3.8036 Eigenvalues: -0.9598 -0.5868 3.8082 33 Bq Isotropic = 6.8820 Anisotropy = 5.4493 5.6651 YX= XX=  $0.2082 \ ZX = -0.0001$ XY =0.1142 YY= 4.4660 ZY= 0.0000XZ=0.0000 YZ= 0.0000 ZZ= 10.5149 Eigenvalues: 4.4447 5.6864 10.5149 34 Bq Isotropic = 9.6161 Anisotropy = 25.3810XX= 1.5802 YX= 0.1508 ZX= -0.3456XY =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 = 1-1.93042 0.52431 -0.00948 С С -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 C	$-3\ 20247\ 1\ 0.8725\ 0\ 0.0473$
ч	-2 69265 -2 8084 -0 00608
и Ц	4 00207 + 81707 + 0.00008
и Ц	-4.99297 - 1.01797 - 0.01000 5 3006 - 0.62841 - 0.0257
П Ц	-5.5000 $0.02041$ $0.02572.24057$ $2.16051$ $0.01224$
II N	-5.5+757 2.10051 0.01254 0.65212 1.00767 0.02602
D	-0.03213 $1.09707$ $-0.020030.20228 0.01480 0.02214$
D C	$0.29338 \ 0.01489 \ -0.02314$
C C	1.64767 - 0.03004 - 0.01323
C	2.44/38 - 1.5230/ -0.00800
C	2.70734 $1.0017$ $0.03432$
	5.85010 - 1.48150 - 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 $-0.83281$
U D	-0.43932 $-1.186/2$ $-0.02089$
Вq	-3.02/55 -0.32254 0.01199
Вq	3.25359 -0.20601 0.01002
Вq	-0.7/837 -0.07847 -0.01674
Вq Da	-0.75013 $-0.08413$ $0.98299$
Bq Da	-0.75589 $-0.08979$ $1.98275$
Бq Da	-0.71103 -0.09343 2.98247
Бų Ра	-0.06941 $-0.10111$ $5.9622$
Dq Da	-5.02755 $-0.52254$ $1.011592 25442 0 21008 1 00004$
р 20 Ва	$J_{100} = 0.0408  \text{Arisotropy} = -4.8426$
29 Dq VV-	7.7465 VY- 0.5606 7Y- 0.0372
$\Lambda\Lambda^{-}$ VV-	7.7403 1 A $-$ 0.3000 Z A $-$ 0.0372 0.8102 VV $-$ 8.0071 ZV $-$ 0.0208
А1- Х7-	0.8193 $11 - 8.9071$ $210.02080.1127$ $V7 - 0.0260$ $77 - 13.1687$
Eigen	-0.1127 120.0209 22 - 15.1007 walkes: 7.4251 0.2280 13.1602
30 F	$R_{a}$ Isotronic = 6.9277 Anisotrony = 5.4397
XX =	5.6483 YX= -0.3942 7X= -0.0921
XY=	-0.2590 YY= $4.5901$ ZY= $-0.1760$
XZ =	-0.0571 YZ= $-0.2789$ ZZ= $10.5448$
Eigen	values: 4.4880 5.7410 10.5542
31 E	3q  Isotropic = 6.2855  Anisotropy = 35.1602

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 = 10.3206XX= -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= -0.4745XZ=1.1092 YZ= -0.1323 ZZ= 5.6047 Eigenvalues: -1.2680 -0.8326 5.6767 35 Bq Isotropic = 0.7621 Anisotropy = 4.5400XX= -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 = 25.66792.2079 YX= 0.3891 ZX= -0.2680XX= XY= 0.7730 YY= 1.3452 ZY = -0.4119XZ=-0.3895 YZ= -0.6834 ZZ= 27.4203 Eigenvalues: 1.0484 2.4885 27.4364 37 Bq Isotropic = 9.6934 Anisotropy = 25.1726XX =1.5938 YX= -0.2143 ZX= -0.0659XY= -0.1868 YY= 1.0497 ZY= -0.9268XZ= 0.9951 YZ= -0.8062 ZZ= 26.4366 0.9652 1.6398 26.4751 Eigenvalues:

d) Thermodynamic calculations in gas phase at 100 °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 m=connectivity int=grid=ultrafine temperature=373.15 \_\_\_\_\_

DAB OptFrq Calculations in gas phase at 100 C

\_\_\_\_\_ Symbolic Z-matrix: Charge = 0 Multiplicity = 1С 1.91966 0.69941 0.10051 С 1.91966 -0.69941 -0.10051 С 3.11417 -1.40302 -0.20527 С 4.31243 -0.6915 -0.10205 С 4.31243 0.6915 0.10206 С 3.11417 1.40302 0.20527 Η 3.11741 -2.47636 -0.36142 Η 5.25447 -1.22169 -0.18022 Η 5.25447 1.22169 0.18023 Η 3.11741 2.47636 0.36142 Η 0.36428 2.08941 0.34006 Η 0.36428 -2.0894 -0.34009 Ν 0.5932 1.12682 0.15641 Ν 0.5932 -1.12682 -0.15643 В -0.28839 0. 0. С -1.84417 0. 0. С -2.57599 -1.17251 0.25838 С -2.57599 1.17251 -0.25838 С -3.96866 -1.17675 0.26014 Η -2.05039 -2.09714 0.47688 С -3.96866 1.17675 -0.26014 Η -2.05039 2.09714 -0.47687 С -4.6699 0. 0. Η -4.50746 -2.09505 0.46695 Η -4.50746 2.09505 -0.46694 Η -5.75429 0. 0. Item Value Threshold Converged? Maximum Force 0.000049 0.000450 YES RMS Force 0.000016 0.000300 YES 0.001440 Maximum Displacement 0.001800 YES RMS Displacement 0.000280 0.001200 YES Predicted change in Energy=-4.958764D-08 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -0.0004 0.0002 0.0005 1.1393 2.5542 6.1169 Low frequencies --- 28.7029 56.0608 80.2429 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ Zero-point correction= 0.208540 (Hartree/Particle)

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 Energie	es= -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

se\BrDAB\BrDAB\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

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## BrDAB OptFrq 100 C DFT GP

Symbolic Z-matrix:

\_\_\_\_\_

Symbolic Z matrix.			
Charge =	0 Multiplicity = $1$		
С	-3.56829 0.69843 -0.10578		
С	-3.56827 -0.69839 0.10603		
С	-4.76261 -1.40151 0.21677		
С	-5.96041 -0.6908 0.10769		
С	-5.96044 0.69066 -0.10805		
С	-4.76266 1.40147 -0.21685		
Н	-4.76575 -2.47347 0.38184		
Н	-6.90252 -1.22007 0.1902		
Н	-6.90257 1.21986 -0.1908		
Н	-4.76584 2.47342 -0.38193		
Н	-2.0134 2.08656 -0.35948		
Н	-2.01332 -2.08647 0.35969		
Ν	-2.24146 1.12595 -0.16437		
Ν	-2.24141 -1.12584 0.16474		
В	-1.36167 0.00006 0.00006		
С	0.19447 $0.00007$ $0.00005$		
С	0.92835 -1.16701 -0.27188		
С	0.9284 1.16711 0.27193		
С	2.32084 -1.17962 -0.27581		
Н	0.40819 -2.09137 -0.50255		
С	2.32089 1.17964 0.27582		
Н	0.40829 2.09148 0.50264		
С	3.0053 00.00001		

Η 2.86453 -2.09016 -0.4932 Η 2.86464 2.09016 0.49317 Br 4.92322 -0.00003 -0.00005 Item Threshold Converged? Value Maximum Force 0.000215 0.000450 YES 0.000045 0.000300 YES RMS Force Maximum Displacement 0.001277 0.001800 YES RMS Displacement 0.000260 0.001200 YES Predicted change in Energy=-1.842745D-07 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -1.0682 0.0045 0.0071 0.0074 0.7293 5.6723 Low frequencies --- 29.6513 34.1906 55.1293 \_\_\_\_\_ - Thermochemistry -------0.198334 (Hartree/Particle) Zero-point correction= Thermal correction to Energy= 0.218064 Thermal correction to Enthalpy= 0.219246 Thermal correction to Gibbs Free Energy= 0.141754 Sum of electronic and zero-point Energies= -3171.865327 Sum of electronic and thermal Energies= -3171.845597 Sum of electronic and thermal Enthalpies= -3171.844415 Sum of electronic and thermal Free Energies= -3171.921907

#### 3. Methoxydiazaborole (4.3)

%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

se\MeODAB\MeODAB\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

\_\_\_\_\_

#### MeODAB DFT 100 C GP

Symbolic Z-matrix:Charge = 0 Multiplicity = 1C-2.78123C-2.835190.66687-0.1C-4.055921.323-0.20774C-5.226330.56384-0.11891C-5.17305-0.819270.07447

C -3.94763 -1.48339 0.18084	
Н -4.10077 2.39669 -0.35515	
Н -6.18791 1.05732 -0.19996	
Н -6.09373 -1.38717 0.1418	
Н -3.90941 -2.55728 0.3289	
Н -1.17603 -2.062 0.33414	
Н -1.33574 2.11945 -0.31555	
N -1.43955 -1.10754 0.15531	
N -1.52649 1.14669 -0.14278	
B -0.59972 0.05472 0.01358	
C 0.95066 0.118 0.02465	
C 1.64179 1.32824 0.23669	
C 1.73823 -1.02377 -0.17783	
C 3.02543 1.39473 0.24642	
Н 1.08394 2.24298 0.41242	
C 3.13265 -0.98294 -0.17424	
Н 1.26072 -1.98188 -0.3598	
C 3.78354 0.23515 0.03912	
H 3.5453 2.33037 0.41513	
H 3.69199 -1.89381 -0.34114	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$C \qquad 5.964 - 0.7416 - 0.13965$	
H $6.98865 - 0.3/828 - 0.08146$	
H $5.80264 - 1.49664 - 0.63/31$	
H 5./9551 -1.18900 -1.124/5	
Maximum Force 0.000021 0.000450 VES	
PMS = 0.000001 + 0.000430 + ES	
Maximum Displacement = 0.001001 = 0.001800 = VES	
RMS Displacement 0.000356 0.001200 VES	
Predicted change in Energy=-4 427050D-09	
Ontimization completed	
Stationary point found	
Full mass-weighted force constant matrix	
Low frequencies0.7365 -0.0004 0.0003 0.0004 1.1839 5.119	90
Low frequencies 24.4338 39.2189 62.1532	Ū
- Thermochemistry -	
Zero-point correction= 0.240707 (Hartree/Particle)	
Thermal correction to Energy= 0.262295	
Thermal correction to Enthalpy= 0.263477	
Thermal correction to Gibbs Free Energy= 0.183293	
Sum of electronic and zero-point Energies= -712.837201	
Sum of electronic and thermal Energies= -712.815613	
Sum of electronic and thermal Enthalpies= -712.814431	

Sum of electronic and thermal Free Energies= -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

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# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo m=connectivity int=grid=ultrafine temperature=373.15

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MeDAB DFT 100 C GP

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

8-	•
С	-1.53051 -0.48573 0.06492
С	-1.44089 0.91231 -0.11794
С	-2.59233 1.67958 -0.22185
С	-3.83075 1.03496 -0.13618
С	-3.93525 -0.34946 0.0507
С	-2.76479 -1.11624 0.15172
Η	-2.53874 2.75358 -0.36417
Н	-4.73681 1.62591 -0.21552
Н	-2.82559 -2.19117 0.29383
Н	-0.06627 -1.97254 0.29973
Н	0.20119 2.20624 -0.32871
Ν	-0.23372 -0.99572 0.12514
Ν	-0.08869 1.25789 -0.15798
В	0.71807 0.07642 -0.01004
С	2.27074 -0.02409 0.00146
С	3.07566 1.09299 0.28679
С	2.92663 -1.2372 -0.27306
С	4.46556 1.00582 0.29864
Н	2.60985 2.04593 0.51883
С	4.31598 -1.33292 -0.26476
Н	2.34345 -2.12131 -0.51233
С	5.09056 -0.20954 0.02202
Н	5.06157 1.88296 0.52624
Н	4.79527 -2.28075 -0.48452
Н	6.17262 -0.28062 0.02985
С	-5.28735 -1.01937 0.14113
Н	-5.41958 -1.76352 -0.6511
Н	-5.41444 -1.5376 1.09717

Η -6.09567 -0.29104 0.04931 Item Value Threshold Converged? Maximum Force 0.000039 0.000450 YES RMS Force 0.000006 0.000300 YES Maximum Displacement 0.001659 0.001800 YES Displacement 0.000468 RMS 0.001200 YES Predicted change in Energy=-8.564478D-09 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -20.9357 -2.7149 -0.0008 -0.0006 0.0003 1.5022 Low frequencies --- 3.2430 27.5071 49.1544 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ Zero-point correction= 0.235536 (Hartree/Particle) Thermal correction to Energy= 0.254886 Thermal correction to Enthalpy= 0.256068 Thermal correction to Gibbs Free Energy= 0.181444 Sum of electronic and zero-point Energies= -637.611599 Sum of electronic and thermal Energies= -637.592249 Sum of electronic and thermal Enthalpies= -637.591067

## 5. N-Methyldiazaborole (4.5)

%nprocshared=4

Will use up to 4 processors via shared memory.

Sum of electronic and thermal Free Energies=

%chk=T:\CHM\deg013\Janaka\_Gaussian\Solvation\Solvation\100 C (373\_15) in gas pha

-637.665691

se\MMDAB\MMDAB\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

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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
 0.18596

3.02023 -2.70616 -0.47085 Η Η 5.19388 -1.51457 -0.28214 Η 5.26317 0.91836 0.13527 Η 3.16777 2.22559 0.36537 Η 0.27299 -2.23784 -0.42651 Ν 0.60156 0.96634 0.15856 Ν 0.5393 -1.29182 -0.20924 В -0.30399 -0.14087 -0.02629 С -1.86457 -0.1418 -0.02696 С -2.5754 -1.1698 0.61895 С -2.61686 0.8474 -0.68518 С -3.9681 -1.20568 0.61617 Η -2.0299 -1.94721 1.14506 С -4.010.81435 -0.69677 -2.1081 Η 1.64571 -1.21558 С -4.69026 -0.21165 -0.04268 Η -4.49004 -2.00665 1.12856 Η -4.56487 1.5864 -1.21888 Η -5.77436 -0.23756 -0.04819 С 0.32556 2.35503 0.47819 Η -0.74354 2.48545 0.63794 Η 0.84692 2.65394 1.39355 Η 0.64278 3.02387 -0.32981 Item Value Threshold Converged? Maximum Force 0.000008 0.000450 YES RMS 0.000002 0.000300 YES Force Maximum Displacement 0.001341 0.001800 YES Displacement 0.000462 0.001200 YES RMS Predicted change in Energy=-1.066894D-08 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -1.8256 -0.0008 -0.0006 0.0006 1.3140 5.0765 Low frequencies --- 42.9245 53.2438 75.2321 \_\_\_\_\_ - Thermochemistry -------0.236406 (Hartree/Particle) Zero-point correction= Thermal correction to Energy= 0.256351 Thermal correction to Enthalpy= 0.257533 Thermal correction to Gibbs Free Energy= 0.182101 Sum of electronic and zero-point Energies= -637.599560 Sum of electronic and thermal Energies= -637.579615 Sum of electronic and thermal Enthalpies= -637.578433 Sum of electronic and thermal Free Energies= -637.653865

# 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

 $se \ bmbab \$ 

# opt=(maxcycle=500,z-matrix,maxstep=30) freq rb3lyp/6-311++g(d,p) geo m=connectivity int=grid=ultrafine temperature=373.15

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## DMDAB 100C GP

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Charge =	0 Multiplicity = $1$
С	1.88427 -0.70225 0.08351
С	1.88427 0.70225 -0.0835
С	3.07942 1.40778 -0.17217
С	4.27909 0.69282 -0.08542
С	4.27909 -0.69282 0.08545
С	3.07942 -1.40778 0.17219
Н	3.08733 2.48372 -0.30103
Н	5.22097 1.22525 -0.15077
Н	5.22097 -1.22525 0.15081
Н	3.08732 -2.48372 0.30104
Ν	0.5622 -1.14336 0.13309
Ν	0.56221 1.14336 -0.13312
В	-0.30558 0.00001 0.00002
С	-1.86991 0.00001 0.00001
С	-2.60169 0.8222 0.87526
С	-2.60168 -0.8222 -0.87524
С	-3.99547 0.82211 0.88037
Н	-2.0742 1.46357 1.57441
С	-3.99546 -0.82211 -0.88036
Н	-2.07418 -1.46357 -1.57438
С	-4.69707 0. 0.
Н	-4.5337 1.46168 1.57166
Н	-4.53368 -1.46168 -1.57165
Н	-5.7815 -0.00001 0.
С	0.23546 -2.53775 0.3672
Н	-0.84474 -2.64609 0.45413
Н	0.58441 -3.17299 -0.45455
Н	0.6936 -2.89689 1.29497
С	0.23546 2.53774 -0.36727
Н	-0.84473 2.64607 -0.45427

0.58435 3.17299 0.4545 Η Η 0.69366 2.89689 -1.29501 Value Threshold Converged? Item Maximum Force 0.000030 0.000450 YES RMS Force 0.000006 0.000300 YES Maximum Displacement 0.001055 0.001800 YES RMS Displacement 0.000373 0.001200 YES Predicted change in Energy=-9.138892D-09 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -2.7251 -0.0008 -0.0006 0.0003 1.3533 2.4140 Low frequencies --- 44.2459 48.9295 69.1108 \_\_\_\_\_ - Thermochemistry -Zero-point correction= 0.264100 (Hartree/Particle) Thermal correction to Energy= 0.286367 0.287549 Thermal correction to Enthalpy= Thermal correction to Gibbs Free Energy= 0.206997 Sum of electronic and zero-point Energies= -676.887787 Sum of electronic and thermal Energies= -676.865519 Sum of electronic and thermal Enthalpies= -676.864338 Sum of electronic and thermal Free Energies= -676.944890

#### 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

se\DOB\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

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DOB at 100 C in GP

5							
Charge =	0 Mul	tiplici	ty = 1				
C							
С	1	B1					
С	2	B2	1	A1			
С	3	B3	2	A2	1	D1	0
С	4	B4	3	A3	2	D2	0
С	1	B5	2	A4	3	D3	0

Н	3 B6	2 A5	1 D4 0	
Н	4 B7	3 A6	2 D5 0	
Н	5 B8	4 A7	3 D6 0	
Н	6 B9	1 A8	2 D7 0	
0	1 B10	6 A9	5 D8 0	
0	2 B11	1 A10	11 D9 0	
В	12 B12	2 A11	1 D10 0	)
С	13 B13	12 A12	2 D11	0
С	14 B14	13 A13	12 D12	0
С	14 B15	13 A14	12 D13	0
С	15 B16	14 A15	13 D14	0
Η	15 B17	14 A16	13 D15	0
С	16 B18	14 A17	13 D16	0
Н	16 B19	14 A18	13 D17	0
С	19 B20	16 A19	14 D18	0
Н	17 B21	15 A20	14 D19	0
Н	19 B22	16 A21	14 D20	0
Н	21 B23	19 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			
<b>B</b> 8	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			
Al	122.02264	5		
A2	116.54768	3		
A3	121.4296	7		
A4	122.02263	3		

A5	121.43485
A6	119.13955
A7	119.43074
A8	121.43482
A9	128.976
A10	109.00137
A11	105.7634
A12	124.76469
A13	120.81873
A14	120.81905
A15	120.87076
A16	119.38114
A17	120.8708
A18	119.38132
A19	119.93251
A20	120.05505
A21	120.05485
A22	119.98447
D1	0.
D2	0.
D3	0.
D4	180.
D5	180.
D6	-180.
D7	180.
D8	-180.
D9	0.
D10	0.
D11	180.
D12	0.
D13	180.
D14	180.
D15	0.
D16	-180.
D17	0.
D18	0.
D19	-180.
D20	180.
D21	180.
Item	Value Threshold Converged?
Maximum Fo	orce 0.000374 0.000450 YES
RMS Force	e 0.000102 0.000300 YES
Maximum Di	isplacement 0.000282 0.001800 YES
KMS Disp	lacement 0.000086 0.001200 YES
Predicted cha	inge in Energy=-1.049895D-07

Optimization completed.

-- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -7.4847 -3.7216 -3.0452 -0.0006 0.0005 0.0005 Low frequencies --- 46.7604 54.8864 79.1531 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ 0.183681 (Hartree/Particle) Zero-point correction= Thermal correction to Energy= 0.200535 Thermal correction to Enthalpy= 0.201717 Thermal correction to Gibbs Free Energy= 0.132564 Sum of electronic and zero-point Energies= -638.088201 Sum of electronic and thermal Energies= -638.071347 -638.070165 Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= -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

se\OAB\OAB\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

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OAB 100 C GP

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

С -3.98677 1.14677 0. Η -2.11879 2.18593 0.00001 С -3.86753 -1.26367 0. Η -1.8929 -2.10714 0.00002 С -4.62566 -0.0931 -0.00001 Η -4.57238 2.05951 -0.00001 Η -4.36132 -2.22922 0. Η -5.70885 -0.1461 -0.00001 Ν 0.61542 1.22583 -0.00002 0 0.53456 -1.05557 -0.00002 В -0.26453 0.09762 0.00003 Value Threshold Converged? Item Maximum Force 0.000088 0.000450 YES RMS Force 0.000030 0.000300 YES 0.001716 Maximum Displacement 0.001800 YES Displacement 0.000719 RMS 0.001200 YES Predicted change in Energy=-9.459937D-08 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -7.1137 -2.4126 -0.7526 -0.0005 0.0003 0.0008 Low frequencies --- 30.9999 55.8366 82.7596 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ 0.196103 (Hartree/Particle) Zero-point correction= Thermal correction to Energy= 0.213400 Thermal correction to Enthalpy= 0.214581 Thermal correction to Gibbs Free Energy= 0.144384 Sum of electronic and zero-point Energies= -618.200297 Sum of electronic and thermal Energies= -618.183001 Sum of electronic and thermal Enthalpies= -618.181819

#### 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

-618.252016

se\N-OAB\N-OAB\DFT CALCULATIONS.chk

Sum of electronic and thermal Free Energies=

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

m=connectivity int=grid=ultrafine temperature=373.15

-----

# N-OAB 100 C GP

-----

Symbolic Z-matrix:	
Charge = $0$ Multiplicity = $1$	
C 1.91819 0.52066 0.04798	
C 1.79736 -0.86738 -0.11448	
C 2.89668 -1.69757 -0.21242	
C 4.16057 -1.09796 -0.14134	
C 4.29381 0.28259 0.02197	
C 3.17328 1.11586 0.11915	
Н 2.7766 -2.76661 -0.33771	
Н 5.04713 -1.71664 -0.21485	
Н 5.28395 0.72062 0.0724	
Н 3.28799 2.18632 0.24089	
N 0.62354 1.04952 0.11518	
B -0.28509 -0.05083 -0.02543	
C -1.83728 -0.10073 -0.02879	
C -2.48347 -1.27299 0.40567	
C -2.64519 0.9622 -0.46948	
C -3.8719 -1.37122 0.42001	
Н -1.88441 -2.11478 0.735	
C -4.03516 0.8656 -0.46522	
Н -2.18893 1.87091 -0.84649	
C -4.65225 -0.29992 -0.01411	
Н -4.34639 -2.28324 0.76542	
Н -4.63627 1.69643 -0.81827	
Н -5.73409 -0.37545 -0.00715	
C 0.39497 2.46038 0.37111	
Н 0.65527 3.07395 -0.49827	
Н -0.65322 2.62324 0.61436	
Н 0.99689 2.79582 1.22118	
O 0.47481 -1.225 -0.15575	
Item Value Threshold Converged?	
Maximum Force 0.000011 0.000450 YES	
RMS Force 0.000003 0.000300 YES	
Maximum Displacement 0.001175 0.001800 YES	
RMS Displacement 0.000280 0.001200 YES	
Predicted change in Energy=-8.633527D-09	
Optimization completed.	
Stationary point found.	
Full mass-weighted force constant matrix:	
Low frequencies3.1667 -1.8129 -0.0004 -0.0003 0.0005 2.5857	
Low frequencies 38.3272 53.9901 83.5102	
- Thermochemistry -	

-----

Zero-point correction=	0.224022 (Hartree/Particle)
Thermal correction to Energy=	0.243546
Thermal correction to Enthalpy=	0.244727
Thermal correction to Gibbs Free E	Energy= 0.169891
Sum of electronic and zero-point E	nergies= -657.487321
Sum of electronic and thermal Ener	rgies= -657.467798
Sum of electronic and thermal Enth	nalpies= -657.466616
Sum of electronic and thermal Free	Energies= -657.541453

e) Thermodynamic calculations in DMSO at 100 °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

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DAB OptFrq Calculations in DMSO at 100 C

Charge =	0 Multiplicity = $1$
С	-1.91966 0.69941 -0.10051
С	-1.91966 -0.69941 0.10051
С	-3.11417 -1.40302 0.20527
С	-4.31243 -0.6915 0.10205
С	-4.31243 0.6915 -0.10206
С	-3.11417 1.40302 -0.20527
Н	-3.11741 -2.47636 0.36142
Н	-5.25447 -1.22169 0.18022
Н	-5.25447 1.22169 -0.18023
Н	-3.11741 2.47636 -0.36142
Н	-0.36428 2.08941 -0.34006
Н	-0.36428 -2.0894 0.34009
Ν	-0.5932 1.12682 -0.15641
Ν	-0.5932 -1.12682 0.15643
В	0.28839 0. 0.
С	1.84417 0. 0.
С	2.57599 -1.17251 -0.25838
С	2.57599 1.17251 0.25838
С	3.96866 -1.17675 -0.26014
Н	2.05039 -2.09714 -0.47688

С 3.96866 1.17675 0.26014 Η 2.05039 2.09714 0.47687 С 4.6699 0. 0. Η 4.50746 -2.09505 -0.46695 Η 4.50746 2.09505 0.46694 Η 5.75429 0. 0. Item Value Threshold Converged? 0.000217 0.000450 YES Maximum Force 0.000057 YES RMS Force 0.000300 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 6.5854 Low frequencies --- 33.1230 56.3973 89.9136 ------ Thermochemistry ------Zero-point correction= 0.208589 (Hartree/Particle) 0.226255 Thermal correction to Energy= Thermal correction to Enthalpy= 0.227437 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\DMSO\BrDAB\ DFT CAL CULATIONS.chk

CULATIONS.CIIK

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# 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

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BrDAB\_OptFrq\_100 C\_DFT\_DMSO

Symbolic Z-matrix: Charge = 0 Multiplicity = 1

С -3.56829 0.69843 -0.10578 С -3.56827 -0.69839 0.10603 С -4.76261 -1.40151 0.21677 С -5.96041 -0.6908 0.10769 С -5.96044 0.69066 -0.10805 С -4.76266 1.40147 -0.21685 Η -4.76575 -2.47347 0.38184 Η -6.90252 -1.22007 0.1902 Η -6.90257 1.21986 -0.1908 Η -4.76584 2.47342 -0.38193 Η -2.0134 2.08656 -0.35948 Η -2.01332 -2.08647 0.35969 Ν -2.24146 1.12595 -0.16437 Ν -2.24141 -1.12584 0.16474 В -1.36167 0.00006 0.00006 С 0.19447 0.00007 0.00005 С 0.92835 -1.16701 -0.27188 С 0.9284 1.16711 0.27193 С 2.32084 -1.17962 -0.27581 Η 0.40819 -2.09137 -0.50255 С 2.32089 1.17964 0.27582 Η 0.40829 2.09148 0.50264 С 3.0053 0. -0.00001Η 2.86453 -2.09016 -0.4932 2.86464 2.09016 0.49317 Η Br 4.92322 -0.00003 -0.00005 Threshold Converged? Item Value Maximum Force 0.000037 0.000450 YES 0.000008 0.000300 RMS Force YES 0.000490 Maximum Displacement 0.001800 YES YES RMS Displacement 0.000189 0.001200 Predicted change in Energy=-9.491802D-09 Optimization completed. -- Stationary point found. Full mass-weighted force constant matrix: Low frequencies --- -3.8228 -3.6182 -0.0059 -0.0009 0.0054 4.3785 Low frequencies --- 32.9064 34.9422 62.0834 ------- Thermochemistry ------Zero-point correction= 0.198336 (Hartree/Particle) Thermal correction to Energy= 0.218024 Thermal correction to Enthalpy= 0.219205 Thermal correction to Gibbs Free Energy= 0.142020 Sum of electronic and zero-point Energies= -3171.875004 Sum of electronic and thermal Energies= -3171.855316
Sum of electronic and thermal Enthalpies=	-3171.854135
Sum of electronic and thermal Free Energies=	-3171.931320

## 3. Methoxydiazaborole (4.3)

%nprocshared=4 Will use up to 4 processors via shared memory.

%chk=T:\CHM\deg013\Janaka\_Gaussian\Solvation\Solvation\MeO.DAB\DMSO\MeOD AB\DFT C ALCULATIONS.chk

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# 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

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### MeODAB DFT 100 C DMSO

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Symbolic Z	-matrix:
Charge = $0$	Multiplicity = 1
С	2.78092 -0.73303 -0.08882
С	2.83556 0.66707 0.09638
С	4.05658 1.32323 0.20086
С	5.22671 0.56343 0.11419
С	5.17276 -0.82037 -0.07365
С	3.94706 -1.48452 -0.17677
Н	4.10179 2.39741 0.34448
Н	6.18852 1.05686 0.19266
Н	6.09316 -1.38893 -0.13925
Н	3.90853 -2.55899 -0.32041
Н	1.17476 -2.06306 -0.32294
Η	1.33735 2.12148 0.30666
Ν	1.43902 -1.1077 -0.15004
Ν	1.52714 1.14759 0.13918
В	0.59971 0.05534 -0.01129
С	-0.95069 0.1189 -0.0212
С	-1.64201 1.32995 -0.22819
С	-1.73821 -1.02385 0.176
С	-3.02566 1.39625 -0.23851
Н	-1.08438 2.24565 -0.39944
С	-3.13266 -0.98333 0.17138
Η	-1.26082 -1.98273 0.35408
С	-3.78361 0.2355 -0.03755
Η	-3.54556 2.33254 -0.40344
Η	-3.69233 -1.89484 0.33379
0	-5.1371 0.39668 -0.06342
С	-5.96379 -0.74331 0.13169

Η -6.98857 -0.38112 0.06899 Η -5.79707 -1.49577 -0.64659 Η -5.79807 -1.19336 1.11642 Value Threshold Converged? Item Maximum Force 0.000025 0.000450 YES 0.000007 0.000300 YES RMS Force Maximum Displacement 0.001002 0.001800 YES RMS Displacement 0.000396 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 -0.0004 0.0004 0.0005 0.9966 3.2452 Low frequencies --- 31.9011 39.3802 68.7954 ------ Thermochemistry -------0.240678 (Hartree/Particle) Zero-point correction= Thermal correction to Energy= 0.262219 Thermal correction to Enthalpy= 0.263401 Thermal correction to Gibbs Free Energy= 0.183677 -712.848650 Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= -712.827108 Sum of electronic and thermal Enthalpies= -712.825926 -712.905650 Sum of electronic and thermal Free Energies=

#### 4. Methyldiazaborole (4.4)

%nprocshared=4 Will use up to 4 processors via shared memory.

%chk=T:\CHM\deg013\Janaka\_Gaussian\Solvation\Me.DAB\DMSO\MeDAB \DFT CAL

CULATIONS.chk

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# 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

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N-methyl DAB\_DFT\_ Calculations t 100 C DMSO

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Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C 1.91231 0.48943 0.07563

C 1.87613 -0.90419 -0.15913

C 4.26814 -0.9591 -0.18362	
C 4.30622 0.41683 0.05489	
C 3.12774 1.15798 0.1878	
Н 3.02234 -2.70488 -0.47437	
Н 5.19485 -1.51207 -0.28449	
Н 5.26253 0.92038 0.13657	
Н 3.16654 2.22568 0.36861	
Н 0.27412 -2.23849 -0.42904	
N 0.60093 0.965 0.16028	
N 0.54008 -1.29268 -0.21035	
В -0.30381 -0.14256 -0.02553	
C -1.86445 -0.1433 -0.02664	
C -2.57674 -1.16652 0.6251	
C -2.6151 0.84272 -0.69136	
C -3.96951 -1.20062 0.62176	
Н -2.03253 -1.94134 1.15637	
C -4.00826 0.81128 -0.70372	
Н -2.10466 1.63715 -1.22602	
C -4.69009 -0.20986 -0.04372	
Н -4.49276 -1.9976 1.139	
Н -4.56187 1.58073 -1.23097	
Н -5.77423 -0.23451 -0.04966	
C 0.32369 2.35343 0.48005	
Н -0.74612 2.48372 0.63519	
Н 0.84129 2.65176 1.39774	
Н 0.64433 3.02271 -0.32619	
Item Value Threshold Converged?	
Maximum Force 0.000023 0.000450 YES	
RMS Force 0.000005 0.000300 YES	
Maximum Displacement 0.001722 0.001800 YES	
RMS Displacement 0.000567 0.001200 YES	
Predicted change in Energy=-9.597019D-09	
Optimization completed.	
Stationary point found	
Full mass-weighted force constant matrix:	
Low frequencies0.0007 -0.0005 -0.0002 1.7050 4.0426 8.6976	
Low frequencies 45.6535 53.5221 77.5961	
- Thermochemistry -	
Zero-point correction= 0.236305 (Hartree/Particle)	
Thermal correction to Energy= 0.256244	
Thermal correction to Enthalpy= 0.257426	
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=	-637.586003
Sum of electronic and thermal Free Energies=	-637.661347

### 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\N-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

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N-methyl DAB\_DFT\_ 100 C DMSO

Symbolic Z-matrix

Symbolic	
Charge =	0 Multiplicity = $1$
С	1.91231 0.48943 0.07563
С	1.87613 -0.90419 -0.15913
С	3.04961 -1.63584 -0.29282
С	4.26814 -0.9591 -0.18362
С	4.30622 0.41683 0.05489
С	3.12774 1.15798 0.1878
Н	3.02234 -2.70488 -0.47437
Н	5.19485 -1.51207 -0.28449
Н	5.26253 0.92038 0.13657
Н	3.16654 2.22568 0.36861
Н	0.27412 -2.23849 -0.42904
Ν	0.60093 0.965 0.16028
Ν	0.54008 -1.29268 -0.21035
В	-0.30381 -0.14256 -0.02553
С	-1.86445 -0.1433 -0.02664
С	-2.57674 -1.16652 0.6251
С	-2.6151 0.84272 -0.69136
С	-3.96951 -1.20062 0.62176
Н	-2.03253 -1.94134 1.15637
С	-4.00826 0.81128 -0.70372
Н	-2.10466 1.63715 -1.22602
С	-4.69009 -0.20986 -0.04372
Η	-4.49276 -1.9976 1.139
Н	-4.56187 1.58073 -1.23097
Н	-5.77423 -0.23451 -0.04966
С	0.32369 2.35343 0.48005
Н	-0.74612 2.48372 0.63519

0.84129 2.65176 1.39774 Η Η 0.64433 3.02271 -0.32619 Value Threshold Converged? Item Maximum Force 0.000023 0.000450 YES RMS Force 0.000005 0.000300 YES Maximum Displacement 0.001723 0.001800 YES Displacement 0.000570 0.001200 RMS 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 4.0455 8.6981 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=	0.257426
Thermal correction to Gibbs Free Energy	v= 0.182082
Sum of electronic and zero-point Energie	es= -637.607123
Sum of electronic and thermal Energies=	-637.587184
Sum of electronic and thermal Enthalpies	s= -637.586002
Sum of electronic and thermal Free Energy	gies= -637.661346

#### 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\DMDAB\DMSO\DMDA B\DFT CALC

ULATIONS.chk

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# 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.

-----

DMDAB 100C DMSO

Symbolic Z-matrix: Charge = 0 Multiplicity = 1 C -1.88424 0.70228 0.08345 C -1.88424 -0.70228 -0.08346

C -3.07942 -1.40766 -0.17238	
C -4.27914 -0.69274 -0.08557	
C -4.27914 0.69274 0.08557	
C -3.07942 1.40766 0.17237	
Н -3.0876 -2.48357 -0.30161	
Н -5.22095 -1.22527 -0.15107	
Н -5.22095 1.22527 0.15108	
Н -3.0876 2.48356 0.30161	
N -0.56215 1.14335 0.13288	
N -0.56215 -1.14335 -0.13289	
B 0.30552 0. 0.	
C 1.86989 0. 0.	
C 2.60141 -0.81323 0.88381	
C 2.60141 0.81323 -0.88381	
C 3.9952 -0.81304 0.88893	
Н 2.07346 -1.44725 1.58929	
C 3.9952 0.81304 -0.88893	
Н 2.07345 1.44725 -1.58929	
C 4.69662 0. 0.	
Н 4.53364 -1.44531 1.58672	
Н 4.53364 1.44531 -1.58672	
Н 5.78107 0. 0.	
C -0.2349 2.53774 0.36639	
Н 0.84534 2.64534 0.45344	
Н -0.5833 3.17272 -0.45577	
Н -0.69298 2.89768 1.29388	
C -0.2349 -2.53774 -0.36638	
Н 0.84534 -2.64534 -0.45348	
Н -0.58326 -3.1727 0.45581	
Н -0.69301 -2.8977 -1.29385	
Item Value Threshold Converged?	
Maximum Force 0.000020 0.000450 YES	
RMS Force 0.000005 0.000300 YES	
Maximum Displacement 0.001463 0.001800 YES	
RMS Displacement 0.000412 0.001200 YES	
Predicted change in Energy=-4.001790D-09	
Optimization completed.	
Stationary point found.	
Full mass-weighted force constant matrix:	
Low frequencies1.5876 -0.0008 -0.0004 0.0002 3.9680 9.302	7
Low frequencies 48.7105 48.9709 70.5935	
- Thermochemistry -	
Zero-point correction= 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 Energie	es= -676.951137

### 7. Dioxaborole (4.7)

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DOB at 100 C in DMSO

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Symbolic Z-matrix:

Charge =	0 Multiplicity = $1$
С	

С	1	B1							
С	2	B2	1	А	1				
С	3	B3	2	A	2	1	D	1	0
С	4	B4	3	A.	3	2	Dź	2	0
С	1	B5	2	A	4	3	D.	3	0
Н	3	B6	2	Α	5	1	D4	4	0
Н	4	<b>B</b> 7	3	А	6	2	D	5	0
Н	5	B8	4	A	7	3	D	6	0
Н	6	B9	1	Α	8	2	Ď	7	0
0	1	B10	6	A	.9	5	D	8	0
0	2	B11	1	A	.10	1	1	D9	0
В	11	B12	1	A	<b>\</b> 11	6	]	D10	0
С	13	B13	1	1.	A12		1	D11	0
С	14	B14	1	3.	A13	•	11	D12	2 0
С	14	B15	1	3.	A14		11	D13	<b>6</b> 0
С	15	B16	14	4	A15		13	D14	0
Н	15	B17	1	4	A16		13	D15	5 0
С	16	B18	14	4.	A17	•	13	D16	5 0
Н	16	B19	1	4	A18		13	D17	7 0
С	19	B20	1	6.	A19		14	D18	<b>3</b> 0

Н	17 B21	15 A20	14 D19
Η	19 B22	16 A21	14 D20
Η	21 B23	19 A22	16 D21
Variable	s:		
B1	1.39339	)	
B2	1.38138	3	
B3	1.40103	3	
B4	1.39722	2	
B5	1.38138	3	
B6	1.08262	2	
B7	1.08356	5	
B8	1.08356	5	
B9	1.08262	2	
B10	1.3778		
B11	1.3778		
B12	1.3941	5	
B13	1.5391		
B14	1.4055	4	
B15	1.4055	4	
B16	1.3917	9	
B17	1.0845	6	
B18	1.3917	9	
B19	1.0845	6	
B20	1.3950	4	
B21	1.0843	6	
B22	1.0843	6	
B23	1.0846		
A1	122.0226	57	
A2	116.5476	55	
A3	121.4296	58	
A4	122.0226	5	
A5	121.4349	)	
A6	119.1395	58	
A7	119.4307	78	
A8	121.4347	77	
A9	128.9760	)3	
A10	109.001	38	
A11	105.763	37	
A12	124.764	82	
A13	120.818	71	
A14	120.819	07	
A15	120.870	75	
A16	119.381	18	
A17	120.870	8	
A18	119.381	27	
A19	119.932	5	

A20	120.05506
A21	120.05484
A22	119.98449
D1	0.
D2	0.
D3	0.
D4	180.
D5	180.
D6	180.
D7	180.
D8	180.
D9	0.
D10	180.
D11	180.
D12	180.
D13	0.
D14	180.
D15	0.
D16	180.
D17	0.
D18	0.
D19	180.
D20	180.
D21	180.
Item	Value Threshold Converged?
Maximum	Force 0.000221 0.000450 YES
RMS F	orce 0.000050 0.000300 YES
Maximum	Displacement 0.000318 0.001800 YES
RMS D	1splacement 0.000082 0.001200 YES
Predicted	change in Energy=-7.254503D-08
Optimizat	ion completed.
Statio	nary point found.
Full mass-	weighted force constant matrix: 142657 + 42641 + 20764 + 0.0005 + 0.0004 + 0.0009
Low frequ	lencies14.365/ -4.3641 -3.9/64 -0.0005 0.0004 0.0008
Low frequ	lencies 40.6555 54.0435 /9.4335
Thormo	
- 1110111100	inclinisti y -
Zero-noint	correction= 0 183462 (Hartree/Particle)
Thermal c	correction to Energy= $0.200353$
Thermal c	correction to Enthalpy $0.200555$
Thermal c	correction to Gibbs Free Energy= 0.132159
Sum of el	ectronic and zero-point Energies= -638 093701
Sum of el	ectronic and thermal Energies= -638.076810
Sum of el	ectronic and thermal Enthalpies= -638.075628
Sum of el	ectronic and thermal Free Energies= -638.145005

## 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 f=(solvent=dmso) geom=connectivity int=grid=ultrafine temperature=373.15

\_\_\_\_\_

#### OAB 100 C DMSO

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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			
Н -3.24272 2.46511 0.			
Н -5.28532 1.04973 -0.00001			
Н -5.12188 -1.41062 0.			
Н -2.88528 -2.53539 0.00001			
Н -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.			
Н 2.11879 2.18593 -0.00001			
C 3.86753 -1.26367 0.			
Н 1.8929 -2.10714 -0.00002			
C 4.62566 -0.0931 0.00001			
Н 4.57238 2.05951 0.00001			
Н 4.36132 -2.22922 0.			
Н 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			
Item Value Threshold Converged?			
Maximum Force 0.000025 0.000450 YES			
RMS Force 0.000005 0.000300 YES			
Maximum Displacement 0.000777 0.001800 YES			

RMS Displacement 0.000335 YES 0.001200 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 0.0007 Low frequencies --- 17.0728 54.9876 84.1848 \_\_\_\_\_ - Thermochemistry -\_\_\_\_\_ Zero-point correction= 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= -618.208389 Sum of electronic and thermal Energies= -618.191061 Sum of electronic and thermal Enthalpies= -618.189879 Sum of electronic and thermal Free Energies= -618.260893

### VITA

EDUCATION		
Master of Science in	Chemistry	Aug 2015-Aug 2017
Sam Houston State U	niversity	
Thesis title	Thesis title DIAZABOROLES: EXPERIMENTAL INVESTIGATIONS OF	
	THEIR DYNAMIC COVALENT	NATURE AND
	COMPUTATIONAL CHEMISTR	Y
GPA	4.00 / 4.00	

Bachelor of Science (Joint Major) in Chemistry and PhysicsSep 2007-June 2012Rajarata University of Sri LankaGPA3.62 (First Class)

# ACADEMIC RESEARCH EXPERIENCE

#### Presentations

<u>Abeysinghe, J. P.</u>; Gross, D. E. Experimental and Computational studies of Diazaborole. *Texas Academy of Science*, 120<sup>th</sup> Annual Meeting, University of Mary Hardin-Baylor, Belton, TX, March 3, 2017.

<u>Abeysinghe, J. P.</u>; 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.

- 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

July 2011-July 2012

Rajarata University of Sri Lanka

- Designed a **Dye Sensitized Solar Cell** by using mesoscopic TiO<sub>2</sub> 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 TiO<sub>2</sub> 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**

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**

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**

Ultracarb, Haycarb PLC, Madampe, Sri Lanka.

Ultracarb is a very special and separate section in Haycarb. Ultracarb is produced very pure (Na,K,Fe<20ppm), small size ( $\mu$ 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

Sep 2015 - Apr 2017

Mar 2012-May 2012

Aug 2012-Aug 2014

Aug 2014-Aug 2015

# 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