Ab Initio Search for Novel BxHy Building Blocks with Potential for Hydrogen Storage

Jared K. Olson
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AB INITIO SEARCH FOR NOVEL BₓHᵧ BUILDING BLOCKS WITH POTENTIAL FOR HYDROGEN STORAGE

by

Jared K. Olson

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry
(Physical Chemistry)

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2010
ABSTRACT

*Ab Initio* Search for Novel BₓHₙ Building Blocks with Potential for Hydrogen Storage

by

Jared K. Olson, Doctor of Philosophy

Utah State University, 2010

Major Professor: Dr. Alexander I. Boldyrev
Department: Chemistry and Biochemistry

On-board hydrogen storage presents a challenging barrier to the use of hydrogen as an energy source because the performance of current storage materials falls short of platform requirements. Because boron is one of the lightest chemical elements that can form strong covalent bonds with hydrogen, it provides an excellent opportunity to design new lightweight materials on the basis of novel boron hydride building blocks. Realizing this potential requires an understanding of the electronic structure, chemical bonding, and stability of neutral and anionic BₓHₙ clusters with variable stoichiometry. While a large number of boron hydride compounds are known, there are still entire classes of yet unknown neutral and anionic BₓHₙ clusters and molecules with various new x/y ratios which may be good candidates for hydrogen storage or as intermediates of borane dehydrogenation. The primary aim of this dissertation was to search for neutral and anionic BₓHₙ clusters that are thermochemically stable towards hydrogen release and to understand the chemical bonding in these novel clusters. These goals were accomplished
by performing an unbiased search for neutral and anionic global minimum B_xH_y clusters using *ab initio* methods.

In addition to finding a rich variety of new neutral and anionic B_xH_y (x = 3 – 6 and y = 4 – 7) clusters that could be building blocks for novel hydrogen-boron materials during the course of conducting this research, optical isomerism was discovered in select neutral and anionic boron-hydride clusters. Furthermore, the transition from planar to 3-dimensional geometries in global minimum B_6H_x^- clusters was discovered using *ab initio* techniques during this study. Chemical bonding analysis using the AdNDP method was performed for all global minimum structures and low-lying isomers. The chemical bonding pattern recovered by the AdNDP method in all cases is consistent with the geometric structure. The theoretical vertical detachment energies presented in this dissertation may help interpret future photoelectron spectroscopic studies of the anions presented here.

(106 pages)
DEDICATION

To Shirlene, Olivia, and Aidan.
ACKNOWLEDGMENTS

I express my sincere gratitude to my advisor, Professor Alexander I. Boldyrev, for all I have learned from him throughout my tenure as a graduate student at Utah State University. He helped me greatly to develop my skills in quantum chemistry, to master the methodology of successful research, and to gain a deep appreciation for the tenacity required to perform such research.

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Jared K. Olson
CONTENTS

Page

ABSTRACT ....................................................................................................................... iii

DEDICATION ..................................................................................................................... v

ACKNOWLEDGMENTS ................................................................................................. vi

LIST OF TABLES ............................................................................................................... x

LIST OF FIGURES ........................................................................................................... xi

CHAPTER

1. INTRODUCTION ................................................................................................. 1

1-1. Background .............................................................................................. 1
1-2. Specific Goals ........................................................................................ 1
1-3. Motivation ............................................................................................... 2
1-4. Relevant Prior Work ............................................................................... 2
1-5. Theoretical Methods ............................................................................ 6
1-6. References ............................................................................................. 9

2. AB INITIO SEARCH FOR GLOBAL MINIMUM STRUCTURES
OF THE NOVEL B₃HY (Y=4-7) NEUTRAL AND ANIONIC
CLUSTERS ........................................................................................................ 17

Abstract ............................................................................................................. 17

2-1. Introduction ........................................................................................... 17
2-2. Computational Details .......................................................................... 20
2-3. Computational Results ......................................................................... 22
2-4. Chemical Bonding in B₃Hₓ and B₃Hₓ⁻ (x=4-7) Species ...................... 26
2-5. Conclusions .......................................................................................... 34
2-6. References ............................................................................................. 34

3. AB INITIO SEARCH FOR GLOBAL MINIMUM STRUCTURES
OF NEUTRAL AND ANIONIC B₄H₄ CLUSTERS .................................................. 40

Abstract ............................................................................................................. 40

3-1. Introduction ........................................................................................... 40
3-2. Computational Details .......................................................................... 41
3-3. Results and Discussion ....................................................................... 43
3-4. Summary and Conclusions ................................................................. 50
### 4. AB INITIO SEARCH FOR GLOBAL MINIMUM STRUCTURES OF NEUTRAL AND ANIONIC B₄H₅ CLUSTERS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>57</td>
</tr>
<tr>
<td>4-1. Computational Details</td>
<td>57</td>
</tr>
<tr>
<td>4-2. Results and Discussion</td>
<td>58</td>
</tr>
<tr>
<td>4-3. Conclusions</td>
<td>64</td>
</tr>
<tr>
<td>4-4. References</td>
<td>65</td>
</tr>
</tbody>
</table>

### 5. AB INITIO DISCOVERY OF THE PLANAR TO 3-DIMENSIONAL TRANSITION IN B₆Hₓ⁻ CLUSTERS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>68</td>
</tr>
<tr>
<td>5-1. Computational Details</td>
<td>69</td>
</tr>
<tr>
<td>5-2. Results and Discussion</td>
<td>70</td>
</tr>
<tr>
<td>5-3. Conclusions</td>
<td>77</td>
</tr>
<tr>
<td>5-4. References</td>
<td>78</td>
</tr>
</tbody>
</table>

### 6. SUMMARY

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-1. Summary</td>
<td>81</td>
</tr>
<tr>
<td>6-2. References</td>
<td>83</td>
</tr>
</tbody>
</table>

### APPENDIX

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDIX</td>
<td>84</td>
</tr>
</tbody>
</table>

### CURRICULUM VITAE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CURRICULUM VITAE</td>
<td>91</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1. Spectroscopic states, electronic configurations, and relative energies of each isomer for each of the neutral B$_3$H$_y$ and anionic B$_3$H$_y^-$ ($y=4-7$) species</td>
<td>25</td>
</tr>
<tr>
<td>2-2. Stability of B$_3$H$_y$ and B$_3$H$_y^-$ ($y=5-7$) species towards H$_2$ release</td>
<td>27</td>
</tr>
<tr>
<td>2-3. Bonds recovered by the AdNDP analysis for the selected isomers of B$_3^-$ and B$_3$H$_4^-$</td>
<td>28</td>
</tr>
<tr>
<td>2-4. Bonds recovered by the AdNDP analysis for the selected isomers of B$_3$H$_5$ and B$_3$H$_5^-$</td>
<td>29</td>
</tr>
<tr>
<td>2-5. Bonds recovered by the AdNDP analysis for the selected isomers of B$_3$H$_6$</td>
<td>30</td>
</tr>
<tr>
<td>2-6. Bonds recovered by the AdNDP analysis for the selected isomers of B$_3$H$_6^-$</td>
<td>31</td>
</tr>
<tr>
<td>2-7. Bonds recovered by the AdNDP analysis for the selected isomers of B$_3$H$_7$ and B$_3$H$_7^-$</td>
<td>32</td>
</tr>
<tr>
<td>3-1. Theoretical Photoelectron Spectrum for structures IV and V of B$_4$H$_4^-$</td>
<td>45</td>
</tr>
<tr>
<td>4-1. Theoretical Photoelectron Spectrum for structure IX of B$_4$H$_5^-$</td>
<td>61</td>
</tr>
<tr>
<td>5-1. Theoretical Photoelectron Spectrum for isomers of B$_x$H$_x^-$</td>
<td>72</td>
</tr>
<tr>
<td>6-1. Stability of B$_x$H$_y$ and B$_x$H$_y^-$ ($x=3, 4, 6; y=2-7$) species towards H$_2$ release</td>
<td>82</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1. Schematic view of a laser vaporization magnetic-bottled PES apparatus</td>
<td>5</td>
</tr>
<tr>
<td>1-2. Logic flow diagram for <em>ab initio</em> study methodology</td>
<td>7</td>
</tr>
<tr>
<td>1-3. Logic flow diagram for the GEGA algorithm</td>
<td>8</td>
</tr>
<tr>
<td>1-4. Logic flow diagram for the Coalescence Kick program</td>
<td>8</td>
</tr>
<tr>
<td>2-1. The lowest energy isomers for neutral $\text{B}_3\text{H}_y$ and anionic $\text{B}_3\text{H}_y^-$ ($y=4-5$) species</td>
<td>23</td>
</tr>
<tr>
<td>2-2. The lowest energy isomers for neutral $\text{B}_3\text{H}_y$ and anionic $\text{B}_3\text{H}_y^-$ ($y=6-7$) species</td>
<td>24</td>
</tr>
<tr>
<td>3-1. Lowest isomers for $\text{B}_4\text{H}_4$ and $\text{B}_4\text{H}_4^-$ with their symmetry, spectroscopic state and relative energies at the CCSD(T) infinite basis set extrapolation in the square brackets, at the CCSD(T)/6-311++G** in curly brackets, at the MP2/6-311++G** in parentheses, otherwise at B3LYP/6-311++G**</td>
<td>44</td>
</tr>
<tr>
<td>3-2. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4$ isomer I</td>
<td>47</td>
</tr>
<tr>
<td>3-3. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4$ isomer I</td>
<td>47</td>
</tr>
<tr>
<td>3-4. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4$ isomer III</td>
<td>47</td>
</tr>
<tr>
<td>3-5. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4^-$ isomer IV. AdNDP analysis was performed for the doubly charged anion $\text{B}_4\text{H}_4^{2-}$ at the optimal geometry of isomers IV of $\text{B}_4\text{H}_4^-$</td>
<td>49</td>
</tr>
<tr>
<td>3-6. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4^-$ isomer V. AdNDP analysis was performed for the doubly charged anion $\text{B}_4\text{H}_4^{2-}$ at the optimal geometry of isomers V of $\text{B}_4\text{H}_4^-$</td>
<td>49</td>
</tr>
<tr>
<td>4-1. Lowest isomers for $\text{B}_4\text{H}_5$ with their symmetry, spectroscopic state and relative energies at the B3LYP/6-311++G** level of theory</td>
<td>59</td>
</tr>
<tr>
<td>4-2. Lowest isomers for $\text{B}_4\text{H}_5^-$ with their symmetry, spectroscopic state and relative energies at the at B3LYP/6-311++G** level of theory</td>
<td>60</td>
</tr>
</tbody>
</table>
4-3. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_5$ isomer I. AdNDP analysis was performed for the $\text{B}_4\text{H}_5^-$ anion at the optimal geometry of isomer I of $\text{B}_4\text{H}_5$ ..........62

4-4. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_5$ isomer III. AdNDP analysis was performed for the $\text{B}_4\text{H}_5^-$ anion at the optimal geometry of isomer I of $\text{B}_4\text{H}_5$ .................................................................63

4-5. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_5$ isomer IX ..............................64

5-1. Lowest isomers for $\text{B}_6\text{H}_2^-$ with their symmetry, spectroscopic state and relative energies at the CCSD(T) infinite basis set extrapolation in curly brackets, at the CCSD(T)/6-311++G** in parentheses, otherwise at B3LYP/6-311++G** ..........70

5-2. Lowest isomers for $\text{B}_6\text{H}_3^-$ with their symmetry, spectroscopic state and relative energies at the B3LYP/6-311+G** level of theory .............................................71

5-3. Lowest isomers for $\text{B}_6\text{H}_4^-$ with their symmetry, spectroscopic state and relative energies at the CCSD(T)/6-311G++** level of theory in parenthesis, otherwise at the B3LYP/6-311++G** level of theory .............................................................71

5-4. Bonds recovered by the AdNDP analysis for $\text{B}_6\text{H}_2^-$ isomer I. AdNDP analysis was performed for the doubly charged $\text{B}_6\text{H}_2^-$ anion at the optimal geometry of isomer I of $\text{B}_6\text{H}_2^-$ ..............................................................................73

5-5. Bonds recovered by the AdNDP analysis for $\text{B}_6\text{H}_3^-$ isomer III ..............................74

5-6. Bonds recovered by the AdNDP analysis for $\text{B}_6\text{H}_3^-$ isomer V ..............................75

5-7. Bonds recovered by the AdNDP analysis for $\text{B}_6\text{H}_4^-$ isomer VIII. AdNDP analysis was performed for the doubly charged $\text{B}_6\text{H}_4^-$ anion at the optimal geometry of isomer VIII of $\text{B}_6\text{H}_4^-$ ..............................................................................76
CHAPTER 1
INTRODUCTION

1-1. Background

Boron is the lightest atom that can form strong covalent bonds with hydrogen and thus provides excellent opportunities to design new light-weight materials on the basis of $\text{B}_x\text{H}_y$ clusters with a potential for high hydrogen storage capacity needed for transportation applications. In order to realize this possibility, one needs to first understand the electronic structure, chemical bonding, and stability of the $\text{B}_x\text{H}_y$ clusters. Borohydride compounds such as $\text{LiBH}_4$, $\text{NH}_4\text{BH}_4(\text{NH}_2)_3$, $\text{NH}_4\text{BH}_4$ and $\text{NH}_3\text{BH}_3$ have been extensively studied with regard to their potential hydrogen storage properties. Boron and hydrogen also form a wide variety of three-dimensional compounds such as the famous closo-boranons and their numerous derivatives with a lesser degree of hydrogenation than the borohydrides mentioned above. Even though a large number of boron-hydrogen compounds are known, there are still entire classes of yet unknown $\text{B}_x\text{H}_y$ clusters and molecules with various new $x/y$ ratios which may be good candidates for hydrogen storage.

1-2. Specific Goals

The major goals of this dissertation were to provide a fundamental understanding of the structures and chemical bonding in $\text{B}_x\text{H}_y^{0-1}$ clusters and to discover new borohydride-based chemical building blocks for potential hydrogen storage materials. These
goals were accomplished through the theoretical study of neutral and anionic $\text{B}_x\text{H}_y$ clusters with systematically varied stoichiometries for $x = 3, 4,$ and $6$ and $y = 4 – 7$.

1-3. Motivation


On-board hydrogen storage is considered to be one of the most challenging barriers to the widespread use of hydrogen because the performance of current hydrogen storage materials and technologies fall far short of vehicle requirements. Research is needed to develop and examine new materials and obtain an atomic- and molecular-level understanding of the physical and chemical processes involved in hydrogen storage and release. These novel storage materials may fall outside of the hydrogen-storage materials that are currently under investigation. \(^8\)

Other systems such as ammonia-borane or metal hydrides do not meet the DOE’s goals, so the motivation of this dissertation was to discover new boron-hydride compounds or building blocks which are different from known compounds based on $\text{BH}_3$, $\text{BH}_4^-$ or $\text{B}_n\text{H}_m^{2-}$ species that may be useful for hydrogen storage and release and may be attractive because of the light weights and high hydrogen storage capacities of boron-hydrogen systems. This motivation led to the generating a large number of clusters from which hydrogen release energies could be calculated, chemical bonding could be studied, and meaningful conclusions could be drawn about the potential for some of these clusters to be used for hydrogen storage.

1-4. Relevant Prior Work

Very limited works on new $\text{B}_x\text{H}_y$ structural units have been carried out previously. In 2003, Boldyrev and co-workers predicted theoretically a new family of planar
aromatic and highly charged boranes,\(^9,10\) such as \(\text{B}_6\text{H}_6^{6-}\) stabilized by six \(\text{Li}^{+}\) cations. An extended analysis of the chemical bonding in the lowest energy planar and non-planar isomers involving \(\text{B}_6\text{H}_6^{6-}\) has been performed.\(^9,10\) The planar \(\text{B}_6\text{H}_6^{6-}\) species can be viewed as a benzene analog. Boron possesses one less valence electron than carbon. Thus, a \(\text{B}^-\) anion becomes isoelectronic to a \(\text{C}\) atom, which underlies the graphite-like network of \(\text{B}\) in \(\text{MgB}_2\) and the benzene-like properties of \(\text{B}_6\text{H}_6^{6-}\). Salts like \(\text{Li}_6\text{B}_6\text{H}_6\) with the \(\text{B}_6\text{H}_6^{6-}\) benzene-like unit remain a theoretical prediction. Fehlner and co-workers\(^{11-13}\) have reported synthesis and crystal structures of two remarkable triple-deck \((\text{Cp}^*\text{ReH}_2)\text{B}_5\text{Cl}_5\) and \((\text{Cp}^*)_2\text{B}_6\text{H}_4\text{Cl}_2\) compounds containing planar \(\text{B}_5\text{Cl}_5\) and \(\text{B}_6\text{H}_4\text{Cl}_2\) structural fragments, respectively. It is believed that the planar \(\text{B}_5\text{Cl}_5\) and \(\text{B}_6\text{H}_4\text{Cl}_2\) structural fragments in Fehlner’s compounds acquire six electrons from the \(\text{Re}\) atom formally and thus become six \(\pi\)-electron aromatic compounds similar to the predicted \(\text{B}_5\text{H}_5^{6-}\) and \(\text{B}_6\text{H}_6^{6-}\) building blocks in the \(\text{Li}_6\text{B}_5\text{H}_5\) and \(\text{Li}_6\text{B}_6\text{H}_6\) salt molecules. Fehlner and co-workers also reported synthesis and characterization of a variety of new compounds containing novel structural groups such as \(\text{B}_3\text{H}_7\),\(^{11}\) \(\text{B}_4\text{H}_7\) and \(\text{B}_4\text{H}_8\),\(^{12}\) and \(\text{B}_4\text{H}_{11}\),\(^{13}\) with highly unusual \(\text{B}:\text{H}\) stoichiometries, thus showing that there are indeed still many new undiscovered structural units with almost continuous \(\text{B}:\text{H}\) ratios.

There have been few prior experimental studies on \(\text{B}_x\text{H}_y^{\text{0-1}}\) type clusters in the gas phase with the only relevant work being done by Anderson and co-workers, who studied the dynamics of \(\text{B}_x^{+}\) cluster \((x = 1 – 16)\) reactions with \(\text{D}_2\).\(^{14}\) They observed the formation of \(\text{B}_x\text{D}^+\) and \(\text{D}_2\) adducts, \(\text{B}_x^+\) (\(\text{D}_2\)), and estimated the \(\text{B}_x^+–\text{D}\) bond energies. This work stimulated a theoretical study by Ricca and Bauschlicher, who calculated the structures of \(\text{B}_x\text{H}^+\) \((x = 1 – 13)\) and the \(\text{H}_x^+–\text{D}\) bond energies.\(^{15}\) They found that the
structures of the $B_xH^+$ clusters are similar to the bare $B_x^+$ clusters with the H atom bonded to the edge of planar or quasi-planar $B_x^+$ clusters.

Extensive experimental work has been performed to validate other systems that were predicted using methods similar to those used in this dissertation and laser vaporization/photoelectron spectroscopy (PES). A schematic diagram of a laser vaporization magnetic-bottled PES apparatus is included as Figure 1-1 for reference. Briefly, anionic clusters can be produced by laser vaporization of target materials of interest in the presence of a helium carrier gas containing H$_2$. Clusters are formed via the reaction of the gas and the target material in a laser-induced plasma. Clusters formed in the nozzle (see Figure 1-1) are entrained in the helium carrier gas, which undergoes a supersonic expansion to form a cluster beam. After passing a skimmer to form a collimated beam, negatively charged clusters are extracted perpendicularly into a time-of-flight mass spectrometer for mass separation. Clusters of interest can be selected via a mass gate and decelerated before being crossed by a laser beam in the interaction zone of the magnetic-bottle PES spectrometer for photodetachment. Photoemitted electrons are collected by the magnetic bottle where time-of-flight spectra are collected and converted into kinetic energy (KE) spectra. The electron binding energy (BE) spectra are obtained by subtracting the KE spectra from the photon energy ($h\nu$) using Einstein’s photoelectric equation: $BE = h\nu – KE$. 
Figure 1-1. Schematic view of a laser vaporization magnetic-bottled PES apparatus.

Using theoretical methods similar to those used in this dissertation and laser vaporization/(PES) method described above, the Boldyrev and Wang groups experimentally produced and confirmed the first 5-atom tetra-coordinated planar carbon molecules,\textsuperscript{16-18} discovered the first all-metal aromatic and antiaromatic clusters,\textsuperscript{19-24} and elucidated the structures and chemical bonding of boron clusters.\textsuperscript{25-34} Recent success in generating a series of Al\textsubscript{x}H\textsubscript{y} clusters in a molecular beam and obtaining their photoelectron spectra by Bowen and co-workers\textsuperscript{35-40} opens a possibility of making B\textsubscript{x}H\textsubscript{y} under similar conditions. Experimental studies on the decomposition of LiBH\textsubscript{4} and Mg(BH\textsubscript{4})\textsubscript{2} by Orimo and co-workers\textsuperscript{41-44} and Her and co-workers\textsuperscript{44} have produced the stable B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-} cluster. An understanding of the methods used in references 41-44 could lead to synthetic methods for producing the borohydrides presented here in bulk quantities.
1-5. Theoretical Methods

A logic flow diagram for the *ab initio* study methodology employed here is included as Figure 1-2. For each given neutral or anionic BxHy species, an unbiased search was performed for the global minima of that species using the hybrid density functional method known as B3LYP\(^{45-47}\) with small split-valence basis sets (3-21G) for energy, gradient, and force calculations. Geometries were then re-optimized and frequencies were calculated for the lowest energy structures using B3LYP with polarized split-valence basis sets (6-311++G**)\(^{48-50}\). Following this re-optimization, for the few lowest structures found at the B3LYP/6-311++G** level of theory, we re-optimized geometries and calculated harmonic frequencies at the second order Moller-Plesset perturbation theory (MP2)\(^{51-53}\) and coupled-cluster with single, double, and non-iterative triple excitations method [CCSD(T)]\(^{54-56}\) using the 6-311++G** basis set for both calculations. A detailed discussion of these methods can be found in references 57-61. Energies of these lowest energy isomers were also recalculated by extrapolating to the infinite basis set at the CCSD(T) level of theory as proposed by Truhlar and co-workers.\(^{62-63}\) Following these energy calculations, chemical bonding was analyzed for all global minimum and low lying isomers, and vertical detachment energies were calculated for the lowest isomers. All *ab initio* calculations were performed using the Gaussian 03 package.\(^{64}\) Molecular visualization was performed using the MOLDEN3.4 program,\(^{65}\) and chemical bonding visualization was completed using the MOLEKEL 4.3 program.\(^{66}\)

The gradient embedded genetic algorithm (GEGA) program written by A. N. Alexandrova\(^{67,68}\) and the coalescence kick (CK) program written by B. B. Averkiev\(^{69,70}\)
were used to conduct the unbiased search for global minimum structures. Logic flow diagrams for these methods are included as Figures 1-3 and 1-4.

Chemical bonding analysis for structures studied in this dissertation was completed using the Adaptive Natural Density Partitioning (AdNDP) method developed by Zubarev and Boldyrev. The AdNDP analysis is based on the concept of electron pairs as the main elements of chemical bonding, is an extension of NBO analysis, and provides is unbiased as no preliminary concept of the bonding pattern is required to perform the analysis. Where NBO represents electronic structure in terms of 2-center-2-electron (2c-2e) and 3-center-3-electron (3c-2e) bonds, AdNDP represents the electronic structure in terms of n-center–two-electron (nc-2e) bonds with n ranging from one to the total number of atoms in the whole cluster. AdNDP recovers both Lewis bonding elements (1c-2e or 2c-2e objects, i.e., lone pairs or two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity.

![Logic flow diagram for ab initio study methodology.](image)

**Figure 1-2.** Logic flow diagram for *ab initio* study methodology.
Figure 1-3. Logic flow diagram for the GEGA algorithm.

Figure 1-4. Logic flow diagram for the Coalescence Kick program
Chapter 2 presents \( B_3H_x \) and \( B_3H_x^- \) (\( x = 4-7 \)) structures identified using the GEGA algorithm, discusses their stability towards hydrogen release, and discusses chemical bonding in these structures by discussing bonds recovered by AdNDP analysis.

Chapter 3 presents the global and lowest local minimum structures for neutral and anionic \( B_4H_4 \) identified using the Coalescence Kick method. Bonds recovered by AdNDP analysis are discussed, and theoretical VDEs are presented with the goal of helping to interpret future photoelectron spectroscopic studies of the \( B_4H_4^- \) anion.

Chapter 4 presents similar data for neutral and anionic \( B_4H_5 \) clusters identified using the Coalescence Kick method.

Chapter 5 presents the discovery of the 2D-3D transition in \( B_6H_x^- \) clusters identified using the Coalescence Kick method, discusses chemical bonding through bonds recovered by AdNDP analysis, presents theoretical VDEs to help interpret future photoelectron spectroscopic studies of the \( B_6H_x^- \) clusters, and discloses the theoretical discovery of optical isomerism in these inorganic clusters.

1-6. References


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CHAPTER 2

AB INITIO SEARCH FOR GLOBAL MINIMUM STRUCTURES OF THE NOVEL B3HY (Y=4-7) NEUTRAL AND ANIONIC CLUSTERS*

Abstract

We sampled potential energy surfaces of neutral and anionic B₃H₄ clusters using the Gradient Embedded Genetic Algorithm (GEGA) program at the B3LYP/3-21G level of theory. The lowest energy isomers were recalculated at the B3LYP/6-311++G**, MP2/6-311++G**, and CCSD(T)/6-311++G** levels of theory. We found a diverse set of global minimum structures and low-lying isomers for the studied clusters. The Adaptive Natural Density Partitioning (AdNDP) method was then used for chemical bonding analysis for all global minimum structures and low-lying isomers. The chemical bonding patterns revealed by the AdNDP analysis can easily explain the geometric structure of even very exotic isomers and global minima.

2-1. Introduction

Boron is one of the lightest chemical elements that can form strong covalent bonds with hydrogen, and thus provides excellent opportunities to design new lightweight materials on the basis of novel boron hydride building blocks, in the form of B₃H₄⁰/n+/n⁻ clusters with a potential for high hydrogen storage capacity. To realize this potential requires an understanding of the electronic structure, chemical bonding, and stability of the B₃H₄⁰/n+/n⁻ clusters with variable stoichiometry. Boron hydride

compounds such as LiBH$_4$, Li$_4$BH$_4$(NH$_2$)$_3$, NH$_4$BH$_4$, NH$_3$BH$_3$, NH$_2$BH$_2$, and NH$_3$B$_3$H$_7$
have been studied extensively with regard to their potential hydrogen storage
properties.$^{1-11}$ Boron and hydrogen also form a wide variety of three-dimensional
compounds such as the well known deltahedral boranes and their numerous derivatives
with a lesser degree of hydrogenation than the above mentioned borohydrides.$^{12-16}$ While
a large number of boron hydride compounds are known, there are still entire classes of
yet unknown B$_x$H$_y$$^{0/n+/n–}$ clusters and molecules with various new $x/y$ ratios which may be
good candidates for hydrogen storage or as intermediates of borane de-hydrogenation.

Very limited work on new B$_x$H$_y$ structural units has been carried out previously.
Fehlner and co-workers$^{17-19}$ have reported synthesis and crystal structures of two
remarkable triple-deck (Cp*ReH$_2$)B$_5$Cl$_5$ and (Cp*)$_2$B$_6$H$_4$Cl$_2$ compounds containing
planar B$_5$Cl$_5$ and B$_6$H$_4$Cl$_2$ structural fragments, respectively. It is believed that the planar
B$_5$Cl$_5$ and B$_6$H$_4$Cl$_2$ structural fragments in Fehlner’s compounds acquire six electrons
from the Re atom formally and thus become six p-electron aromatic compounds similar
to the predicted B$_5$H$_5$$^6–$ and B$_6$H$_6$$^6–$ building blocks in the Li$_6$B$_5$H$_5$ and Li$_6$B$_6$H$_6$ salt
molecules.$^{20,21}$ Fehlner and co-workers also reported the synthesis and characterization
of a variety of new compounds containing novel structural groups such as B$_3$H$_7$,$^{17}$ B$_4$H$_7$
and B$_6$H$_8$,$^{18}$ and B$_4$H$_{11},^{19}$ with highly unusual B:H stoichiometries. Surprisingly, there
have been few prior experimental works on B$_x$H$_y$$^{0/n+/n–}$ type clusters in the gas phase. To
the best of our knowledge, the only relevant work is by Anderson et al., who studied the
dynamics of B$_x^+$ cluster ($x = 1–16$) reactions with D$_2$.$^{22}$ Among the various reaction
channels, they observed the formation of B$_x$D$^+$ and D$_2$ adducts, B$_x^–$(D$_2$), and estimated
the B$_x^+$–D bond energies. Interactions of the B$_3$ cluster with H atoms and H$_2$ molecules
have been studied by Hernandez and Simons.\textsuperscript{23} This work stimulated a theoretical study by Ricca and Bauschlicher, who calculated the structures of $\text{B}_x\text{H}^+$ ($x = 1\text{–}13$) and the $\text{B}_x^+\text{H}$ bond energies.\textsuperscript{24} Interestingly, they found that the structures of the $\text{B}_x\text{H}^+$ clusters are similar to the bare $\text{B}_x^+$ clusters with the $\text{H}$ atom bonded to the edge of planar or quasi-planar $\text{B}_x^+$ clusters. Alexandrova et al.\textsuperscript{25} performed a global minimum structure search and rationalized chemical bonding in terms of aromaticity/antiaromaticity in the $\text{B}_7\text{H}_2^-$ cluster anion. Alexandrova et al.\textsuperscript{26} also studied series of boron-hydrogen anions analogous to planar aromatic hydrocarbons. A few groups have previously studied the $\text{B}_3\text{H}_7$ cluster.\textsuperscript{27-30} Five different isomers were found in early theoretical studies with geometry optimization at the Hartree-Fock level with small basis sets.\textsuperscript{27} In follow up studies,\textsuperscript{28-30} high-level calculations were performed for one,\textsuperscript{28} two,\textsuperscript{29} or three\textsuperscript{30} isomers of $\text{B}_3\text{H}_7$.

There are still many new undiscovered structural units with almost continuous B:H ratios. The non-stoichiometric and non-conventional boron hydride clusters with three boron atoms and variable number of hydrogen atoms $\text{B}_3\text{H}_y^{0/-1}$ will be the main focus of the research presented in this paper. Counter cations may affect the relative stability of the corresponding anionic $\text{B}_3\text{H}_y^-$ isomers. In this article, however, we will concentrate on the intrinsic properties of these anions free of such influence. We believe that understanding the structure, stability and bonding of bare $\text{B}_3\text{H}_y^-$ anions is an important first step in predicting novel boron-hydrogen species. We plan to study the influence on $\text{B}_3\text{H}_y^-$ from counter cations in our future works.
2-2. Computational Details

We initially performed searches for the global minimum of B₃Hₓ and B₃Hₓ⁻ (y=4-7) using our gradient embedded genetic algorithm (GEGA) program written by A. N. Alexandrova.³¹,³² Briefly, within the GEGA procedure, the initial geometries of individuals in a population are randomly generated and optimized to the nearest local minima on the potential energy surface using the Gaussian 03 package. If a saddle point is encountered, the normal mode of the first imaginary frequency is followed until a local minimum is found. Further, the population, composed of the thus selected good individuals, undergoes breeding and mutations. Probabilities to be bred are assigned according to the best-fit (lowest-energy) criterion. Based on the probabilities, couples of parents are randomly selected. The geometries of parents are cut by a random cutting plane, and the newly obtained halves (genes) are then recombined either in a simple or head-to-tail manner forming a child. The number of atoms in the newly generated geometry is checked, and the child is optimized to the nearest local minimum. After the number of individuals in the population is doubled within the breeding process, the best-fit group is selected and convergence of the algorithm is checked. GEGA is considered as converged if the current lowest energy species (global minimum or at least very stable local minimum) remains leading for 20 iterations. If the convergence is not yet met, the highest energy species in the population undergo mutations. The mutation rate is set to 33.33%. Mutations are shifts of random atoms of a species in random directions, with the purpose of changing the initial geometry so as to push the structure out of the current local minimum to another well on the potential energy surface. Mutants are then optimized to the nearest local minima. After this optimization, the algorithm proceeds
with the new cycle of breeding. All low-lying isomers are detected and stored throughout
the execution of the GEGA algorithm and are reported to the user at the end of the run. A
few runs of GEGA are done on the system of interest in order to confirm the global
minimum structure which is discovered. A more complete description of the GEGA
algorithm is contained in reference 31.

For the global minimum search, we used a hybrid method known as B3LYP\textsuperscript{33-35}
with small split-valence basis sets (3-21G) for energy, gradient, and force calculations.
Geometries were then re-optimized and frequencies were calculated for the lowest energy
structures using B3LYP with polarized split-valence basis sets (6-311++G**).\textsuperscript{36-38}
Following this re-optimization, for the few lowest structures found at the
B3LYP/6-311++G** level of theory, we re-optimized geometries and calculated
harmonic frequencies at the second order Moller-Plesset perturbation theory (MP2)\textsuperscript{39-41}
and coupled-cluster with single, double, and non-iterative triple excitations method
[CCSD(T)]\textsuperscript{42-44} using the 6-311++G** basis set for both calculations. Relative energies
reported in this work were corrected for zero-point energies (ZPE) at the corresponding
level of theory.

To understand the relationship between chemical bonding and structure in
B\textsubscript{3}H\textsubscript{y}\textsuperscript{0-1} clusters, we performed chemical bonding analysis for the lowest energy isomers
using the recently developed Adaptive Natural Density Partitioning (AdNDP)
method.\textsuperscript{45-47} AdNDP performs analysis of the first-order reduced density matrix with the
purpose of obtaining its local block eigenfunctions with optimal convergence properties
for describing the electron density. The local blocks of the first-order reduced density
matrix correspond to the sets of \( n \) atoms (from one to all the atoms of the molecule) that
are tested for the presence of a two-electron object (nc-2e bonds, including core electrons and lone pairs as a special case of \( n=1 \)) associated with this particular set of \( n \) atoms. The \( n \)-atomic sets are formed and checked in an exhaustive manner, so that the recovered \( nc-2e \) bonding elements always correspond to the point-group symmetry of the system after these bonding elements are superimposed onto the molecular frame. For the given \( n \)-atomic block those eigenvectors are accepted whose occupation numbers (eigenvalues) exceed the established threshold value, usually close to 2.00 |e|. Thus Lewis's idea of an electronic pair as the essential element of bonding is preserved. The AdNDP procedure is numerically efficient since it involves only a series of diagonalizations of density matrix blocks. It is unbiased in the sense that no preliminary ideas of the bonding pattern are required to perform the analysis.

The B3LYP, R(U)MP2, R(U)CCSD(T) calculations were performed using the Gaussian 03 program. Molecular visualization was performed using the MOLDEN3.4 program, and molecular orbital visualization was completed using the MOLEKEL 4.3 program.

2-3. Computational Results

We initially performed GEGA searches for the global minimum of the neutral \( \text{B}_3\text{H}_y \) and anionic \( \text{B}_3\text{H}_y^- \) (\( y=4-7 \)) isomers at the B3LYP/3-21G level of theory. The lowest energy isomers were then recalculated at the B3LYP/6-311++G**, MP2/6-311++G**, and CCSD(T)/6-311++G** levels of theory. Figures 2-1 and 2-2 show the lowest energy structures identified in our scanning of the potential energy surfaces for the neutral \( \text{B}_3\text{H}_y \) and anionic \( \text{B}_3\text{H}_y^- \) (\( y=4-7 \)) species.
**Figure 2-1.** The lowest energy isomers for neutral B$_3$H$_y$ and anionic B$_3$H$_y^-$ (y=4-5) species.
**Figure 2-2.** The lowest energy isomers for neutral B$_3$H$_y$ and anionic B$_3$H$_y^-$ (y=6-7) species.
The corresponding spectroscopic states, electronic configurations, and relative energies of each isomer (at the B3LYP/6-311++G**, MP2/6-311++G**, and CCSD(T)/6-311++G** levels of theory) for each of the neutral $\text{B}_3\text{H}_y$ and anionic $\text{B}_3\text{H}_y^-$ ($y=4-7$) species are summarized in Table 2-1.

### Table 2-1. Spectroscopic states, electronic configurations, and relative energies of each isomer for each of the neutral $\text{B}_3\text{H}_y$ and anionic $\text{B}_3\text{H}_y^-$ ($y=4-7$) species.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Isomer</th>
<th>State</th>
<th>Relative Energy$^1$</th>
<th>B3LYP$^2$</th>
<th>MP2$^2$</th>
<th>CCSD(T)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_3\text{H}_4$</td>
<td>I</td>
<td>C$_{2v}$, 2B$_2$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>D$_{2h}$, 2B$_2$1a$_g$2b$_2$1b$_1$2b$_1$2a$_g$4b$_u$1b$_u$</td>
<td>7.9</td>
<td>16.7</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_4^-$</td>
<td>III</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2b$_2$1b$_1$2b$_2$4a$_u$1b$_1$</td>
<td>2.0</td>
<td>2.3</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>D$_{2h}$, 1A$_u$, 2a$_g$1b$_2$1a$_g$2b$_2$1b$_1$2b$_1$2b$_u$</td>
<td>6.4</td>
<td>17.6</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_4$</td>
<td>VI</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VII</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0.4</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VIII</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2b$_2$1b$_1$2b$_2$1a$_g$2a$_u$1b$_1$</td>
<td>14.1</td>
<td>23.3</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IX</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>18.9</td>
<td>23.0</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2b$_2$1b$_1$2b$_2$1a$_g$2a$_u$1b$_1$2b$_2$</td>
<td>27.3</td>
<td>29.9</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_5$</td>
<td>XI</td>
<td>C$_{2v}$, 2A$_u$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XII</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>6.5</td>
<td>7.0</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XIII</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>8.9</td>
<td>6.8</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_5$</td>
<td>XIV</td>
<td>C$_{2v}$, 2B$_2$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XV</td>
<td>C$_{2v}$, 2B$_2$, 1a$_g$2b$_2$1b$_1$2b$_2$1a$_g$2a$_u$1b$_1$2b$_2$</td>
<td>3.7</td>
<td>1.2</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_6$</td>
<td>XVI</td>
<td>C$_{1v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XVII</td>
<td>D$<em>{2h}$, 1A$</em>{ig}$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>-0.2</td>
<td>6.7</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_6^-$</td>
<td>XVIII</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XIX</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>1.8</td>
<td>3.7</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XX</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>6.8</td>
<td>9.1</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_7$</td>
<td>XXI</td>
<td>C$_{2v}$, 2B$_2$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XXII</td>
<td>C$_{2v}$, 1A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>21.7</td>
<td>24.3</td>
<td>30.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XXIII</td>
<td>C$_{2v}$, 2A$_1$, 1a$_g$2a$_u$1b$_2$2a$_g$4a$_u$1b$_1$2b$_2$</td>
<td>25.9</td>
<td>28.6</td>
<td>30.4</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ Relative energy was corrected by zero-point vibrational energies at the corresponding level of theory.

$^2$ Calculations were performed with the 6-311++G** basis set.
From our calculations we found that isomers with the lowest possible multiplicities were found to be the lowest energy states for all clusters studied here. Several of the neutral \( \text{B}_3\text{H}_y \) and anionic \( \text{B}_3\text{H}_y^- \) \((y=4-7)\) species have two or more structures competing for the global minimum isomer. The low-lying isomers were found to be structures with the triangular and linear core \( \text{B}_3 \) units. There is no clear pattern why for some species, isomers with the triangular \( \text{B}_3 \) core are more stable, while for others isomers with the linear \( \text{B}_3 \) core are more stable. Previously reported results\(^{27-30}\) on \( \text{B}_3\text{H}_7 \) clusters showing that isomer XVIII is the most stable structure with isomers XIX and XX being the second and third most stable structures are in excellent agreement with our results.

Table 2-2 summarizes the dissociation energies for \( \text{B}_3\text{H}_y \) and \( \text{B}_3\text{H}_y^- \) \((y=5-7)\) species for \( \text{H}_2 \) release. All of the \( \text{B}_3\text{H}_y \) and \( \text{B}_3\text{H}_y^- \) \((y=5-7)\) species, except for the \( \text{B}_3\text{H}_5^- \), are thermochemically stable towards spontaneous hydrogen release.

### 2-4. Chemical Bonding in \( \text{B}_3\text{H}_x \) and \( \text{B}_3\text{H}_x^- \) \((x=4-7)\) Species

In order to facilitate the understanding between bonding and structure for \( \text{B}_3\text{H}_y \) and \( \text{B}_3\text{H}_y^- \) \((y=4-7)\) species we performed chemical bonding analysis for the lowest isomers of each species using our newly developed AdNDP analysis. We briefly discussed this method in the Computational Details. A more extensive discussion on this method and its application to boron clusters, aromatic organic molecules and golden clusters can be found in references 45-48. The bonding pattern recovered in a particular chemical species by the AdNDP analysis depends on how close the recovered bonds are to the ideal \( 2.00 \, |e| \) the occupation numbers (ON). Therefore we report ON for a
particular bond for each isomer discussed in this section. We found that in all isomers ONs are indeed very close to the ideal values, thus providing us with confidence in our chemical bonding pattern. The results of the AdNDP analysis, including pictorial representations of the recovered “bond,” are presented and summarized in Tables 2-3 through 2-7.

Table 2-2. Stability of $\text{B}_3\text{H}_y$ and $\text{B}_3\text{H}_y^-$ ($y=5-7$) species towards $\text{H}_2$ release.

<table>
<thead>
<tr>
<th>Dissociation channel</th>
<th>Dissociation energy$^{1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_3\text{H}<em>5$ VI ($C</em>{2v}$, $^1A_1$) $\rightarrow$ $\text{B}_3\text{H}<em>4$ I ($C</em>{2v}$, $^2B_2$) $+ 1/2\text{H}_2$</td>
<td>+ 31.2 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>5^-$ XI ($C</em>{3v}$, $^2A''$) $\rightarrow$ $\text{B}_3\text{H}<em>4^-$ III ($C</em>{2v}$, $^1A_1$) $+ 1/2\text{H}_2$</td>
<td>- 6.5 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>6$ XIV ($C</em>{2v}$, $^2B_2$) $\rightarrow$ $\text{B}_3\text{H}<em>5$ VI ($C</em>{2v}$, $^1A_1$) $+ 1/2\text{H}_2$</td>
<td>- 15.6 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>6$ XIV ($C</em>{2v}$, $^2B_2$) $\rightarrow$ $\text{B}_3\text{H}<em>4$ I ($C</em>{2v}$, $^2B_2$) $+ \text{H}_2$</td>
<td>+ 15.6 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_6^-$ XVI ($C_1$, $^1A$) $\rightarrow$ $\text{B}_3\text{H}<em>5^-$ XI ($C</em>{3v}$, $^2A''$) $+ 1/2\text{H}_2$</td>
<td>+ 25.8 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}_6^-$ XVI ($C_1$, $^1A$) $\rightarrow$ $\text{B}_3\text{H}<em>4^-$ III ($C</em>{2v}$, $^1A_1$) $+ \text{H}_2$</td>
<td>+ 19.3 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>7$ XVIII ($C</em>{3v}$, $^1A'$) $\rightarrow$ $\text{B}_3\text{H}<em>6$ XIV ($C</em>{2v}$, $^2B_2$) $+ 1/2\text{H}_2$</td>
<td>+ 34.3 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>7$ XVIII ($C</em>{3v}$, $^1A'$) $\rightarrow$ $\text{B}_3\text{H}<em>5$ VI ($C</em>{2v}$, $^1A_1$) $+ \text{H}_2$</td>
<td>+ 18.7 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>7^-$ XXI ($C</em>{2v}$, $^2B_2$) $\rightarrow$ $\text{B}_3\text{H}_6^-$ XVI ($C_1$, $^1A$) $+ 1/2\text{H}_2$</td>
<td>+ 11.2 kcal/mol</td>
</tr>
<tr>
<td>$\text{B}_3\text{H}<em>7^-$ XXI ($C</em>{2v}$, $^2B_2$) $\rightarrow$ $\text{B}_3\text{H}<em>5^-$ XI ($C</em>{3v}$, $^2A''$) $+ \text{H}_2$</td>
<td>+ 37.0 kcal/mol</td>
</tr>
</tbody>
</table>

$^{1)}$ $\Delta E$ calculated at the CCSD(T)/6-311++G**+ZPE/CCSD(T)/6-311++G** level of theory.
Table 2-3. Bonds recovered by the AdNDP analysis for the selected isomers of $\text{B}_3^-$ and $\text{B}_3\text{H}_4^-$.

| Cluster, Isomer | Structure | Occupation Number ( |e| ) |
|-----------------|-----------|-------------------|
| $\text{B}_3^-$ | ![Structure](image) | (B1–B2)=2.00  
(B1–B3)=2.00  
(B2–B3)=2.00  
(B1–B2–B3)=2.00  
(B1–B2–B3)=2.00 |
| $\text{B}_3\text{H}_4^-$, III | ![Structure](image) | (B3–H5)=1.98  
(B1–H2)=1.99  
(B4–H6)=1.99  
(B1–B3)=1.89  
(B1–B4)=1.89  
(B3–B4–H7)=2.00  
(B1–B3–B4)=1.96 |

Bonding in the bare $\text{B}_3^-$ cluster was studied previously,\textsuperscript{45,51-53} and it was shown that this cluster has three 2c-2e σ-B-B bonds, one 3c-2e σ-bond and one 3c-2e π-bonds. Thus, this cluster is a doubly (σ- and π-) aromatic system. This double aromaticity explains its high symmetry cyclic structure and high atomization energy. The addition of four hydrogen atoms to $\text{B}_3^-$ results in the global minimum structure III of the $\text{B}_3\text{H}_4^-$ anion.
Table 2-4. Bonds recovered by the AdNDP analysis for the selected isomers of $B_3H_5$ and $B_3H_5^-$. 

| Cluster, Isomer | Structure | Occupation Number (|e|) |
|-----------------|-----------|--------------------------|
| $B_3H_5$, VI    |           | (B4–H8)=1.97             |
|                 |           | (B1–H2)=1.97             |
|                 |           | (B3–H7)=1.97             |
|                 |           | (B1–B4–H6)=1.99          |
|                 |           | (B1–B3–H5)=1.99          |
|                 |           | (B1–B3–B4)=1.88          |
|                 |           | (B1–B3–B4)=2.00          |
| $B_3H_5$, VII   |           | (B2–H7)=2.00             |
|                 |           | (B2–H8)=2.00             |
|                 |           | (B3–H5)=2.00             |
|                 |           | (B4–H6)=2.00             |
|                 |           | (B2–B3–B4)=1.92          |
|                 |           | (B2–B3–B4)=1.99          |
|                 |           | (B3–B4–H1)=2.00          |
| $B_3H_5^{-1}$, XI | | (B1–B2)=2.00 |
|                 |           | (B1–B3)=2.00             |
|                 |           | (B1–B2)=1.96             |
|                 |           | (B2–H5)=1.97             |
|                 |           | (B2–H4)=1.97             |
|                 |           | (B3–H6)=1.97             |
|                 |           | (B3–H7)=1.97             |
|                 |           | (B3–H8)=1.97             |

1) The AdNDP analysis for this isomer was performed for the doubly charged anion by adding one extra electron to the singly occupied MO (SOMO).
Table 2-5. Bonds recovered by the AdNDP analysis for the selected isomers of B\textsubscript{3}H\textsubscript{6}.

| Cluster, Isomer | Structure | Occupation Number ( |e| ) |
|-----------------|-----------|-------------------|
| B\textsubscript{3}H\textsubscript{6}, XIV | ![Structure](image) | (B1–B4)=1.93 (B1–B5)=1.93 (B4–H7)=1.97 (B1–H2)=1.97 (B5–H9)=1.97 (B4–H6)=1.97 (B5–H8)=1.97 (B4–B5–H3)=1.97 |

The AdNDP analysis for this isomer was performed for the anionic state by adding one extra electron to the SOMO.

According to the AdNDP analysis the global minimum structure of B\textsubscript{3}H\textsubscript{4} has three 2c-2e σ-B-H bonds, one 3c-2e BHB σ-bond, two 2c-2e σ-B-B bonds and one 3c-2e π-bond. Thus, this anion is only a π-aromatic system. Compared to the B\textsubscript{3} \textsuperscript{−} anion, in the B\textsubscript{3}H\textsubscript{4} \textsuperscript{−} anion, the addition of four hydrogen atoms led to the formation of three new B-H σ-bonds, the substitution of a 3c-2e BHB bridged σ-bond for a 2c-2e B-B σ-bond, and the removal of the delocalized 3c-2e BBB σ-bond responsible for aromaticity of B\textsubscript{3} \textsuperscript{−}.
Table 2-6. Bonds recovered by the AdNDP analysis for the selected isomers of B₃H₆⁻.

| Cluster, Isomer | Structure | Occupation Number (|e|) |
|-----------------|-----------|---------------------|
| B₃H₆⁻, XVI     | ![Structure](image1) | (B2–B3)=1.99  
(B3–H6)=1.98  
(B3–H4)=1.98  
(B1–H7)=1.98  
(B1–H5)=1.98  
(B2–H8)=1.98  
(B1–B2–H9)=1.99  
(B3–B2–B1)=1.94 |
| B₃H₆⁻, XVII    | ![Structure](image2) | (B1–B2)=1.93  
(B1–B3)=1.93  
(B2–H6)=2.00  
(B2–H4)=2.00  
(B2–H5)=2.00  
(B3–H8)=2.00  
(B3–H7)=2.00  
(B3–H9)=2.00 |

Addition of a H⁺ to B₃H₄⁻ with the formation of B₃H₅ led to the substitution of one 2c-2e B-B σ-bond by the 3c-2e BHB bridged σ-bond. The B₃H₅ cluster is still a π-aromatic system. The second lowest energy B₃H₅ isomer VI has three 2c-2e B-H σ-bonds, two 3c-2e BHB σ-bonds, one delocalized 3c-2e σ-bond and one delocalized 3c-2e π-bond. Thus, isomer VI regains double (σ- and π-) aromaticity. When an extra electron is added to the B₃H₅ cluster, chemical bonding (performed for the B₃H₅²⁻ dianion at the optimal geometry of the B₃H₅⁻ anion) in the global minimum structure XI of the B₃H₅⁻ species can be rationalized in terms of the classical structure with five 2c-2e B-H bonds, a
single σ-bond between H₃B and the central boron atom, and a double (σ- and π-) bond between the central atom and the BH₂ fragment.

**Table 2-7.** Bonds recovered by the AdNDP analysis for the selected isomers of B₃H₇ and B₃H₇⁻.

| Cluster, Isomer | Structure | Occupation Number (|$|e|\$) |
|-----------------|-----------|----------------------|
| B₃H₇, XVIII     |           | (B₁–B₂–H₅)=2.00      |
|                 |           | (B₁–B₃–H₄)=2.00      |
|                 |           | (B₁–B₂–B₃)=1.90      |
|                 |           | (B₂–H₉)=1.97         |
|                 |           | (B₃–H₈)=1.97         |
|                 |           | (B₂–H₇)=1.97         |
|                 |           | (B₃–H₆)=1.97         |
|                 |           | (B₁–H₁₀)=1.97        |
| B₃H₇, XIX       |           | (B₁–B₂–B₃)=1.96      |
|                 |           | (B₂–B₃–H₁₀)=2.00     |
|                 |           | (B₁–H₅)=1.94         |
|                 |           | (B₁–H₄)=1.94         |
|                 |           | (B₂–H₆)=1.94         |
|                 |           | (B₃–H₈)=1.94         |
|                 |           | (B₂–H₇)=1.94         |
|                 |           | (B₃–H₉)=1.94         |
| B₃H₇⁻, XXI      |           | (B₁–B₂)=1.94         |
|                 |           | (B₁–B₃)=1.94         |
|                 |           | (B₁–H₄)=1.99         |
|                 |           | (B₁–H₅)=1.99         |
|                 |           | (B₂–H₆)=1.99         |
|                 |           | (B₃–H₈)=1.99         |
|                 |           | (B₂–H₇)=1.99         |
|                 |           | (B₃–H₉)=1.99         |
|                 |           | (B₂–B₃–H₁₀)=1.97     |

1) The AdNDP analysis for this isomer was performed for the doubly charged anion by adding one extra electron to the singly occupied MO (SOMO).
The B$_3$H$_6$ cluster has two low-lying isomers XIV and XV. Chemical bonding analysis was performed for the closed shell anionic isomer XIV and XV at the optimal geometries of the neutral clusters. In the global minimum structure XIV, we found five 2c-2e B-H $\sigma$-bonds, two 2c-2e B-B $\sigma$-bonds and one bridged 3c-2e BHB bond. In the second isomer XV we found four 2c-2e B-H $\sigma$-bonds, two 2c-2e B-B $\sigma$-bonds, and two 3c-2e BHB bonds. The transition of one of the terminal hydrogen atoms to a bridged position does not cost much energy, apparently. The two lowest isomers XVI and XVII of the B$_3$H$_6^-$ species are truly remarkable structures. In isomer XVI we found three types on bonding: the 2c-2e B-B $\sigma$-bond between B2 and B3, 3c-2e BHB $\sigma$-bond between B1 and B2, and the 3c-2e $\sigma$-bond responsible for bonding between B1 and B3. That chemical bonding pattern can easily explain the unusual geometric structure of the isomer XVI. The classical type structure of the isomer XVII can also be easily understood from the AdNDP analysis. Two BH$_3$ groups are attached to the central boron atom through two dative 2c-2e B-B $\sigma$-bonds. The two lowest isomers XVIII and XIX of the B$_3$H$_7$ species have similar bonding patterns with the exception that one hydrogen atom migrates from the bridged position in isomer XVII to the terminal position in isomer XVIII. We noticed that such migrations do not cost much energy in the hydrogen-boron clusters discussed here. Finally, in isomer XXI we found that it has two classical 2c-2e B-B sbonds, one 3c-2e BHB bond which keep the boron kernel together, with all other electron pairs used for the 2c-2e B-H $\sigma$-bonds.

The overall chemical bonding patterns revealed by the AdNDP analysis can easily explain the geometric structure of even very exotic isomers and global minima.
2-5. Conclusions

We found global minimum structures and low-lying isomers for a series of B$_3$H$_y$ and B$_3$H$_y^-$ species using the GEGA method. We refined the relative energies at the CCSD(T)/6-311++G** level of theory, and found a very diverse set of structures for global minimum and low-lying isomers of the studied species. All of the B$_3$H$_y$ and B$_3$H$_y^-$ (y=5-7) species, except for the B$_3$H$_5^-$, are thermochemically stable towards hydrogen release. Chemical bonding in the global minimum and low-lying isomers was analyzed using the AdNDP method; from this analysis we found the chemical bonding patterns in all cases were consistent with the geometric structures of the studied clusters.

We hope that predictions made in our work will be tested in follow-up photoelectron studies of the anionic species studied in this work. We also hope that the bonding patterns presented here recovered by the AdNDP analysis will be useful for the future rational design of novel boron-hydrogen compounds. This is our first step in the probing of non-stoichiometric B$_x$H$_y^{n+/0/n-}$ species.

2-6. References


(18) Lei, X.; Shang, M.; Fehlner, T.P. *Organometal.* **2000**, *19*, 118-120.


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CHAPTER 3

*AB INITIO SEARCH FOR GLOBAL MINIMUM STRUCTURES OF NEUTRAL AND ANIONIC B₄H₄ CLUSTERS*

Abstract

Potential energy surfaces of neutral and anionic B₄H₄ clusters were sampled using a coalescence kick method. A diverse set of global minimum structures and low-lying isomers was found for the studied clusters. Theoretical vertical electron detachment energies were calculated for the two lowest isomers of B₄H₄⁻, which could help to assign them in the future experimentally observed photoelectron spectra of the anion. Chemical bonding analysis for the global minimum structures and low-lying isomers of B₄H₄ and B₄H₄⁻ was performed using the Adaptive Natural Density Partitioning method.

3-1. Introduction

Boron hydrides are as diverse as hydrocarbons and they play an important role in advancing chemical bonding in chemistry. [1-7] In particular, the recognition of bridge structure for diborane (B₂H₆) [8,9] led to the introduction of the three center – two electron (3c-2e) bond in chemistry. [10] Another important breakthrough made due to the study of boron hydrides was the introduction of three-dimensional aromaticity [11-13] in order to explain extra stability of deltahedral boranes BₙHₙ²⁻. Longuet-Higgins and Roberts [14] provided molecular orbital arguments for the necessity of two extra

electrons in the deltahedral boranes $B_nH_n^{2-}$. The $B_4H_4$ tetrahedron was found to be a “black sheep” in the $B_nH_n^{2-}$ family, however. While $B_4H_4$ has never been experimentally observed, its $B_4Cl_4$ and $B_4(t-Bu)_4$ derivatives have been synthesized [15-17] and their geometric structure [17,18] was shown to be tetrahedral without two extra electrons. Quantum chemical calculations [19-25] have shown that the lowest unoccupied MO (LUMO) is a doubly degenerate e-MO and thus in order to avoid the Jahn-Teller distortion one needs to add four extra electrons rather than two in the singlet coupling. In 1994, Mavridis and co-workers [26] made an amazing discovery, that the global minimum structure of $B_4H_4$ is not a tetrahedron, but rather planar low-symmetry ($C_3$) structure. In 2007, Guvenc and co-workers [27] confirmed Mavridis and co-workers prediction, that $B_4H_4$ has a planar low-symmetry global minimum.

As mentioned above, there are no experimental data on $B_4H_4$, but recent success in generating in molecular beam a series of $Al_xH_y^-$ clusters and obtaining their photoelectron spectra by Bowen and co-workers [28-33] opens a possibility of making $B_4H_4^-$ under similar conditions. Comparison of the theoretical and experimental photoelectron spectra could provide experimental evidence on the geometric structure of $B_4H_4^-$ and possibly on $B_4H_4$.

3-2. Computational Details

In this article we performed an unbiased search for the global minima of $B_4H_4$ and $B_4H_4^-$ using a Coalescence Kick (CK) method program written in our group by Averkiev [34,35]. The Coalescence Kick method subjects large populations of randomly generated structures to a coalescence procedure with all atoms gradually pushed to the molecular
center of mass to avoid generation of fragmented structures and then optimizes them to the nearest local minima. For the global minimum search, we used a hybrid method known as B3LYP [36-38] with small split-valence basis sets (3-21G) for energy and gradient calculations. Geometries were then re-optimized and frequencies were calculated for the lowest energy structures using B3LYP with polarized split-valence basis sets (6-311++G**). [39-41] Following this re-optimization, for the few lowest structures found at the B3LYP/6-311++G** level of theory, we re-optimized geometries and calculated harmonic frequencies at the second order Moller-Plesset perturbation theory (MP2) [42-44] and coupled-cluster with single, double, and non-iterative triple excitations method [CCSD(T)] [45-47] using the 6-311++G** basis set for both calculations. The B3LYP, MP2, and CCSD(T) calculations were performed using the Gaussian 03. [48] Molecular structure visualization was done using the MOLDEN 3.4 program. [49] Relative energies reported in this work were corrected for zero-point energies (ZPE) at the corresponding level of theory. Energies of these lowest energy isomers were also recalculated by extrapolating to the infinite basis set from correlation–consistent polarized valence double and triple zeta (aug-cc-pvDZ and aug-cc-pvTZ) basis sets [50-54] at the CCSD(T) level of theory as proposed by Truhlar and co-workers. [55,56] Theoretical vertical electron detachment energies (VDEs) were calculated using three levels of theory: CCSD(T)/aug-cc-PVTZ method, the outer valence Green Function method [UOVGF/aug-cc-PVTZ] [57-59] at the CCSD(T)/6-311++G** geometries, and the time-dependent DFT method [TD-B3LYP/aug-cc-PVTZ] [60,61] at the optimized B3LYP/6-311++G** geometries. In the last approach, the first VDE was calculated at the B3LYP level of theory as the lowest transition from the anion into the neutral cluster.
The vertical excitation energies of the neutral species (at the TD-B3LYP level) were then added to the first VDE to obtain the second and higher VDEs. Core electrons were frozen in treating the electron correlation at the RCCSD(T) and ROVGF levels of theory.

3-3. Results and Discussion

Spectroscopic states and relative energies of each isomer of the neutral and anionic B₄H₄ species are included in Figure 3-1.

We confirmed that structure I, previously reported by Mavridis and co-workers [26] and Guvenc and co-workers, [27] is a global minimum for B₄H₄. According to our CCSD(T) extrapolation to the infinite basis set the planar structure I is more stable than tetrahedral structure II by 6.6 kcal/mol (ZPE corrections were used from the CCSD(T)/6-311++G** level of theory). When the geometries of structures with imaginary frequencies identified by Guvenc and co-workers [27] (see B₄H₄ – II (mul1) and B₄H₄ – III (mul1)) are optimized at the higher levels of theory indicated in this paper, the planar structures presented by Guvenc and co-workers converge to structures I or III in Figure 1.

We are not aware of any quantum chemical calculations of B₄H₄⁻. Our CK global minimum search for B₄H₄⁻ revealed that the distorted tetrahedral structure IV is a global minimum at all our levels of theory. The second lowest structure V was found to be 5.0 kcal/mol at the CCSD(T) extrapolating to the infinite basis set. The second isomer can potentially contribute to the photoelectron spectra of B₄H₄⁻.

In order to facilitate photoelectron spectroscopic identification of the B₄H₄⁻ global minimum structure, we calculated theoretical VDEs using three levels of theory:
CCSD(T)/aug-cc-PVTZ method, ROVGF/aug-cc-PVTZ and TD-B3LYP/aug-cc-PVTZ (see Table 3-1).

\[ \text{Figure 3-1. Lowest isomers for } B_4H_4 \text{ and } B_4H_4^- \text{ with their symmetry, spectroscopic state and relative energies at the CCSD(T) infinite basis set extrapolation in the square brackets, at the CCSD(T)/6-311++G** in curly brackets, at the MP2/6-311++G** in parentheses, otherwise at B3LYP/6-311++G**.} \]
Table 3-1. Theoretical Photoelectron Spectrum for structures IV and V of B$_4$H$_4^+$. 

<table>
<thead>
<tr>
<th>Cluster, Isomer</th>
<th>Final State and Electronic Configuration</th>
<th>VDE (theo, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TD-B3LYPa</td>
</tr>
<tr>
<td>B$_4$H$_4^-$</td>
<td>$^1A_1$, $1b_2^22a_1^22e^24b_2^21b_1^0$</td>
<td>2.12</td>
</tr>
<tr>
<td>IV (D$_{2d}$)</td>
<td>$^3A_2$, $1b_2^22a_1^22e^24b_2^21b_1^1$</td>
<td>3.53</td>
</tr>
<tr>
<td></td>
<td>$^1A_2$, $1b_2^22a_1^22e^24b_2^21b_1^1$</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td>$^3E$, $1b_2^22a_1^22e^24b_2^21b_1^1$</td>
<td>4.10</td>
</tr>
<tr>
<td></td>
<td>$^1E$, $1b_2^22a_1^23e^24e^12b_2^21b_1^1$</td>
<td>5.19</td>
</tr>
<tr>
<td>B$_4$H$_4^-$</td>
<td>$^1A$, $3a^24a^25a^26a^27a^28a^29a^0$</td>
<td>2.75</td>
</tr>
<tr>
<td>V (C$_1$)</td>
<td>$^3A$, $3a^24a^25a^26a^27a^28a^29a^110a^0$</td>
<td>3.09</td>
</tr>
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<td></td>
<td>$^1A$, $3a^24a^25a^26a^27a^28a^29a^1$</td>
<td>3.62</td>
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<td>$^3A$, $3a^24a^25a^26a^27a^28a^29a^110a^0$</td>
<td>3.86</td>
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<td>$^1A$, $3a^24a^25a^26a^27a^28a^29a^1$</td>
<td>4.91</td>
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<td>$^3A$, $3a^24a^25a^26a^27a^28a^29a^110a^0$</td>
<td>5.18</td>
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<tr>
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<td>$^3A$, $3a^24a^25a^26a^27a^28a^29a^110a^0$</td>
<td>5.73</td>
</tr>
</tbody>
</table>

a VDEs were calculated at TD-B3LYP/aug-cc-pvTZ//B3LYP/6-311++G**
b VDEs were calculated at CCSD(T)/aug-cc-pvTZ//CCSD(T)/6-311++G**
c VDEs were calculated at OVGF/aug-cc-pvTZ//CCSD(T)/6-311++G**
d VDE cannot be calculated at this level of theory

The two lowest B$_4$H$_4^+$ isomers should be easily recognized in the experimental photoelectron spectra, since isomer IV has the first and second peaks at about 1.9 eV and 3.7 eV, respectively. The second peak should be more intense than the first one because the final state for the first peak is a singlet state and the second final state is a triplet state.

For isomer V, however, the first and the second peaks should be at about 2.7 eV and 3.2 eV, respectively. Again, the second peak should be more intense than the first one, because the final state for the first peak is a singlet state and the second final state is a triplet state. Thus, two much smaller peaks from isomer V could potentially be observed inside of two more prominent peaks from isomer IV since isomer V is about 5.0 kcal/mol
higher in energy than isomer IV. We hope that experimentalists will verify our theoretical prediction. The presence of isomer V in the experimental photoelectron spectra will be a confirmation that the planar isomer I is the global minimum of B₄H₄ since we used the same level of theory for the anion and the neutral species.

We performed chemical bonding analysis for the global minimum structure and two low-lying isomers of B₄H₄ using the Adaptive Natural Density Partitioning (AdNDP) method developed by Zubarev and Boldyrev. [62-64] The AdNDP analysis is based on the concept of electron pairs as the main elements of chemical bonding. It represents the electronic structure in terms of $n$-center–two-electron ($nc$-2e) bonds with $n$ ranging from one to the total number of atoms in the whole cluster. AdNDP recovers both Lewis bonding elements (1c-2e or 2c-2e objects, i.e., lone pairs or two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity. Pictures of bonds recovered by the AdNDP analysis of B₄H₄ were made using the MOLEKEL program [65] and are presented in Figures 3-2, 3-2, and 3-4.

According to the AdNDP analysis, the global minimum structure has three 2c-2e B-H $\sigma$-bonds, one 2c-2e B-B $\sigma$-bond, one 3c-2e B-H-B $\sigma$-bond, two 3c-2e B-B-B $\sigma$-bonds and one 4c-2e delocalized over four boron atoms $\pi$-bond. Calculated occupation numbers (ONs) were found to be very close to the ideal 2.00 $|e|$ number for all recovered bonds (see Figure 3-2). Thus, bonding in the boron framework is $\sigma$-antiaromatic (4 electrons on two delocalized $\sigma$-bonds) and $\pi$-aromatic (2 electrons on one delocalized $\pi$-bond).
Figure 3-2. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4$ isomer I.

Figure 3-3. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4$ isomer II.

Figure 3-4. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4$ isomer III.
This is not the first time a structure with conflicting aromaticity was found to be a global minimum structure. It was previously shown that the B₅⁻ cluster has a global minimum structure with conflicting aromaticity. [66-69] For the second tetrahedral structure II our AdNDP analysis revealed exactly the same chemical bonding pattern as was established by Hall and Lipscomb in 1974, [70] using the Boys localization method. Specifically, we found four 2c-2e B-H σ-bonds and four 3c-2e B-B-B bonds located over each face of the B₄H₄ tetrahedron. While structure III is very similar to the global minimum structure differing only in the location of the bridged atom, the bonding pattern is somewhat different from that of the global minimum structure. Structure III has three 2c-2e B-H σ-bond, two 2c-2e B-B σ-bonds, one 3c-2e B-H-B σ-bond, one 3c-2e B-B-B σ-bond, and one 4c-2e delocalized over a four boron atom π-bond. Thus, compared to the global minimum structure, in isomer III one 3c-2e B-B-B σ-bond is substituted by the 2c-2e B-B σ-bond. This could provide one explanation for why this isomer is less stable than structure I.

In order to obtain a simple chemical bonding picture and avoid complications due to spin-polarization, we performed the AdNDP analysis for doubly charged anions B₄H₄²⁻ (an extra electron was added to the semioccupied HOMO) at the optimized geometry of structures IV and V. Results of our analysis are presented in Figure 3-5 and Figure 3-6.

The addition of an electron pair to the tetrahedral structure B₄H₄ makes a dramatic change in chemical bonding. In the global minimum structure IV we now have four 2c-2e B-B σ-bonds and one 4c-2e bond delocalized over four boron atoms in a π-like bond instead of the four 3c-2e bonds in structure II. In structure V the AdNDP analysis
Figure 3-5. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4^-$ isomer IV. AdNDP analysis was performed for the doubly charged anion $\text{B}_4\text{H}_4^{3-}$ at the optimal geometry of isomer IV of $\text{B}_4\text{H}_4^-$. 

Figure 3-6. Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_4^-$ isomer V. AdNDP analysis was performed for the doubly charged anion $\text{B}_4\text{H}_4^{3-}$ at the optimal geometry of isomer V of $\text{B}_4\text{H}_4^-$. 
revealed four 2c-2e B-H $\sigma$-bonds, two 3c-2e B-B-B $\sigma$-bonds and one 3c-2e B-B-B $\pi$-bond. The chemical bonding patterns revealed by the AdNDP analysis is consistent with the geometric structures of all isomers and global minima presented here, similar to our findings for $B_3H_y$ and $B_3H_y^-$ ($y=4-7$) clusters. [71]

3-4. Summary and Conclusions

In the present work using our unbiased CK search for the global minima we confirmed that $B_4H_4$ has a planar rather than a tetrahedral global minimum structure in agreement with previously reported results by Mavridis and co-workers [26] and Guvenc and co-workers.[27] We predicted the global minimum structure for the $B_4H_4^-$ anion, which is a distorted tetrahedral structure, and calculated its VDEs. We believe our VDEs can help interpret future photoelectron spectroscopic study of this anion. Our chemical bonding analysis using the AdNDP method revealed a chemical bonding picture which includes multicenter bonding and are consistent with the geometric structure of all isomers studied here.

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CHAPTER 4

AB INITIO SEARCH FOR GLOBAL MINIMUM STRUCTURES OF NEUTRAL AND ANIONIC B₄H₅ CLUSTERS

Abstract

Potential energy surfaces of neutral and anionic B₄H₅ clusters were sampled using the Coalescence Kick (CK) method at the B3LYP/3-21G level of theory. The lowest energy isomers were recalculated at the B3LYP/6-311++G** and CCSD(T)/6-311++G** levels of theory. The Adaptive Natural Density Partitioning (AdNDP) method was used for chemical bonding analysis for all global minimum structures and low-lying isomers. The chemical bonding patterns revealed by the AdNDP analysis can easily explain the geometric structure of even very exotic isomers and global minima. Theoretical Vertical Detachment Energies (VDEs) were calculated for comparison with future experimental work.

4-1. Computational Details

An unbiased search for the global minimum structures of B₄H₅ and B₄H₅⁻ was conducted using the Coalescence Kick method as described in Chapter 3. For the global minimum search, the hybrid method known as B3LYP¹⁻³ was used with small split-valence basis sets (3-21G) for energy, gradient, and force calculations. Geometries were re-optimized and frequencies were calculated for the lowest energy structures using B3LYP with polarized split-valence basis sets (6-311++G**).⁴⁻⁶ Following this re-optimization, for the few lowest structures found at the B3LYP/6-311++G** level of theory, geometries were re-optimized and harmonic frequencies were calculated at the
coupled-cluster level of theory with single, double, and non-iterative triple excitations method [CCSD(T)]\textsuperscript{7-9} using the 6-311++G** basis set calculations. Relative energies reported in this chapter were corrected for zero-point energies (ZPE) at the corresponding level of theory. Energies of these lowest energy isomers were recalculated by extrapolating to the infinite basis set as described in Chapter 3, and theoretical vertical electron detachment energies (VDEs) were calculated using the outer valence Green Function method and the time-dependent DFT method also as described in Chapter 3. Energy and frequency calculations were performed using the Gaussian 03 program.\textsuperscript{10} Molecular visualization was performed using the MOLDEN3.4 program,\textsuperscript{11} and molecular orbital and chemical bonding visualization was completed using the MOLEKEL 4.3 program.\textsuperscript{12}

4-2. Results and Discussion

Spectroscopic states and relative energies of each isomer of the neutral B\textsubscript{4}H\textsubscript{5} species are included in Figure 4-1. Spectroscopic states and relative energies of each isomer of the anionic B\textsubscript{4}H\textsubscript{5}\textsuperscript{-} species are included in Figure 4-2.

While the optical isomerism appearing in the global minima (and other low lying isomers) for the neutral B\textsubscript{4}H\textsubscript{5} species is interesting, currently available experimental methods can not be used to observe the neutral species. The presence of isomer IX in the experimental photoelectron spectra may be a confirmation that isomer I and its optical isomer are the global minimum of B\textsubscript{4}H\textsubscript{5}, however, since the same level of theory was used for the anion and the neutral species.
Figure 4-1. Lowest isomers for B₄H₅ with their symmetry, spectroscopic state and relative energies at the B3LYP/6-311++G** level of theory.
**Figure 4-2.** Lowest isomers for B$_4$H$_5^-$ with their symmetry, spectroscopic state and relative energies at the B3LYP/6-311++G** level of theory.
In order to facilitate photoelectron spectroscopic identification of the B₄H₅⁻ global minimum structure, theoretical VDEs were calculated as described in Chapter 3. Theoretical VDEs are contained in Table 4-1.

**Table 4-1.** Theoretical Photoelectron Spectrum for structure IX of B₄H₅⁻.

<table>
<thead>
<tr>
<th>Cluster, Isomer</th>
<th>Final State and Electronic Configuration</th>
<th>VDE (theo, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₄H₅⁻ IX (C₅)</td>
<td>²A', 1a''(2)2a''(2)3a''(2)4a''(2)5a''(2)1a''(1)6a''(1)2a''(2)7a''(2)</td>
<td>3.2 3.0 (0.91)</td>
</tr>
<tr>
<td></td>
<td>²A'', 1a''(2)2a''(2)3a''(2)4a''(2)5a''(2)1a''(1)6a''(1)2a''(2)7a''(2)</td>
<td>3.4 3.2 (0.90)</td>
</tr>
<tr>
<td></td>
<td>²A', 1a''(2)2a''(2)3a''(2)4a''(2)5a''(2)1a''(1)6a''(1)2a''(2)7a''(2)</td>
<td>5.2 5.4 (0.88)</td>
</tr>
<tr>
<td></td>
<td>²A'', 1a''(2)2a''(2)3a''(2)4a''(2)5a''(2)1a''(1)6a''(1)2a''(2)7a''(2)</td>
<td>6.5 7.5 (0.89)</td>
</tr>
</tbody>
</table>

a VDEs were calculated at TD-B3LYP/aug-cc-pvTZ//B3LYP/6-311++G**
b VDEs were calculated at OVGF/aug-cc-pvTZ//CCSD(T)/6-311++G**

The lowest B₄H₅⁻ isomer should be observed in the experimental photoelectron spectra, with first and second peaks at about 3.2 eV and 3.4 eV, respectively, for isomer IX. The large gap between the second and third VDEs in these calculations can be used as a signature of isomer IX of B₄H₅⁻ in future PES experiments.

Chemical bonding analysis was performed for the global minimum structure and one low-lying isomer of B₄H₅ and the global minimum B₄H₅⁻ structure using the Adaptive Natural Density Partitioning (AdNDP) method. In all three isomers, Occupation Numbers (ONs) are very close to the ideal values; this provides confidence in the chemical bonding pattern presented here. In order to obtain a simple chemical bonding picture for the B₄H₅ structures and avoid complications due to spin-polarization, AdNDP analysis was performed for B₄H₅⁻ anions (an extra electron was added to the semioccupied HOMO) at the optimized geometry of structures I and III. Results of the analysis are presented in Figures 4-3, 4-4, and 4-5.
According to the AdNDP analysis, the global minimum structure (see Figure 4-3) has four 2c-2e B-H σ-bonds ($|e| = 1.98$–$1.99$), one 3c-2e B-H-B σ-bond ($|e| = 1.99$), three 2c-2e B-B-B σ-bonds ($|e| = 1.71$–$1.88$), and one 4c-2e delocalized over four boron atoms π-bond ($|e| = 1.98$). AdNDP analysis of the low-lying isomer III (see Figure 4-4) reveals five 2c-2e B-H σ-bonds ($|e| = 1.93$–$1.99$), two 2c-2e B-B σ-bonds ($|e| = 1.91$), one 3c-2e B-H-B σ-bond ($|e| = 1.95$), and one 4c-2e delocalized over four boron atoms π-bond ($|e| = 2.00$).

**Figure 4-3.** Bonds recovered by the AdNDP analysis for $\text{B}_4\text{H}_5$ isomer I. AdNDP analysis was performed for the $\text{B}_4\text{H}_5^-$ anion at the optimal geometry of isomer I of $\text{B}_4\text{H}_5$. 
AdNDP analysis of the global minimum $B_4H_5^-$ isomer IX reveals four 2c-2e B-H σ-bonds ($|e| = 1.95 - 1.99$), one 3c-2e B-H-B σ-bond ($|e| = 2.00$), one 2c-2e B-B σ-bonds ($|e| = 1.95$), one 3c-2e B-B-B σ-bond ($|e| = 1.94$), one 3c-2e B-B-B π-bond ($|e| = 1.96$), and one 4c-2e delocalized over four boron atoms σ-bond ($|e| = 1.96$).

For $B_4H_5$ and $B_4H_5^-$ we found that the chemical bonding consists of 2c-2e and 3c-2e B-H and B-H-B bonds, 2c-2e, 3c-2e and 4c-2e B-B, B-B-B, and four center BBBB bonds. Two-center and three-center bonds are typical for borohydrides. The four-center two-electron BBBB bonds identified in this research are reported for only the second time,
Figure 4-5. Bonds recovered by the AdNDP analysis for B₄H₅ isomer IX.

with the first being our B₄H₄/B₄H₄⁻ paper¹⁶ included as Chapter 3. The chemical bonding patterns revealed by the AdNDP analysis are consistent with the geometric structures of all isomers and global minima presented here, similar to findings presented elsewhere in this dissertation.

4-3. Conclusions

Global minimum structures and low-lying isomers were found for a series of B₄H₅ and B₄H₅⁻ species using the CK method. Relative energies were refined at the CCSD(T)/6-311++G** level of theory and extrapolated to the infinite basis set.

Chemical bonding in the global minimum and low-lying isomers was analyzed using the AdNDP method; from this analysis it was found that the chemical bonding
patterns in all cases were consistent with the geometric structures of the studied clusters. In addition to two-center two-electron and three-center two-electron bonds typical for borohydrides, we identified four-center two-electron bonds in B₄H₅ and B₄H₅⁻, which are reported for only the second time, with the first being our B₄H₄/B₄H₄⁻ paper included as Chapter 3.

The global minimum structure for the B₄H₅⁻ anion was predicted, and its VDEs were calculated. The VDEs can help interpret future photoelectron spectroscopic study of this anion.

4-4. References


CHAPTER 5

AB INITIO DISCOVERY OF THE PLANAR TO 3-DIMENSIONAL TRANSITION IN B₆Hₓ⁻ CLUSTERS

Abstract

In the B₆Hₓ⁻ (x = 6 – 12) clusters, there exist a known series of stable deltahedral boranes, BₙHₙ⁻ (n = 6 – 12). It was expected that the singly charged BₙHₙ⁻ species should also possess 3D structures,¹ which may be distorted relative to the doubly charged parents due to the Jahn-Teller effect. Pure boron clusters in this size range are all planar, however. Previous calculations by Ricca and Bauschlicher on BₓH⁺ indicate that the H atom bonds to the peripheral of the planar Bₓ⁺ clusters.² This raises an interesting question regarding the 2D to 3D transition as a function of y for a given x for each BₓHₓ⁻ series. This is an important issue because this transition would suggest a major structural change as a function of de-hydrogenation for the stoichiometric BₙHₙ⁻ polyhedral boranes, and has been studied on other systems.³-⁶

To search for this transition in B₆Hₓ⁻ clusters, potential energy surfaces of anionic B₆Hₓ⁻ (x = 2 – 4) clusters were sampled using the Coalescence Kick (CK) method at the B3LYP/3-21G level of theory. The lowest energy isomers were recalculated at the B3LYP/6-311++G** and CCSD(T)/6-311++G** levels of theory. The Adaptive Natural Density Partitioning (AdNDP) method was used for chemical bonding analysis for all global minimum structures and low-lying isomers. The chemical bonding patterns revealed by the AdNDP analysis can easily explain the geometric structure of even very
exotic isomers and global minima. Theoretical Vertical Detachment Energies (VDEs) were calculated for comparison with future experimental work.

5-1. Computational Details

An unbiased search for the global minimum B₆Hₓ⁻ structures of was conducted using the Coalescence Kick method as described in Chapter 3. For the global minimum search, the hybrid method known as B3LYP was used with small split-valence basis sets (3-21G) for energy, gradient, and force calculations. Geometries were re-optimized and frequencies were calculated for the lowest energy structures using B3LYP with polarized split-valence basis sets (6-311++G**). Following this re-optimization, for the few lowest structures found at the B3LYP/6-311++G** level of theory, geometries were re-optimized and harmonic frequencies were calculated at the coupled-cluster level of theory with single, double, and non-iterative triple excitations method [CCSD(T)] using the 6-311++G** basis set calculations. Relative energies reported in this chapter were corrected for zero-point energies (ZPE) at the corresponding level of theory. Energies of these lowest energy isomers were recalculated by extrapolating to the infinite basis set as described in Chapter 3, and theoretical vertical electron detachment energies (VDEs) were calculated using the outer valence Green Function method and the time-dependent DFT method also as described in Chapter 3. Energy and frequency calculations were performed using the Gaussian 03 program. Molecular visualization was performed using the MOLDEN3.4 program, and molecular orbital and chemical bonding visualization was completed using the MOLEKEL 4.3 program.
5-2. Results and Discussion

The 2D-3D transition in B₆Hₓ⁻ occurs when x = 4. Another interesting result is the presence of quasi-planar optical isomers as the global minima when x = 3. Spectroscopic states and relative energies of each global minimum and low lying isomer of the B₆Hₓ⁻ (x = 2 – 4) species are included in Figures 5-1, 5-2, and 5-3.

In order to facilitate photoelectron spectroscopic identification of the B₆Hₓ⁻ global minimum structures, theoretical VDEs were calculated as described in Chapter 3. Theoretical VDEs are contained in Table 5-1.

![B₆H₂⁻](image)

**Figure 5-1.** Lowest isomers for B₆Hₓ⁻ with their symmetry, spectroscopic state and relative energies at the CCSD(T) infinite basis set extrapolation in curly brackets, at the CCSD(T)/6-311++G** in parentheses, otherwise at B3LYP/6-311++G**.
**Figure 5-2.** Lowest isomers for $\text{B}_6\text{H}_3^-$ with their symmetry, spectroscopic state and relative energies at the B3LYP/6-311++G** level of theory.

**Figure 5-3.** Lowest isomers for $\text{B}_6\text{H}_4^-$ with their symmetry, spectroscopic state and relative energies at the CCSD(T)/6-311G++** level of theory in parenthesis, otherwise at the B3LYP/6-311++G** level of theory.
Table 5-1. Theoretical Photoelectron Spectrum for isomers of B₆Hₓ⁻.

<table>
<thead>
<tr>
<th>Cluster, Isomer</th>
<th>Final State and Electronic Configuration</th>
<th>VDE (theo, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TD-B3LYPa</td>
</tr>
<tr>
<td>B₆H₂⁻ I (C₂h)</td>
<td>1A₁g, 1a₁g 1b₁u 2a₂g 2b₂u 3b₂u 3a₂g 1a₄u 2a₄g 2b₄u 3a₄g 5a₂g 1b₂g</td>
<td>2.8</td>
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<tr>
<td></td>
<td>1B₂g, 1a₁g 1b₁u 2a₂g 2b₂u 3b₂u 3a₂g 1a₄u 2a₄g 2b₄u 3a₄g 5a₂g 1b₂g</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>3A₈g, 1a₁g 1b₂u 2a₂g 2b₂u 3b₂u 3a₂g 1a₄u 2a₄g 2b₄u 3a₄g 5a₂g 1b₂g</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>1A₈u, 1a₁g 1b₁u 2a₂g 2b₂u 3b₂u 3a₂g 1a₄u 2a₄g 2b₄u 3a₄g 5a₂g 1b₂g</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>3A₈g, 1a₁g 1b₂u 2a₂g 2b₂u 3b₂u 3a₂g 1a₄u 2a₄g 2b₄u 3a₄g 5a₂g 1b₂g</td>
<td>5.2</td>
</tr>
<tr>
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<td>5.7</td>
</tr>
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<td>5.9</td>
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<tr>
<td>B₆H₃⁻ V (C₅)</td>
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<td>6.4</td>
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<tr>
<td>B₆H₄⁻ VIII (D₄h)</td>
<td>3A₂g, 1a₁g 2a₁g 4a₁g 2a₄g 1b₁g 2e₁g 4a₄g 1b₂g 3a₁g</td>
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<td>1A₂g, 1a₁g 2a₁g 4a₁g 2a₄g 1b₁g 2e₁g 4a₄g 1b₂g 3a₁g</td>
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<td>5.84</td>
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a VDEs were calculated at TD-B3LYP/aug-cc-pvTZ/B3LYP/6-311++G**

b VDEs were calculated at OVGF/aug-cc-pvTZ/CCSD(T)/6-311++G**

The lowest B₆H₂⁻ isomer should be observed in the experimental photoelectron spectra, with first and second peaks at about 2.8 eV and 3.7 eV, respectively, for isomer I. The large gap between these first two VDEs can be used as a signature of isomer I of B₆H₂⁻ in future PES experiments. The large gap between the third and fourth VDEs may be used to identify the lowest B₆H₄⁻ isomer VIII.

Chemical bonding analysis was performed for the global minimum and low-lying isomers of B₆Hₓ⁻ using the Adaptive Natural Density Partitioning (AdNDP) method.19-21
In order to obtain a simple chemical bonding picture and avoid complications due to spin-polarization, the AdNDP analysis was performed for doubly charged anions B$_6$H$_2^{7-}$ and B$_6$H$_4^{2-}$ (an extra electron was added to the semioccupied HOMO) at the optimized geometry of structures I and VIII. Results of the analysis are presented in Figures 5-4, 5-5, 5-6, and 5-7.

**Figure 5-4.** Bonds recovered by the AdNDP analysis for B$_6$H$_2^{-}$ isomer I. AdNDP analysis was performed for the doubly charged B$_6$H$_2^{-}$ anion at the optimal geometry of isomer I of B$_6$H$_2^{-}$. 
Figure 5-5. Bonds recovered by the AdNDP analysis for $B_6H_3^-$ isomer III.
Figure 5-6. Bonds recovered by the AdNDP analysis for B₆H₃⁻ isomer V.
**Figure 5-7.** Bonds recovered by the AdNDP analysis for B₆H₄⁻ isomer VIII. AdNDP analysis was performed for the doubly charged B₆H₄²⁻ anion at the optimal geometry of isomer VIII of B₆H₄⁻.

According to the AdNDP analysis, the global minimum B₆H₂⁻ isomer (see Figure 5-4) has two 2c-2e B-H σ-bonds (|e| = 1.99), six 2c-2e B-B σ-bonds (|e| = 1.74 – 1.96), one 4c-2e B-B-B σ-bond (|e| = 1.90), and two 4c-2e B-B-B π-bonds (|e| = 1.97). Thus, this cluster is σ-aromatic and π-antiaromatic.

AdNDP analysis of the low-lying isomer III (see Figure 5-5) reveals two 2c-2e B-H σ-bonds (|e| = 1.99), one 3c-2e B-H-B σ-bond (|e| = 1.98), four 2c-2e B-B σ-bonds (|e| = 1.774 – 1.95), two 3c-2e B-B-B σ-bonds (|e| = 1.79 – 1.98), and two 3c-2e B-B-B π-bonds (|e| = 1.73 – 1.86). Thus, this bonding in the boron framework in this cluster is π-antiaromatic.

The AdNDP bonding analysis of low-lying isomer V (see Figure 5-6) reveals three 2c-2e B-H σ-bonds (|e| = 1.94 – 1.99), six 2c-2e B-B σ-bonds (|e| = 1.69 – 1.96),
one 4c-2e B-B-B-B σ-bond ($|e| = 1.92$), and one 5c-2e delocalized over five boron atoms π-bond ($|e| = 1.99$).

AdNDP analysis of the global minimum $B_6H_5^-$ isomer VIII (see figure 5-7) reveals four 2c-2e B-H σ-bonds ($|e| = 1.99$) and eight 3c-2e B-B-B σ-bonds ($|e| = 1.99$).

For $B_6H_x^-$, we found that the chemical bonding consists of 2c-2e and 3c-2e B-H and B-H-B bonds, 2c-2e, 3c-2e, 4c-2e, 5c-2e B-B, B-B-B, four center BBBB, and five center BBBBB bonds. The chemical bonding patterns revealed by the AdNDP analysis are consistent with the geometric structures of all isomers and global minima presented here, similar to findings presented elsewhere in this dissertation.

5-3. Conclusions

Global minimum structures and low-lying isomers were found for a series of $B_6H_x^-$ species using the CK method. Relative energies were refined at the CCSD(T)/6-311++G** level of theory and extrapolated to the infinite basis set. The 2D-3D transition occurs when $x = 4$. This is an important discovery because this transition suggests a major structural change as a function of de-hydrogenation for the stoichiometric $B_nH_n^-$ polyhedral boranes.

Chemical bonding in the global minimum and low-lying isomers was analyzed using the AdNDP method; from this analysis it was found that the chemical bonding patterns in all cases were consistent with the geometric structures of the studied clusters.

The global minimum structure for the $B_6H_x^-$ ($x = 2 – 4$) anions were predicted, and their VDEs were calculated. The VDEs can help interpret future photoelectron spectroscopic study of these anions.
5-4. References


6-1. Summary

The main result of this dissertation is the prediction of a rich variety of new neutral and anionic \( \text{B}_x\text{H}_y \) \((x = 3 – 6 \text{ and } y = 4 – 7)\) clusters which could be building blocks for novel hydrogen-boron materials. In particular, it is hoped that these clusters could be formed by stopping the thermal decomposition of \( \text{LiBH}_4 \) in the early stages of the process, which could lead to experimental synthesis of these theoretically predicted boron-hydride clusters for use as borohydride building blocks. Such compounds may have a potential use as hydrogen storage materials. In fact, during the time which has elapsed between submitting the draft dissertation to the committee and this final draft, Jensen and co-workers\(^1\) have published a paper disclosing the production of \( \text{Mg(B}_3\text{H}_8)_2 \) via the decomposition of \( \text{Mg(BH}_4)_2 \) in a reversible process at 250 °C under 120 atm \( \text{H}_2 \).

The hydrogen release energies of clusters presented in this dissertation are included below in table 6-1. Species in the table with positive hydrogen release energies less than \(~20 \text{ kcal/mol}\) may be useful for potential hydrogen storage materials.

Chemical bonding analysis was performed using AdNDP analysis for all global minimum structures and low lying isomers of neutral and anionic \( \text{B}_x\text{H}_y \) \((x = 3 – 6 \text{ and } y = 2 – 7)\) clusters. It was shown here that the chemical bonding picture obtained by AdNDP is consistent with the geometric structure found in our calculations.
Table 6-1. Stability of BₙHₙ and BₙHₙ⁻ (x=3, 4, 6; y=2-7) species towards H₂ release

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<tr>
<th>Reaction</th>
<th>ΔE (kcal/mol)</th>
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<tr>
<td>2B₃H₅⁻ → 2B₃H₄⁻ + H₂</td>
<td>62.4</td>
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<tr>
<td>2B₃H₆⁻ → 2B₃H₅⁻ + H₂</td>
<td>-31.2</td>
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<tr>
<td>B₃H₆⁻ → B₃H₅⁻ + H₂</td>
<td>15.6</td>
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<tr>
<td>2B₃H₇⁻ → 2B₃H₆⁻ + H₂</td>
<td>68.6</td>
</tr>
<tr>
<td>B₃H₇⁻ → B₃H₆⁻ + H₂</td>
<td>18.7</td>
</tr>
<tr>
<td>2B₃H₅⁻ → 2B₃H₄⁻ + H₂</td>
<td>-13.0</td>
</tr>
<tr>
<td>2B₃H₆⁻ → 2B₃H₅⁻ + H₂</td>
<td>51.6</td>
</tr>
<tr>
<td>B₃H₆⁻ → B₃H₅⁻ + H₂</td>
<td>19.3</td>
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<tr>
<td>2B₃H₇⁻ → 2B₃H₆⁻ + H₂</td>
<td>22.4</td>
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<td>B₃H₇⁻ → B₃H₆⁻ + H₂</td>
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<tr>
<td>2B₄H₅⁻ → 2B₄H₄⁻ + H₂</td>
<td>-22.4</td>
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<td>2B₄H₅⁻ → 2B₄H₄⁻ + H₂</td>
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<td>2B₄H₅⁻ → 2B₄H₄⁻ + H₂</td>
<td>55.8</td>
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<tr>
<td>B₆H₄⁻ → B₆H₃⁻ + H₂</td>
<td>-64.9</td>
</tr>
<tr>
<td>2B₆H₃⁻ → 2B₆H₂⁻ + H₂</td>
<td>-185.6</td>
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Theoretical VDEs were calculated for the global minimum and low lying isomers of anionic BₙHₙ⁻ (x = 4 – 6 and y = 4 – 7) clusters. These theoretical VDEs will be used for comparison with experiment which will be performed by Kit H. Bowen at Johns Hopkins University. Such joint theoretical and experimental work is essential for verifying the theoretical predictions contained here.

Secondary results of this dissertation are the discovery of optical isomerism in borohydrides and the discovery of the 2D-3D transition in B₆H₅⁻ clusters. While the global minimum neutral B₄H₅ cluster has an optical isomer, it is not experimentally
observable with currently developed experimental methods. On further review after discovering optical isomerism in the neutral and anionic B₄H₅ clusters, it was noted that the global minimum B₃H₆⁻ structure (isomer XVI in chapter 2) and the global minimum B₆H₃⁻ structure (isomer III in chapter 5) have optical isomers. These clusters should be experimentally observable via photoelectron spectroscopy. Any cluster lacking symmetry (i.e. having C₁ point group symmetry) should, in theory, have an optical isomer with identical energy. This can be confirmed by taking the z-matrix for a cluster with C₁ symmetry, replacing its dihedral angles with the negative of the original dihedral angles, and calculating the new cluster’s energy and normal vibrational frequencies to correct for the zero point energy.

The discovery of the 2D-3D transition is exciting because of the radical change in chemical bonding that occurs during that transition.

6-2. References

(1) Chong, M.; Karkamkar, A.; Autrey, T.; Orimo, S.; Jalisatgi, S.; Jensen, C. M.

APPENDIX
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(November 2010)

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2. (Presentation) Growth and characterization of GeTe, Sb₂Te₃, and Ge₂Sb₂Te₅ thin film chalcogenide glasses (at the American Physical Society March Meeting 2004, Montreal, Quebec, Canada, 22-26 March 2004).

3. (Presentation) *Ab Initio* search for global minimum structures of the novel BₓHᵧ (y=4-7) neutral and anionic clusters (at the Intermountain Graduate Research Symposium, Logan UT, 31 March 2010).

4. (Poster) *Ab initio* search for global minimum structures of novel BₓHᵧ (x=3-4, y=4–7) neutral and anionic clusters and theoretical photoelectron spectroscopic study of anionic BₓHᵧ clusters (at the 240th American Chemical Society National Meeting & Exposition, Boston, MA, 22-26 August 2010).

AWARDS AND HONORS


PUBLICATIONS


5. Master’s Thesis: Growth and Characterization of Thin Film Telluride Glasses, University of Utah, 2004


PATENTS


3. Doll, D.W.; Olson, J.K.; Cragun, R.B.; Moore, M.A. NIR Chemiluminescent 40mm Target Marker, (Pending, unpublished application number).