THE USE OF POLYHEDRAL BORANE DERIVATIVES
AS MOLECULAR ELECTRONIC SCAFFOLDS

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by
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AS MOLECULAR ELECTRONIC SCAFFOLDS

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Chapter 1: Introduction

This work seeks to elucidate the electronic and mechanical properties of derivatives and analogues of the icosahedral polyhedral borane, closo-dodecahydrides, or more commonly dodecaborate, with an emphasis towards generating a novel and multifunctional nanomachine scaffold.

The approach taken to actuate such an endeavor has been primarily computational. The first aim of this project was to understand the fundamental electronic properties of dodecaborate. To that end, extensive density functional theory calculations were performed on the icosahedron with a variety of substituents, including halogens, chalcogens, ethers, and aromatic rings. These foundational calculations detail the oxidation pathway available to dodecaborate, showing the Jahn-Teller effects it has on the cage, as well as the π-back donation support from the substituents. The π-back donation was examined in more detail by using a natural bond order (NBO) analysis of these species. With this knowledge of the system, two specific nanomachines were explored: a single-molecule transistor (SMT) and a molecular rotor.

Electronics is a field that tends towards the miniaturization of its goods. At this time, the theoretical knowledge and manufacturing abilities are in a transitory period. Now, electronic components, particularly the vital transistor, may not be produced any smaller due to lithography limitations and tunneling leakages. To answer this dilemma, researchers have responded with single molecular components. Dodecaborate could serve as a highly advantageous scaffold for such a device. The reasons for this are numerous and varied, and will be developed more fully throughout this work. To begin with, dodecaborate contains 26 delocalized electrons within its
frameworks, has 12 points of possible functionalization, and exhibits unique electronic properties in its different oxidation states.

In addition to the detailed exploration of these two specific nanomachine applications, other fundamental principles in the chemistry of dodecaborate were explored. Most significant is the exhaustively described π-back donation that is believed to stabilize cage oxidation. This effect though purported has yet to be fully described in the literature.

A General Background of Polyhedral Boranes

Polyhedral boranes represent a unique class of molecules known as molecular polyhedral, adopting an array of three-dimensional geometric shapes. Loosely defined, a molecular polyhedral refers to a cluster of atoms for which any given atom is bound to at least two other atoms of the same kind.\(^1\) The range of structures and bonding types is so great that several organizational schemes have been proposed.\(^2-4\) For the purpose of this work, where only a few types of these molecular polyhedral boranes are considered, only a narrow view into the larger scope of structures is needed.

This work exclusively considers the closo polyhedral boranes. The name for these structures derives from the Greek word for cage, clovo. They are so named due to their three-dimensionally closed shape, as each vertex of a closo-polyhedral borane has a boron atom with a terminal hydrogen atom.\(^1\) Though the closo structures represent an important class of molecules, their existence was heavily debated, due to the high coordination numbers experienced by a formally electron-deficient boron atom.
The electronic structure of these *closo*-polyhedral boranes may be described in the same terms as the 3-center, 2-electron bond in diborne. Briefly, to elucidate this consider dodecaborate, or \( \text{B}_{12}\text{H}_{12}^2^- \), shown below. Each boron atom has 3 valence electrons. One of those valence electrons will be shared with the terminal hydrogen atom to form a “normal” \( \sigma \) bond. This leaves 26 electrons for the structure of the cage.\(^3\) Rather than forming more traditional bonds, these remaining electrons delocalize over the entire cage.\(^1\) As such, each boron atom has two empty p-orbitals that are normal to the surface of the cage with reference at each vertex. Thus, a shell of empty orbitals surround the cage, potentially serving as a pathway for electron density to and from the cage. Furthermore, this extensive delocalization causes dodecaborate and the rest of the *closo*-polyhedral borane to be aromatic, affording them an interesting array of properties.\(^5\)

All of the *closo* polyhedral boranes exhibit similar properties; however, it is useful to discuss these properties in terms of dodecaborate, which shows them most clearly. This is in part due to the high degree of symmetry seen in dodecaborate.\(^6\) Though initially contested\(^7\), it has been shown that dodecaborate has \( \text{I}_\text{H} \) symmetry\(^8\), existing as an icosahedron. Despite this, dodecaborate is not a large structure.\(^1\) In fact, the cage volume is comparable to the volume generated by benzene spinning on its C2 axis. Moving from physical to chemical properties, salts of dodecaborate have high thermal stability due to their thermodynamics and have low thermal reactivity due to a variety of kinetic factors.\(^9\) As an example, the cesium salt may be heated to 810°C in an evacuated quartz tube without decomposition.\(^9\) While the cage exhibits low oxidative reactivity, derivatives of dodecaborate have a highly advantageous oxidation pathway available to them.
Several derivatives, as will be discussed below in Chapters 2 – 7, of dodecaborate can undergo two, one-electron oxidations.\textsuperscript{10} The first oxidation generates the radical monoanion, which is often intense in color.\textsuperscript{10} The second oxidation forms the once again diamagnetic neutral closomer.

\textit{A General Background of Dodecaborate}

Dodecaborate, as described by Wade’s Rules, is constructed from 26 delocalized, framework electrons.\textsuperscript{11} So vital are these electrons to the structural integrity of the cage that unsubstituted dodecaborate cannot be oxidized.\textsuperscript{12} Thus, for the two, one-step oxidation pathway to be available, electron density must be added to support the structure of the cage during oxidation. Several groups have suggested that $\pi$-back donation does just that for a large number of dodecaborate’s derivatives.\textsuperscript{13} In this way, certain substituents are able to $\pi$-back donate electron density into the empty $p$–orbitals from the boron atoms surrounding the cage. Though this potentially central electronic exchange has not yet been described in the literature in full, several experimental manifestations can be found.

Hawthorne et al. synthesized a variety of homogenously persubstituted ethers, $B_{12}(OR)_{12}^{2-}$, examining their electrochemical properties.\textsuperscript{10} Variation of the $R$ group led to a wide range in oxidation potential for the first and second step in the pathway. This observation alone demonstrates that ethers, known electron-donors, stabilize the neutral species such that the oxidation pathway is available. Further, it shows that certain ethers promote a more favorable pathway. In addition to this very informative electrochemistry data, the paper also includes a discussion of the differences in crystal structures between the dianion and neutral species. The boron-oxygen bond distance between the cage and substituent shortened upon oxidation. For
such a shortening to occur additional electron density must be present in the neutral species that was not in the dianion. This bond distance shortening has been suggested to derive from π-back donation.

In beginning to examine π-back donation, it would first be useful to place it in context with polyhedral boranes. From a purely theoretical argument, a few general rules can be used to gauge a substituent’s propensity to be a π-back donor. Greater orbital overlap between the substituent and the apical cage orbitals leads to an increased chance of π-back donation. More practically this means that substituents more closely bound to the cage are better able to stabilize the oxidation pathway. Quantum mechanically, for that overlap to be constructive, those orbitals must be of similar size and energy. With this loose framework in mind, previous electrochemical data could be used to categorize substituents.

Because π-back donation is such an important factor during the oxidation of dodecaborate, the properties of the cage orbitals necessarily must be discussed. Dodecaborate has a quadrupally degenerate ground electronic state, where the sum of the four highest occupied molecular orbitals (HOMOs) provide a uniform shell of electron density in the framework of the cage. During oxidation, it has been suggested that the cage undergoes a Jahn-Teller distortion to increase stability in the neutral state.$^{14}$ This effect can be observed in the expansion of the cage upon oxidation, as well as the anisotropy generated in the boron-boron bond distances of the framework.

The consequences of oxidation, including Jahn – Teller distortions and π – back bonding have been examined for the disubstituted derivatives of closo- hexahydrohexaborate, or $\text{B}_6\text{H}_4\text{X}_2^2$, $[\text{X} = \text{OH}, \text{SH}, \text{NH}_2]$. $^{15}$ In this work, a hybrid DFT calculation using B3LYP – 6-311+G** was used to examine “exopolyhedral multiple bonding” of π-character. This paper suggested that
substituents could form multiple bonds to help stabilize the cage during oxidation. The multiplicity of those bonds were examined using Wilberg bond orders with an NBO routine. The generation of those bonds follows the same logic described earlier for π-back bonding in dodecaborate.

Polyhedral Borane History

Dodecaborate and the other closo-BₙH₂⁻ polyhedral boranes exist in quite unique electronic structures, requiring a formally electron deficient boron atom to have a coordination number as large as six. While the structures of these polyhedral are now well-understood and accepted by the scientific community, this was not always the case. The history of polyhedral boranes is one full of intellectual debate and resourceful innovation. In the early 1900’s, Alfred Stock described the synthesis of a wide variety of polyhedral boranes, which were being tested and use for certain proprietary uses.¹⁶ Driven by their applications, the scientific community began to speculate about the bonding and structures of the polyhedral boranes, focusing on the simple, yet essential, diborane, B₂H₆, structure.

The theoretical problem with understanding or even predicting diborane’s structure was accounting for twelve bonding electrons, but what might appear to be five to seven bonds. Very early on in 1921, Dilthey¹⁷ and later Core¹⁸ in 1927 proposed the currently accepted structure, shown in Figure 1.1 below, that accounted for this electron-bonding discrepancy by using what would later coined “bridging hydrogen atoms”.
Figure 1.1. Currently accepted structure for diborane

In this way, two of the hydrogen atoms are placed between the boron atoms, one above and one below the plane of the molecule, forming a “4-membered ring bond or bridge”. Though the correct structure was proposed in the 1920’s, it was so controversial, or at least inexplicable with the then current bonding theory that by the 1940’s another structure emerged.

In a 1942 review\textsuperscript{19}, Bauer, addressing the difficulty in determining the structure of several polyhedral boranes proposed the ethane-like structure for diborane, shown in Figure 1.2 below.

Figure 1.2. Bauer’s “ethane-like” proposed structure

The bonding of the ethane-like structure was explained through a complicated set of resonance forms, containing two-electron, one-electron, and non-bonding orbitals between the boron and hydrogen atoms. Bauer’s theory expanded to all polyhedral boranes, conforming their structures to hydrocarbon-like connectivity. Unlike for Dilthey and Core, Bauer’s theory was published alongside experimental work.\textsuperscript{20,21} Bauer and his mentor, Linus Pauling, carried out electron diffraction studies on several polyhedral boranes, which Bauer used to found his
hydrocarbon-like structure theory. While Bauer’s structures were novel, the utility of resonance in polyhedral borane bonding was not.

Just preceding Bauer’s review, Nekrasov in 1940 and Diatkina in 1941 proposed structures for diborane, both of which relied on resonance. Shown in Figures 1.3 a-b below, the proposed structures resonated between either ionic or covalent linkages, respectively.

![Figure 1.3a. Nekrasov’s covalent resonance structures for diborane](image)

![Figure 1.3b. Diatkina’s ionic resonance structures for diborane](image)

The scientific community from this time favored the resonance and hydrocarbon-like theory over the bridging-hydrogen atom theory. Certainly, the hydrocarbon-like structures were more amenable to the theories of bonding at that time; however, advances in electronic structure and a few keen observations would inevitably shift the theory back to this unusual bridging – hydrogen atom bond.

The first revival of the bridging structure came by Schlesinger, again, just before Bauer’s review, but unfortunately went unpublished. Schlesinger wrote to Pauling about the bridging structure to which Pauling said he did “not feel very friendly toward.” In the end, Schlesinger discussed the properties of a few of the polyhedral boranes in terms of Bauer’s hydrocarbon-like structures in his own review concomitant to Bauer’s in 1942.
In spite of such overwhelming individual and literature support for the hydrocarbon-like structures, Longuet-Higgins re-proposed and validated the bridging structures in 1943.\textsuperscript{26} Though his argument makes several significant points, perhaps the most persuasive piece of evidence is the observed diamagnetism of diborane. Bauer’s hydrocarbon-like structure of diborane would have unpaired electrons, and would of course, then be paramagnetic, contradictory to its observed properties. The bridging structure, on the other hand, would be diamagnetic. This very important entry to the discourse provided substantial evidence for the bridging structure.

In the immediate wake of this paper, several ideas were added to the theory from experimentalists and theoreticians alike. Schomaker used electron diffraction data to completely disprove the ethane-like structure.\textsuperscript{27} In 1945, Pitzer dubbed the bridging – hydrogen atom bond, a “protonated double bond” in an attempt to provide some theoretical framework for bonding of this type.\textsuperscript{28} Importantly, his theory would allow for conjugation with nearby bridging – hydrogen atoms. Sanderson\textsuperscript{29} noticed that the bridging – hydrogen atoms must be partially negative. Adding to the theory, Castellan used molecular orbital theory and Jahn-Teller distortions to make an argument against the ethane-like structures and for the bridging structure.\textsuperscript{30} In this work, Castellan built off Mulliken’s electronic calculations.\textsuperscript{31} All of this important groundwork was carefully observed and compiled in a work that would result in Lipscomb’s 1976 Nobel Prize.\textsuperscript{32}

The pivotal “two electron-three center” bond was established in 1954, as it applies to polyhedral boranes.\textsuperscript{32} In this paper, there is a very descriptive exposition on the nature of bonding in polyhedral boranes, including nomenclature and theory. The scientists first describe the use of styx rules, which are still used to describe the electronic structure of polyhedral boranes today. It is in this work where dodecaborate is first significantly discussed. Though the researchers did not perform the calculations on B\textsubscript{12}H\textsubscript{12} due to the complexity, they extrapolated
data from their B₆H₆ calculation and theory. Through this they surmised that B₁₂H₁₂ could not exist as an icosahedron.

A year later, Longuet-Higgins performed electronic structure calculations on polyhedral boranes, including B₁₂H₁₂, predicting that an icosahedron with a boron atom at each vertex could exist, but only as a dianion.⁸ Half a decade later, experiment verified the existence of B₁₂H₁₂²⁻.³² Soon after, several review articles and books were published explaining the theory and chemistry⁶,³⁴-³⁵ and providing various organizational schemes³,³⁵,³⁷-³⁹ of these polyhedral.

\textit{Dodecaborate as a Scaffold for a Single – Molecule Transistor}

The field of molecular electronics tends to the smaller fabrication of devices and an increase in processing.⁴⁰ As an essential component of an electric circuit, the transistor has been central to these studies.⁴¹,⁴² The most widely used transistor in modern electronics is the MOSFET (metal-oxide semiconductor field-effect transistor). This is a three-terminal, layered device with a somewhat lengthy manufacturing process.⁴³ The primary function of a transistor is to act as an on/off switch in the circuit. Generally, electrons are carefully channeled from a source to a drain with a gate controlling the amount of current to pass. The MOSFET uses a voltage gate.

The performance of a MOSFET is described by its packing density, or how many gates the device has per unit area of circuit.⁴⁰ To increase performance then, several research groups have focused on creating smaller gates, which are now at the limit of 20 nm.⁴⁴,⁴⁵ The gate size is controlled practically by lithography and fundamentally by tunneling. Lithography is a two-fold problem. First, it is expensive, accounting for an estimated 30% of production costs.⁴⁶ Second,
its resolution is limited by diffraction. Recently, a group created a “doughnut” double-beam lithography technique capable of resolution as low as 52 nm.\textsuperscript{47}

Even once lithography allows for the manufacturing of smaller transistors with a higher packing density, electron tunneling causes excess leakage and diminishes the processing power.\textsuperscript{48} Generally, in larger transistors the gates are far enough apart from one another and sufficiently coated by an oxide layer to make electron tunneling negligible. However, as these smaller transistors are being made, electron tunneling probability becomes significant. To account for this, a new type of transistor, the TFET (tunneling field-effect transistor), has been in research development.\textsuperscript{49,50} TFETs use electron tunneling probability as a gate. These devices are still layered and therefore limited by lithography.

Molecular electronics would solve the problems stated previously with modern bulk electronics and theoretically increase performance. Several groups have developed models for single molecule transistors (SMTs). Within this research, there are two clear areas of work to be done. First, the fundamental nature of electron transport within a single molecule must be better understood. Second, a gated, molecule must be characterized and manufactured as a candidate for an SMT. Several groups have begun research on these topics. The work up leading up the projects described in Chapters 2 – 10 are detailed below.

Generally, a candidate molecule will have an electron donor and acceptor pair in place of the typical source and drain. The most studied pair is the -NH\textsubscript{2} and -NO\textsubscript{2} combination. Between these two groups an “island” or area of conjugated \(\pi\)-electrons must exist. Islands tested include large organic chains \textsuperscript{41}, benzene derivatives\textsuperscript{48,51}, and fullerenes\textsuperscript{52}. These all exhibit low on/off ratios for conductivity\textsuperscript{3}, which is a measure of transistor performance.\textsuperscript{53} Also, few of these have been made and tested. Arguably, one of the largest problems with these devices is the need for a
third terminal to act as a gate, a need that has not been addressed yet. Considerable theoretical work has been done on these types of systems, indicating that the electrons travel through the antibonding (σ* or π*) orbitals of the island.

Dodecahydrododecaborate, B_{12}H_{12}^{2-}, or more commonly dodecaborate, exhibits extraordinary potential as an SMT scaffold. First, it has several points of functionalization, expanding the possible geometries of the devices and current flow. Second, the conductivity on/off ratio would be greatly increased, as it has 26 delocalized electrons. Further, extensive computational studies (mentioned in the preliminary work) indicate that the cage is highly polarizable. Third, a gate would not be needed. Because the dipole moment and the HOMO/LUMO (LUMO : lowest unoccupied molecular orbital) gaps have such a pronounced change upon oxidation, the derivatives would essentially be redox gates. This means that in one oxidation state the structure would conduct and in another it would not. Fourth, the derivatives have high thermal resistance and would not overheat.
References


24. A photocopy of this letter was graciously given by the Pauling Archive Special Collections at Oregon State University and is available for academic use.


44. Han, J. J. Kor. Phys. Soc. 2014, 64,1441-1445.


47. Gu, M.; Gan, Z.; Cao, Y.; Evans, R. SPIE Newsroom. 2013.


53. Han, J. J. Kor. Phys. Soc. 2014, 64, 1441-1445.

Chapter 2: Ionization Properties of the Perhalogenated Derivatives of \textit{closo-}\textit{Dodecahydrododecaborate}

The three-dimentional molecular polyhedra, \([\text{B}_{12}\text{H}_{12}]^{2-}\), or dodecaborate, is constructed of seemingly electron deficient boron atoms arranged in such way to make the 26 cage electrons aromatic.\textsuperscript{1} This unique electronic motif originates from the simple concept of the two-electron, three- center bond.\textsuperscript{2} The electron deficient nature of the individual boron atom necessitates the electron delocalization of the cage as a whole. Further consideration of the electronic configuration of an individual boron atom shows that two empty p-orbitals are found on each boron atom. This configuration generates a shell of empty orbitals around the cage. This shell provides a location for electrons to move into and out of the cage during oxidation.

Though dodecaborate exists most stably as a dianion,\textsuperscript{3} derivatives of it have a two, one-electron oxidation pathway.\textsuperscript{4} The structural integrity of the cage depends on the 26 electrons, thereby requiring some means of electron density support during oxidation. This support has been suggested to come from substituents through \(\pi\)-back bonding using the empty orbital shell around the cage for transport.\textsuperscript{5,6}

In this work, a computational examination of the oxidation properties, including the possibility of \(\pi\)-back donation, will be done on the perhalogenated derivatives of dodecaborate, or \([\text{B}_{12}\text{X}_{12}]\).

\textit{Computational Methods}

All calculations were performed using DFT as found in the Gaussian 09 suite of programs\textsuperscript{7}. Geometry optimizations and vibrational frequencies were completed at the
BPV86/cc-pVTZ level of theory. To optimize the neutral hyperclosomer species and the corresponding radical monoanion, the stable dianion structure for that species was used as a starting geometry. For validation of the model, the perhalogenated, or $\text{B}_{12}\text{X}_{12}$, boron–halogen bond distances and ionization energies were compared to experimental values found in the literature\(^9\). The particular level of theory was chosen, as the literature\(^5,8-9\) found it to be reliable for systems of this type. An aug–cc–pVTZ basis set was also assessed, but was found not to increase the consistency with experimental data for the $\text{B}_{12}\text{Cl}_{12}^{2-/0}$ species.

All values used for comparisons were taken as a change between oxidation states. In all cases, the change in the general property, $P$, may be represented as:

$$\Delta P = P_{\text{neutral}} - P_{\text{dianion}}$$

Values taken in this way were cage expansion ($\Delta \text{BB}$), substituent support ($\Delta \text{BX}$), and overall ionization energy.

Isodensity plots were prepared for each dianion in GaussView 5.0.9\(^10\). Plots of the four-degenerate HOMO and the nondegenerate LUMO orbitals were obtained.

**Results and Discussion**

Bond Distances and Isodensity Plots

The average cage-substituent bond distance for each perhalogenated species may be seen in Table 2.1. A stable structure was not found for the monoanion or neutral species of $\text{B}_{12}\text{H}_{12}^\times$, which correlates with previous reports\(^2\) stating that the structure forms a dimer upon ionization. Also, no stable species was located for the monoanion or neutral species of $\text{B}_{12}\text{Br}_{12}^\times$. This result and the bond distance changes seen in the $\text{B}_{12}\text{F}_{12}^\times$ and $\text{B}_{12}\text{Cl}_{12}^\times$ species could be explained by $\pi$-
back donation, which becomes more effective as the distance between donor and acceptor is shortened.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Dianion</th>
<th>Monoanion</th>
<th>Neutral</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(<em>{12})H(</em>{12})(^{2-})</td>
<td>120.4357</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>B(<em>{12})F(</em>{12})(^{2-})</td>
<td>140.2751</td>
<td>137.2585</td>
<td>134.6462</td>
<td>-5.6289</td>
</tr>
<tr>
<td>B(<em>{12})Cl(</em>{12})(^{2-})</td>
<td>181.9230</td>
<td>179.3145</td>
<td>177.0158</td>
<td>-4.9072</td>
</tr>
<tr>
<td>B(<em>{12})Br(</em>{12})(^{2-})</td>
<td>197.3261</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*aAll units are pm.*

The average boron-boron bond distance within the cage for each species may be seen in Table 2.2. Each perhalogenated closomer expands upon oxidation, as the electrons vital to the structure of the cage are removed. The greater expansion seen in the B\(_{12}\)F\(_{12}\)\(^{2-}\) species is due to the electronegative nature of the fluorine atoms. Even in the most stable, dianion state, the cage size is different among the perhalogenated species. Here, the electronegativity becomes a major factor, as it determines how much electron density is lost from the cage.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Dianion</th>
<th>Monoanion</th>
<th>Neutral</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(<em>{12})H(</em>{12})(^{2-})</td>
<td>178.2570</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>B(<em>{12})F(</em>{12})(^{2-})</td>
<td>180.1452</td>
<td>181.9919</td>
<td>184.8211</td>
<td>4.6759</td>
</tr>
<tr>
<td>B(<em>{12})Cl(</em>{12})(^{2-})</td>
<td>180.6002</td>
<td>182.2346</td>
<td>188.7110</td>
<td>3.1108</td>
</tr>
<tr>
<td>B(<em>{12})Br(</em>{12})(^{2-})</td>
<td>179.4849</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*aAll units are pm.*

The isodensity plots for the HOMO and LUMO orbitals of each optimized dianion may be seen in Figure 2.1 a-d. Each dianion structure exhibits four degenerate HOMO levels, where the electron density becomes evenly distributed amongst the cage, conserving I\(_{h}\) symmetry. Only one of these structures is shown below. This degeneracy is lost upon oxidation, creating electronic anisotropy within the cage.
Figure 2.1a. HOMO and LUMO Isodensity Plot for B_{12}H_{12}^{2-} taken with an isovalue of 0.02

Figure 2.1b. HOMO and LUMO Isodensity Plot for B_{12}F_{12}^{2-} taken with an isovalue of 0.02

Figure 2.1c. HOMO and LUMO Isodensity Plot for B_{12}Cl_{12}^{2-} taken with an isovalue of 0.02

Figure 2.1d. HOMO and LUMO Isodensity Plot for B_{12}Br_{12}^{2-} taken with an isovalue of 0.02
The LUMO isodensity plots show each cage being surrounded by electron density with \( \text{B}_{12}\text{H}_{12}^{2-} \) having a sphere around it. The perhalogenated structures have a slightly deformed sphere surrounding the cage, a deformation that suggests orbital interaction between the halogen and cage. The \( \text{B}_{12}\text{F}_{12}^{2-} \) structure exhibits the most deformation due to its shorter B – X bond distance and greater ability for orbital interaction.

Ionization Energies

The calculated and experimental 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) ionization energies for each species may be seen in Table 2.3. Each perhalogenated structure exhibits a much higher 2\(^{\text{nd}}\) ionization energy than the 1\(^{\text{st}}\), in part from the weakening stability of the species during oxidation. \( \text{B}_{12}\text{F}_{12}^{x} \) is 233.60 kJ mol\(^{-1}\) easier to ionize than \( \text{B}_{12}\text{Cl}_{12}^{x} \), which may seem counterintuitive following from electronegativity trends. However, considering the importance of \( \pi \)-back donation in these species, the more favorable ionization of \( \text{B}_{12}\text{F}_{12}^{x} \) follows from a shorter bond distance between the fluorine atom and the cage – boron atoms, as shown in Table 2.3.

<table>
<thead>
<tr>
<th>Structure</th>
<th>1(^{\text{st}}) Ionization Energy</th>
<th>1(^{\text{st}}) Ionization Energy</th>
<th>2(^{\text{nd}}) Ionization Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}<em>{12}\text{H}</em>{12}^{x} )</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>( \text{B}<em>{12}\text{F}</em>{12}^{x} )</td>
<td>102.93</td>
<td>131</td>
<td>500.06</td>
</tr>
<tr>
<td>( \text{B}<em>{12}\text{Cl}</em>{12}^{x} )</td>
<td>234.05</td>
<td>229</td>
<td>601.78</td>
</tr>
<tr>
<td>( \text{B}<em>{12}\text{Br}</em>{12}^{x} )</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\(^{a}\)All units are kJ mol\(^{-1}\)

HOMO/LUMO Gaps

The calculated HOMO / LUMO energy gaps may be seen in Table 2.4. Within a given structure, the dianion species shows the largest HOMO/LUMO gap, as it exhibits no \( \pi \)-back donation. The gap decreases in the monoanion and then the neutral species, as the \( \pi \)-back donation increases.
Table 2.4. HOMO / LUMO Gaps\(^a\) for Perhalogenated Species

<table>
<thead>
<tr>
<th>Structure</th>
<th>Dianion</th>
<th>Monoanion</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(<em>{12})H(</em>{12})(^x)</td>
<td>620.42</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>B(<em>{12})F(</em>{12})(^x)</td>
<td>346.85</td>
<td>200.02</td>
<td>85.62</td>
</tr>
<tr>
<td>B(<em>{12})Cl(</em>{12})(^x)</td>
<td>406.53</td>
<td>221.56</td>
<td>47.15</td>
</tr>
<tr>
<td>B(<em>{12})Br(</em>{12})(^x)</td>
<td>354.31</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\(^a\)All units are kJ mol\(^{-1}\).

Conclusion

From these studies, it has been shown that halogenating the cage allows for ionization by stabilizing the monoanion and neutral species. These data and previous literature’s suggestions would indicate that ionization is allowed via \(\pi\)-back donation. Ionization of the cage breaks degeneracy, forming electronic point defects in the cage. The LUMO isodensity plots show evidence of orbital interaction between the cage and substituents, which could lead to \(\pi\)-back bonding. Further, the ionization energies trend may be accounted for by \(\pi\)-back bonding. Future studies, should include an examination of functionalized perhalogenated derivatives for candidacy as a material for molecular electronics and an examination into the nature of \(\pi\)-back donation.
References

Chapter 3: Ionization Properties of the Perhalogenated Hydroxyl Derivatives of \textit{closo}-Dodecahydrododecaborate

The highly symmetric, three-dimensional cluster \([\text{B}_{12}\text{H}_{12}]^{2-}\) has been researched over the last few decades in terms of functionalization,\textsuperscript{1-14} mechanistic studies of derivatives,\textsuperscript{15-17} and DFT.\textsuperscript{18-21} The recent investigations stem from the scaffolding ability of the cluster in a wide variety of applications, spanning Boron Neutron Capture Therapy,\textsuperscript{22-25} lithium-ion batteries,\textsuperscript{26-28} molecular imaging,\textsuperscript{29} ionic liquids,\textsuperscript{30} enzyme inhibitors,\textsuperscript{31-33} and lipid membrane interlopers.\textsuperscript{34-35}

\textit{Closo}-dododecahydrododecaborate, or more commonly dodecaborate, is a member of the molecular polyhedral borane structural class. Loosely defined, a molecular polyhedral refers to a cluster constructed of atoms bound to at least two of the same kind.\textsuperscript{36} The range of structures and bonding types is so great that several organization schemes have been proposed.\textsuperscript{37-39} Relevant to dodecaborate is the classification of \textit{closo}, dictating that the cluster has the basic formula \text{B}_n\text{H}_n^{2-} and a cage electron count of \(2n + 2\), where \(n\) is the number of vertices.\textsuperscript{38c} This classification, along with the electron count changes with the oxidation state of the cluster and is shown below in Figures 3.1 and 3.2. In addition to this classification, dodecaborate has a specific numbering system.\textsuperscript{40}

\textit{Figure 3.1:} Conventional numbering scheme for dodecaborate established in 1963 by Adams\textsuperscript{40}
Figure 3.2: Two, one-electron oxidation pathways for dodecaborate of the closo dianion (26) to the hyper-closo radical (25) to the hyper-closo neutral (24) species

Dodecaborate exists with a unique electronic structure that allows for a seemingly electron deficient boron atom to have a coordination number of six. The theoretical bonding model used to describe dodecaborate and other molecular polyhedral boranes stems from the “two electron – three-center” bond established by Lipscomb in 1975 for systems of this type. Dodecaborate is a three-dimensional molecular polyhedral of $I_3^H$ symmetry. Considering the electronic configuration, each boron atom has three valence electrons, one of which is shared with terminal hydrogen atoms to form a $\sigma$-bond. This leaves 24 valence electrons from the boron atoms and two additional electrons due to the charge to form the structure of the cage. When the structure of dodecaborate was first being predicted Longuet-Higgins proposed that it must have these 26 electrons, leading to the currently accepted theory that closo polyhedral boranes exist most stably as dianions. Furthermore, it has been shown that the 26 electrons are delocalized across the framework of the cage, yielding a three-dimensionally aromatic cage. Revisiting the electronic configuration of the boron atoms, it would be noticed that each boron atom has two empty p-orbital. Importantly, they are normal to the surface of the cage with reference given at each vertex. Thus, a shell of empty orbitals surrounds the cage, potentially serving as a pathway for electron density to and from the cage.

As alluded to previously, derivatives of dodecaborate have a well-known oxidation pathway, ranging from the stable dianion to the neutral species. Though the unsubstituted cage
dimerizes upon oxidation, several derivatives are able to utilize the full oxidation pathway.\textsuperscript{45} Recently, a variety of perether derivatives of dodecaborate were prepared and their oxidation and reduction potentials were characterized electrochemically.\textsuperscript{46} As a consequence of the oxidation of these clusters from the native 26-electron \textit{closo} species, to the stable 25-electron \textit{hypercloso} radical anion species, and to the stable 24-electron \textit{hypercloso} neutral species, it was observed that the cage-oxygen bond distances shorten during oxidation. $\Pi$-back donation has been suggested as the process by which this occurs. Within the literature, other groups have ascribed several oxidation properties to $\pi$-back donation.\textsuperscript{21,47} However, very little detail or any method of quantification has been proposed. Similar characterization has been done for dative bonding using NBO analysis.\textsuperscript{48} This analysis has been used on the periodated derivative of dodecaborate to describe the natural charges.\textsuperscript{49} In this work, we seek to show the utility of an NBO analysis in the quantifying description of $\pi$-back donation.

Consider the two-fold necessity of the stabilization provided by $\pi$-back donation. Most paramount, the framework of the dianion is held together by 26 delocalized electrons, therefore, $\pi$-back donation could stabilize the pathway by increasing electron density in the cage during oxidation, a concept that has been pictorially described below in Figure 3.3.\textsuperscript{50} In addition to this, there has been some discussion about Jahn-Teller distortions of the cage, in-describing the effects of oxidation on the cage.\textsuperscript{51} Similarly to $\pi$-back donation, these effects have not been fully elucidated with respect to their impact on the cage.
Included in this work is a discussion of the optimized substitution patterns of the cluster, which first began with Lipscomb in 1962. In his work, Lipscomb used an LCAO-MO approach to determine the substitution patterns on \([\text{B}_{12}\text{H}_{12}]^{2-}\) to \([\text{B}_{12}\text{X}_{12}]^{2-}\) \([\text{X=}\text{F,Cl,Br,I}]\) via sequential electrophilic attack. Lipscomb premised his predictions on two assumptions: the attack by halogen is electrophilic and will therefore occur at the most negative vertex and successive attacks occur sequentially, rather than simultaneously. Herein, substitution patterns of similar species with agreement to Lipscomb’s early predictions are observed.

**Computational Methods**

All calculations were performed using DFT as found in the Gaussian 09 suite of programs. Geometry optimizations and vibrational frequencies were completed at the BPV86/cc-pVTZ level of theory. For validation of the model, the perhalogenated, or \(\text{B}_{12}\text{X}_{12}\), boron – halogen bond distances and ionization energies were compared to experimental values found in the literature. The particular level of theory was chosen, as the literature found it to be reliable for systems of this type. An aug – cc – pVTZ basis set was also assessed, but was found not to increase the consistency with experimental data for the \(\text{B}_{12}\text{Cl}_{12}^{2-}\) species.
The perhalogenated hydroxyl derivatives of dodecaborane, or \( \text{B}_{12}(\text{OH})_n\text{X}_{12-n} \), were tested in this manner. Let a series be defined as a halogen-hydroxyl combination over all possible \( n \)-values and isomers. For \( n \)-values between 2 and 10 several possible isomers exist theoretically. For each series the most stable isomer was determined as having the minimum energy in the dianion oxidation state relative to the other isomers of the \( n \)-value in that series. Average values were also generated by comparing data from isomers with a relative energy less than 10 kJ mol\(^{-1} \).

All values used for trend comparisons were taken as a change between oxidation states. In all cases, the change in the general property, \( P \), may be represented as:

\[
\Delta P = P_{\text{neutral}} - P_{\text{dianion}}
\]

Values taken in this way were cage expansion (\( \Delta \text{BB} \)), substituent support (\( \Delta \text{BX}, \Delta \text{BOH}, \) and \( \Delta (X+\text{BOH}) \)), and overall ionization energy.

Additionally, an NBO\(^{54} \) analysis was performed on the most stable isomers of the \([\text{B}_{12}(\text{OH})_n\text{F}_{12-n}] \) series for both the dianion and neutral oxidation state.

**Results and Discussion**

The most stable isomers, as determined by the minimum total energy for a given \( n \)-value are shown in Table 3.1, along with Lipscomb’s\(^{52} \) early predictions. In comparison of the unique substitution patterns of the series \([\text{B}_{12}(\text{OH})_n\text{X}_{12-n}] \), an increase in distance between substituents trends as \( \text{F} < \text{Cl} < \text{Br} \). This might arise due to either halogen inductivity or atomic radius. In an attempt to understand this more, the calculated substitution patterns in this work were compared to Lipscomb’s predictions. In Lipscomb’s model, the charge distribution across the cage was used to determine isomer stability after each sequential addition of a halogen. Thus, an inductive
substituent was added to an unsubstituted cage. A series would have a similar substitution pattern as Lipscomb’s prediction, if the added substituent was more inductive than the substituent already present. Considering this and the substitution patterns for [B_{12}(OH)_nX_{12-n}], deviations from Lipscomb’s predictions increase as Br < Cl < F, suggesting inductivity drives the isomer stability.

<table>
<thead>
<tr>
<th>Series</th>
<th>[B_{12}(OH)<em>nF</em>{12-n}]</th>
<th>[B_{12}(OH)<em>nCl</em>{12-n}]</th>
<th>[B_{12}(OH)<em>nBr</em>{12-n}]</th>
<th>Lipscomb’s Predictions$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1,2</td>
<td>1,7</td>
<td>1,7</td>
<td>1,7</td>
</tr>
<tr>
<td>3</td>
<td>1,2,3</td>
<td>1,7,9</td>
<td>1,7,9</td>
<td>1,7,9</td>
</tr>
<tr>
<td>4</td>
<td>1,2,3,5</td>
<td>1,2,10,12</td>
<td>1,2,9,11</td>
<td>1,2,9,11</td>
</tr>
<tr>
<td>5</td>
<td>1,2,3,10,12</td>
<td>1,2,4,7,12</td>
<td>1,2,4,8,11</td>
<td>1,2,3,9,11</td>
</tr>
<tr>
<td>6</td>
<td>1,2,3,5,10,11</td>
<td>1,2,4,7,9,12</td>
<td>1,2,4,7,9,11</td>
<td>1,2,4,8,9,11</td>
</tr>
<tr>
<td>7</td>
<td>REV$^{[b]}$: 1,2,3,10,12</td>
<td>REV: 1,2,4,8,11</td>
<td>REV:1,2,4,11,12</td>
<td>REV: 1,2,4,9,11</td>
</tr>
<tr>
<td>8</td>
<td>REV:1,2,10,12</td>
<td>REV:1,2,9,11</td>
<td>REV: 1,2,9,11</td>
<td>REV: 1,2,9,11</td>
</tr>
<tr>
<td>9</td>
<td>REV: 1,2,4</td>
<td>REV: 1,2,9</td>
<td>REV: 1,7,9</td>
<td>REV: 1,7,9</td>
</tr>
<tr>
<td>10</td>
<td>REV: 1,7</td>
<td>REV: 1,7,12</td>
<td>REV: 1,7</td>
<td>REV: 1,7</td>
</tr>
</tbody>
</table>

$^a$n refers to the number of hydroxyl substituents on the cage

$^b$REV refers to nomenclature that numbers the halogen first

Several properties, including boron-boron bond distance in the dianion state, Δ BB, Δ BX, Δ BOH, Δ B(X+OH), overall ionization energy, and π-back bonding occupancy were compared to the relative energies within a given n-value of a series; however, no correlation was found. For all trends used, two data sets are available—those from the most stable species only and those from averaging the isomers within 10 kJ mol$^{-1}$. No significant deviation between the two was apparent; therefore, throughout this article only the latter will be considered.

NBO Analysis

In an effort to better elucidate the potential for π-back bonding in these species, an NBO analysis was performed on the [B_{12}(OH)_nF_{12-n}] series. The π-back bond was identified as being
an additional cage-substituent bond, which was entirely of p-character. A computer representation of one is shown in Figure 3.4. In each case this bond was only observed for the neutral species, suggesting that π-back donation is indeed a consequence of oxidation. In addition to this, the NBO analysis also provides a way to qualify the substituent’s significance as a potential π-back donor. Shown below in Figure 3.5 is the fraction of π-bonds formed during the oxidation of $[\text{B}_{12}(\text{OH})_n\text{X}_{12-n}]^{2-}$ to $[\text{B}_{12}(\text{OH})_n\text{X}_{12-n}]^0$ per substituent as a function of n. For each n-value, the hydroxyl substituent provides a greater fraction of π-back bonds than the fluorine atom substituent. This difference in substituent back donation increases with n. Knowing the extent of π-back bonds formed, it is useful to consider the occupancy of these bonds. This information is detailed in Table 3.2. From this data, it is observed that a fluorine atom is a more prolific donor of electron density when F is a major species than the hydroxyl substituent.

Figure 3.4: NBO image capture of π-back bond between the cage and an oxygen substituent on the B$_{12}$(OH)$_8$F$_4^0$
Figure 3.5. The fraction of π-back bonds of a given type (blue: BF; orange: BOH) per the number of possible π-back bonds of that type.

Table 3.2. Average Occupancy[a] of π-Back Bonds

<table>
<thead>
<tr>
<th>n[b]</th>
<th>B-F occupancy</th>
<th>B-O occupancy</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>1</td>
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<td>3</td>
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</tr>
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<td>4</td>
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</tr>
<tr>
<td>12</td>
<td>n/a</td>
<td>1.96</td>
</tr>
</tbody>
</table>

[a]Average occupancy refers to the average number of electrons in the π-back bond found in the NBO analysis of the neutral species.

[b]n refers to the number of OH substituents on the cage.

π-Back Donation

The concept that π-back donation stabilizes the oxidation of the persubstituted dodecaborate species was first proposed based on experimental bond distance shortening observed in single crystal X-Ray structure\textsuperscript{46}. As such, π-back bonding was predicted and
quantified here for these species and is depicted as a function of n in Figure 3.6 below. Considering the \([B_{12}(OH)_nF_{12-n}]\) series first, increasing the value of n results in less bond distance shortening. The change in bond distance correlates to the degree of \(\pi\)-back donation occurring. From the NBO data, the fluorine substituents contribute more electron density through \(\pi\)-back donation than the hydroxyl substituents, and so, the decrease in bond distance is more pronounced for lower n-values. The opposite trend is seen with the other halogens, presumably due to the mismatch in orbital energy between the valence electrons of boron atoms and those of chlorine and bromine atoms. Thus, the halogen substituents may be ranked from weak to strong \(\pi\)-back donors for this system as follows: \(\text{Br} < \text{Cl} < \text{F}\).

**Figure 3.6.** The combined substituent support of species \(B_{12}(OH)_nX_{12-n}\) for each halogen as defined as the summation of the change in bond distance of both substituents upon the two-electron oxidation.
Overall Ionization Energy

The overall ionization energy was computed to evaluate the favorability of each oxidation pathway and is compared to electrochemical data found in the literature. These values have been plotted against n for all three series in Figure 3.7. For each value of n, the \([B_{12}(OH)_nF_{12-n}]\) series is the most favorable. This result arises from the calculated relative strength of a fluorine atom as a \(\pi\)-back donor compared to other halogens. Furthermore, this may be quantified by considering the regressions of these trends, tabulated below. Though replacement of any halogen with a hydroxyl group is favorable, the \([B_{12}(OH)_nF_{12-n}]\) slope is smaller than for the other halogens, again suggesting that a fluorine atom is the strongest \(\pi\)-back donor among the halogens.

The overall ionization energy describes how the cage uses \(\pi\)-back bonds. Considering the NBO data on \(\pi\)-back bonding, the significance of a negative slope in the \([B_{12}(OH)_nF_{12-n}]\) series may be discussed. The negative slope is a result of the hydroxyl substituent providing greater overall stabilization than a fluorine substituent. This means that multiple \(\pi\)-back bonds provide greater stabilization than a locally strong \(\pi\)-back bond. The preference for homogeneous stabilization becomes particularly important when considering distortions caused by oxidation.

| Table 3.3. Overall Ionization Energy Slopes\(^{[a]}\) |
|-----------------|-----------|-----------|
| Series          | Slope     | Correlation Factor |
| F/OH            | -29.9     | 97.5       |
| Cl/OH           | -45.3     | 97.5       |
| Br/OH           | -44.7     | 99.5       |

\(^{[a]}\)The slopes were taken using the linear regression software found in EXCEL 2013.
Figure 3.7. The overall ionization energy of the two-electron pathway from \([\text{B}_{12}(\text{OH})_{n}\text{X}_{12-n}]^{2-}\) to \([\text{B}_{12}(\text{OH})_{n}\text{X}_{12-n}]^{0}\).

**Jahn-Teller Distortions**

Oxidation of the 26 electron *closo* dianion to the 24 electron *hypercloso* neutral species results in cage expansion. This arises due to the loss of two framework bonding electrons during oxidation. A process that adds electron density during oxidation, such as \(\pi\)-back donation might then be thought to decrease cage expansion. To measure this the average boron-boron distance as a function of \(n\) has been computed.
Figure 3.8. The expansion of the cage defined by the change in average boron-boron distance upon the two-electron oxidation from \([\text{B}_{12}(\text{OH})_nX_{12-n}]^2-\) to \([\text{B}_{12}(\text{OH})_nX_{12-n}]^0\).

With respect to both the \([\text{B}_{12}(\text{OH})_n\text{Cl}_{12-n}]\) and \([\text{B}_{12}(\text{OH})_n\text{Br}_{12-n}]\) the replacement of the halogen with a hydroxyl group actually increases cage expansion in Figure 3.8. Considering similar orbital overlap and energy, the hydroxyl group would be predicted to be the more dominant \(\pi\)-back donor than either a chlorine or bromine atom. This suggests two competing factors in \(\pi\)-back bonding metrics. First, consider the occupancy of \(\pi\)-back bonds. The fluorine substituents provided greater occupancy of \(\pi\)-back bonds that the hydroxyl substituents, resulting in a the fluorine atoms causing a greater bond distance contraction than the hydroxyl group. Second, consider the number of \(\pi\)-back bonds. The hydroxyl group provides a higher percent of \(\pi\)-back bonds than the fluorine atoms do, resulting in a perhydroxy cage having a more favorable oxidation pathway than a perfluoro cage.
To probe the system further an examination of the boron-boron ranges in both oxidation states was performed. For each halogen system, the oxidative product had a significant jump in this range across all n-values, shown in Figure 3.9. This anisotropic expansion and the previous cage expansion trends may be explained through Jahn-Teller distortions. The significant difference in range values for the two oxidation states arises from the loss of symmetry during the oxidation. This loss of symmetry is, at least in part, due to the unique electronic environments around the cage and the proximity of electron density generated by the substituents. Thus, a substituent with a filled orbital nearer to the cage will induce a greater distortion and cause the cage to expand more than a substituent further from the cage. This may be corroborated by the cage expansion trends, where the increasing number of hydroxyl groups, which are closer to the cage than either a chlorine or bromine atom, causes greater cage expansion.

![Figure 3.9. The oxidation-based bimodal ranges in framework boron-boron bond distances for B_{12}(OH)_nX_{12-n}](image-url)
Conclusion:

In this work an accurate and computationally efficient methodology has been described to examine a wide range of dodecaborate functionalities. The specific derivatives examined were $\text{B}_{12}(\text{OH})_n\text{X}_{12-n}$ [$n=0$-$12$; $\text{X}=\text{F,Cl,Br}$] of which the most stable isomers were determined. In an effort to understand the highly applicable oxidation pathway of these species, two important factors became apparent. First, $\pi$-back donation was seen to be the predominant stabilizing force for these species. An NBO analysis was done to quantify the $\pi$-back bonds for the first time in the literature. Second, Jahn-Teller distortions were observed for the cage as a response to oxidation. These oxidation-induced distortions show the harsh nature of oxidation and how significant the $\pi$-back donation is for these species.
References


   Sieglova, I.; Plesek, J.; Sicha, V.; Gruner, B.; Oberwinkler, H.; Sedlacek, J.; Krausslich, H.; Hobza, P.; 


   *163*, 64-73.


Chapter 4 : A Comparison of Chalcogen Effects on Ionization Properties in Perfluorinated Derivatives of \textit{closo}-Dodecahydrododecaborate

With a defined computational methodology in place to describe the ionization properties, including quantifying \( \pi \)-back donation, further functionalities can be systematically evaluated. As the halogens have undergone such evaluation in the preceding chapters, this chapter will focus on the chalcogen substituent.

How the hydroxyl groups acts as a substituent and its effect on the oxidation pathway is important to know, as it serves as a synthetic branching point for several other functional groups, such as ethers.\(^1\) Similarly, the thiol group is of interest. Though a thiol group would potentially act as a sythetic precursor, it can also facilitate other meaningful experiments, such as conductive – Atomic Force Microscopy.\(^2\)

Thus, this chapter focuses on a computational examination of the thiol – fluorine series, or \( \text{B}_{12}(\text{SH})_n\text{F}_{12-n} \) \( [n=0-12] \).

\textit{Computational Methods}

All calculations were performed using DFT as found in the Gaussian 09 suite of programs\(^3\). Geometry optimizations and vibrational frequencies were completed at the BPV86/cc-pVTZ level of theory. For validation of the model, the perhalogenated, or \( \text{B}_{12}\text{X}_{12} \), boron – halogen bond distances and ionization energies were compared to experimental values found in the literature\(^20\). The particular level of theory was chosen, as the literature\(^19\)–\(^21\) found it to be reliable for systems of this type. An aug – cc – pVTZ basis set was also assessed, but was found not to increase the consistency with experimental data for the \( \text{B}_{12}\text{Cl}_{12}^{2-/0} \) species.
The perfluorinated thiol derivatives of dodecaborane, or B_{12}(SH)_nF_{12-n}, were tested in the following manner. Let a series be defined as a fluorine-thiol combination over all possible n-values and isomers. For n-values between 2 and 10 several possible isomers exist theoretically. For each series the most stable isomer was determined as having the minimum energy in the dianion oxidation state relative to the other isomers of the n-value in that series.

All values used for trend comparisons were taken as a change between oxidation states. In all cases, the change in the general property, P, may be represented as:

$$\Delta P = P_{neutral} - P_{dianion}$$

Values taken in this way were cage expansion (\(\Delta BB\)), substituent support (\(\Delta BF\), \(\Delta BSH\), and \(\Delta(F+BSH)\)), and overall ionization energy.

Additionally, an NBO\(^7\) analysis was performed on the most stable isomers of the \([B_{12}(SH)_nF_{12-n}]\) series for both the dianion and neutral oxidation state.

Results & Discussion:

The most stable isomers, as determined by the minimum total energy for a given n-value are shown in Table 4.1, along with Lipscomb’s\(^8\) early predictions. It was previously shown in Chapter 3 that inductivity drives isomer stability with greater induction leading to greater deviations from Lipscomb’s predictions. Thus, the \([B_{12}(SH)_nF_{12-n}]\) series may be seen to adhere slightly more to those early predictions than the \([B_{12}(OH)_nF_{12-n}]\) series. However, there is still great deviation due to the large inductivity of a fluorine atom.
Table 4.1. Most Stable Isomers of a n-value for Each Series

<table>
<thead>
<tr>
<th>Series</th>
<th>( [\text{B}_{12}(\text{OH})<em>n\text{F}</em>{12-n}] )</th>
<th>( [\text{B}_{12}(\text{SH})<em>n\text{F}</em>{12-n}] )</th>
<th>Lipscomb's Predictions(^{52})</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (^{[a]})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1,2</td>
<td>1,12</td>
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</tr>
<tr>
<td>3</td>
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<td>1,2,3,5,7,9</td>
<td>1,2,4,8,9,11</td>
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<tr>
<td>7</td>
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<td>REV: 1,2,4,11,12</td>
<td>REV: 1,2,4,9,11</td>
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<td>8</td>
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<td>REV: 1,2,10,12</td>
<td>REV: 1,2,9,11</td>
</tr>
<tr>
<td>9</td>
<td>REV: 1,2,4</td>
<td>REV: 1,7,9</td>
<td>REV: 1,7,9</td>
</tr>
<tr>
<td>10</td>
<td>REV: 1,7</td>
<td>REV: 1,12</td>
<td>REV: 1,7</td>
</tr>
</tbody>
</table>

\(^{[a]}\)n refers to the number of hydroxyl substituents on the cage

\(^{[b]}\)REV refers to nomenclature that numbers the fluorine substituent first

**NBO Analysis**

To compare the \(\pi\)-back bonding potential for the two chalcogens, an NBO analysis was performed on both \( [\text{B}_{12}(\text{YH})_n\text{F}_{12-n}] \) series. The \(\pi\)-back bond was identified as being an additional cage-substituent bond, which was entirely of p-character. As with the discussion in the previous chapter, such a \(\pi\)-back bond was only found in the neutral species. Comparing first the quantity of \(\pi\)-back bonds, Figure 4.1 below shows the fraction of \(\pi\)-bonds formed during the oxidation of \( [\text{B}_{12}(\text{YH})_n\text{F}_{12-n}]^2^- \) to \( [\text{B}_{12}(\text{YH})_n\text{F}_{12-n}]^0 \) per substituent as a function of \(n\).
Figure 4.1. The fraction of π-back bonds of a given type (red: BF (F/OH series); yellow: BOH (F/OH series); green: BF (F/SH series); purples: BSH (F/SH series) per the number of possible π-back bonds of that type.

For both series $[\text{B}_{12}(\text{YH})_n\text{F}_{12-n}]$, the chalcogen provides a greater fraction of π-back bonds for most $n$-values. As the $n$-value increases, the chalogen participates in a greater fraction of π-back bonds. The thiol group contributes the same or a lower fraction of π-back bonds than the hydroxyl groups for any given $n$-value. Next, consider the quality of these π-back bonds as described by the average electron density present in the π-back bonds shown in Table 4.2. From this data, it is observed that the hydroxyl group is a more prolific donor than the thiol group for any given $n$-value.
Table 4.2. Average Occupancy\(^{[a]}\) of π-Back Bonds

<table>
<thead>
<tr>
<th>n(^{[b]})</th>
<th>B-F occupancy</th>
<th>B-O occupancy</th>
<th>B-F occupancy</th>
<th>B-S occupancy</th>
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<td>1.96</td>
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<tr>
<td>12</td>
<td>n/a</td>
<td>1.96</td>
<td>n/a</td>
<td>1.86</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Average occupancy refers to the average number of electrons in the π-back bond found in the NBO analysis of the neutral species.

\(^{[b]}\)n refers to the number of YH substituents on the cage.

π-Back Donation

The effect of π-back donation may be monitored experimentally through bond distance shortening between the cage and substituent. Figure 4.2 below shows this bond distance shortening for the \([\text{B}_{12}(\text{YH})_n\text{F}_{12-n}]\) series as a function of n. The \([\text{B}_{12}(\text{SH})_n\text{F}_{12-n}]\) experiences less bond distance shortening for all n-values except 1 and 2. This correlates well with the NBO data that depicted the thiol group as providing π-back bonds less often and with less electron density than the hydroxyl group. This trend between the two chalcogens might manifest itself from the longer bond distance between the thiol group and the cage compared to the hydroxyl group and the cage. Thus, the chalcogen substituents may be ranked from weak to strong π-back donors for this system as follows: SH < OH.
Figure 4.2. The combined substituent support of species $B_{12}(YH)_nF_{12-n}$ for each chalcogen as defined as the summation of the change in bond distance of both substituents upon the two-electron oxidation.

**Overall Ionization Energy**

The overall ionization energy was calculated to compare the favorability of the oxidation pathways of the chalcogens. These values have been plotted against $n$ for both series in Figure 4.3. For any given $n$-value the $[B_{12}(OH)_nF_{12-n}]$ series provides the more favorable oxidation pathway compared to $[B_{12}(SH)_nF_{12-n}]$. This arises from the greater calculated $\pi$-back donation support provided by the hydroxyl group compared to the thiol group. This may be further quantified by considering the regression of these trends, tabulated below. In general, replacement of a fluorine substituent with either chalcogen is preferable. However, the preference for the replacement to be a thiol group is not nearly as strong as for it to be a hydroxyl group. Additionally, the favorability for the replacement of a fluorine atom with a thiol group is not always present, as the correlation factor is low for this trend.
Figure 4.3. The overall ionization energy of the two-electron pathway from \([B_{12}(YH)_nX_{12-n}]^{2-}\) to \([B_{12}(YH)_nX_{12-n}]^0\).

| Table 4.3. Overall Ionization Energy Slopes\(^{[a]}\) |
|-----------------|-------|-----------------|
| Series          | Slope | Correlation Factor |
| F/OH            | -29.9 | 97.5            |
| F/SH            | -1.48 | 6.9             |

\(^{[a]}\)The slopes were taken using the linear regression software found in EXCEL 2013.

**Jahn-Teller Distortions**

Oxidation of the 26 electron *closo* dianion to the 24 electron *hypercloso* neutral species results in cage expansion. This arises due to the loss of two framework bonding electrons during oxidation. A process that adds electron density during oxidation, such as π-back donation might then be thought to decrease cage expansion. This effect has been monitored by calculating the change in boron-boron bond distance as a function of \(n\).
Figure 4.4. The expansion of the cage defined by the change in average boron-boron distance upon the two-electron oxidation from $[\text{B}_{12}(\text{YH})_n\text{F}_{12-n}]^{2-}$ to $[\text{B}_{12}(\text{YH})_n\text{F}_{12-n}]^0$.

For each given n-value the $[\text{B}_{12}(\text{SH})_n\text{F}_{12-n}]$ series experienced less cage expansion than the $[\text{B}_{12}(\text{OH})_n\text{F}_{12-n}]$ series shown in Figure 4.4. This result may be better understood in the context of the Jahn-Teller distortion argument presented in the previous chapter. The hydroxyl groups are nearer than cage than the thiol groups, and thus induce a greater distortion upon oxidation.

Conclusion:

In this work, the computational method described previously to examine the ionization properties of dodecaborate derivatives was used to compare the chalcogen groups SH and OH on the perfluorinated cage. In comparison of the two chalcogens, the NBO analysis revealed that the thiol group provides $\pi$-back bonds less often and with less electron density than the hydroxyl groups. Further calculations correlated this to the thiol derivatives experiencing a more energetic oxidation pathway and less Jahn-Teller distortions that the hydroxyl derivatives. These trends arise due to the greater distance from the cage between the thiol group compared to the hydroxyl group.
References

Chapter 5: Ionization Properties of the Perchlorinated Monosubstituted Ether Derivatives of \textit{closo} - Dodecahydrododecaborate

For dodecaborate to be useful towards molecular machinery scaffolding, systematic and informative studies on derivatives of dodecaborate must be performed. In previous chapters, a methodology to test various ionization properties has been developed and described in rigor. Such an examination begins with observing the favorability of the ionization pathway total energy values, and then uses a variety of other properties to observe the cage’s response to ionization. In an effort to examine the ionization properties of practical derivatives of dodecaborate, a variety of mono-substituted ether derivatives were computationally examined.

Ether functional groups are a suitable starting point for functionalization, as other groups have provided synthetic methods for producing them and have begun detailing their properties.

\textit{Computational Methods}

All calculations were performed using DFT as found in the Gaussian 09 suite of programs\textsuperscript{1}. Geometry optimizations and vibrational frequencies were completed at the BPV86/cc-pVTZ level of theory. For validation of the model, the perhalogenated, or B\textsubscript{12}X\textsubscript{12}, boron – halogen bond distances and ionization energies were compared to experimental values found in the literature\textsuperscript{20}. The particular level of theory was chosen, as the literature\textsuperscript{19-21} found it to be reliable for systems of this type. An aug – cc – pVTZ basis set was also assessed, but was found not to increase the consistency with experimental data for the B\textsubscript{12}Cl\textsubscript{12}\textsuperscript{2/-0} species.

All values used for trend comparisons were taken as a change between oxidation states. In all cases, the change in the general property, P, may be represented as:
\[ \Delta P = P_{\text{neutral}} - P_{\text{dianion}} \]

Values taken in this way were cage expansion (\( \Delta \text{BB} \)), substituent support (\( \Delta \text{BX}, \Delta \text{BOR} \), \( \Delta (\text{BCl}+\text{BOR}) \), \( \Delta \text{CC}_{\text{alkene}} \), and \( \Delta \text{CC}_{\text{benzene}} \)), and overall ionization energy.

**Results and Discussion**

**Overall Ionization Energy**

The overall ionization energy quantifies the favorability of the two-electron oxidation pathway for the ether derivatives: \([\text{B}_{12}\text{ORCl}_{11}]\). The computed energies for the ether derivativess are shown below in Table 5.1. Each saturated alkyl group, 2 – 5, lowered the ionization energy relative to the unsubstituted hydroxyl derivative. As these alkyl groups are a part of a \( \pi \)-system, they are slightly electron-donating, which allows them to shuttle some extra electron density into the oxidized cage. More notably, the oxidation pathway is most stabilized for the species with the most \( \pi \)-rich substituents, i.e. 9 and 10. The additional \( \pi \)-electrons available to the oxidized cage, allows support for the oxidation product, providing a more favorable ionization pathway for these ether derivatives. When these ether derivatives are oxidized, they undergo other phenomena whose observation yields greater clarity on the ionization pathway and the forces that influence its energetics.
Table 5.1. Overall Ionization Energy\(^{[a]}\) of the Mono-Substituted Ether Derivatives of \textit{closo-}
Dodecahydrododecaborate

<table>
<thead>
<tr>
<th>Species</th>
<th>R</th>
<th>Overall Ionization Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>683.5</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>661.0</td>
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<td>662.0</td>
</tr>
<tr>
<td>5</td>
<td>t-Bu</td>
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<td>C=CH(_2)</td>
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<tr>
<td>7</td>
<td>C=CH</td>
<td>691.8</td>
</tr>
<tr>
<td>8</td>
<td>Ph</td>
<td>650.9</td>
</tr>
<tr>
<td>9</td>
<td>C=CHPh</td>
<td>632.1</td>
</tr>
<tr>
<td>10</td>
<td>C=C(Ph)(_2)</td>
<td>601.4</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Overall ionization energy refers to the calculated difference in total energy between the two species: \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^0\) and \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^{-2}\)

Cage Expansion

When these species are oxidized, two framework electrons are lost from the cage, resulting in an expansion of the cage itself. This property may be diminished slightly with the addition of electrons from the substituents during oxidation. For the ether species, the cage expansion results have been tabulated below in Table 5.2. The cage expansion for the ether species may be grouped into three categories of magnitude. The first category includes species 1 – 5, the saturated alkyl groups and the unsubstituted hydroxyl group. Though the alkyl groups are electron donating, they do not provide much electron density into the cage, and so this category experiences the greatest cage expansion of the ether groups. The third category includes species 9 – 10, the substituents with the most π-electrons. This group of ether derivatives experiences the least amount of cage expansion due to the availability of π-electrons during oxidation. The second group, species 6 – 8, is intermediate between the first and third categories in terms of both cage expansion and the amount of π-electrons. The strong correlation between these two variables suggests that cage expansion is a function of the availability of π-electrons to the oxidized cage.
Table 5.2. Cage Expansion$^a$ of the Mono-Substituted Ether Derivatives of *closo*-Dodecahydrododecaborate

<table>
<thead>
<tr>
<th>Species</th>
<th>R</th>
<th>Cage Expansion (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>3.48</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>3.56</td>
</tr>
<tr>
<td>3</td>
<td>i-Pr</td>
<td>3.38</td>
</tr>
<tr>
<td>4</td>
<td>n-Bu</td>
<td>3.23</td>
</tr>
<tr>
<td>5</td>
<td>t-Bu</td>
<td>3.35</td>
</tr>
<tr>
<td>6</td>
<td>C=CH$_2$</td>
<td>2.56</td>
</tr>
<tr>
<td>7</td>
<td>C≡CH</td>
<td>2.66</td>
</tr>
<tr>
<td>8</td>
<td>Ph</td>
<td>2.32</td>
</tr>
<tr>
<td>9</td>
<td>C=CHPh</td>
<td>1.71</td>
</tr>
<tr>
<td>10</td>
<td>C=C(Ph)$_2$</td>
<td>1.31</td>
</tr>
</tbody>
</table>

$^a$Cage expansion refers to the calculated difference in the average boron-boron bond distance between the two species: $[\text{B}_{12}(\text{OR})\text{Cl}_{11}]^0$ and $[\text{B}_{12}(\text{OR})\text{Cl}_{11}]^2$.

Combined Substituent Support

As with previous chapters, the manifestation of $\pi$-back donation may be observed through cage-substituent bond distance shortening during oxidation. Here, the combined substituent contraction will be used to monitor this phenomenon, as shown in Table 5.3. The ether derivatives may be categorized into the same three categories as before. Category 1, including species 1 – 5, experience the greatest bond distance contraction, suggesting that the species in the category experience the most $\pi$-back bonding. Again, category 2, species 6 – 8, is an intermediate. Category 3, those species with the most $\pi$-electrons, or species 9 – 10, experiences the least bond distance contraction upon oxidation. For the ether species, it seems that the addition of $\pi$-electrons renders the need for $\pi$-back donation less necessary, and thus, the bond contraction becomes less apparent. For the category 3 compounds, there must exist an ulterior bond distance contraction or lengthening that could be used to monitor the shuttle of $\pi$-electrons into the cage upon oxidation.
Table 5.3. Combined Substituent Support\(^{[a]}\) of the Mono-Substituted Ether Derivatives of closo-Dodecahydrododecaborate

<table>
<thead>
<tr>
<th>Species</th>
<th>R</th>
<th>Combined Substituent Contraction (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>-10.31</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>-10.65</td>
</tr>
<tr>
<td>3</td>
<td>i-Pr</td>
<td>-11.34</td>
</tr>
<tr>
<td>4</td>
<td>n-Bu</td>
<td>-10.90</td>
</tr>
<tr>
<td>5</td>
<td>t-Bu</td>
<td>-11.61</td>
</tr>
<tr>
<td>6</td>
<td>C=CH(_2)</td>
<td>-8.38</td>
</tr>
<tr>
<td>7</td>
<td>C≡CH</td>
<td>-7.92</td>
</tr>
<tr>
<td>8</td>
<td>Ph</td>
<td>-8.03</td>
</tr>
<tr>
<td>9</td>
<td>C=CH(_2)</td>
<td>-5.66</td>
</tr>
<tr>
<td>10</td>
<td>C=C(Ph(_2))</td>
<td>-4.65</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Combined substituent support refers to the calculated difference in the sum of the bond length between the cage and both substituents (B-Cl distances were averaged.) between the two species: \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^0\) and \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^{-2}\)

Alkene and Benzene Contraction

To examine the nature of the conjugated systems more, it was noticed that the alkene bond lengthened and the benzene bond shortened upon oxidation. These bonds are shown in Figure 5.1 below for clarity. For the relevant species, these values are tabulated below.

Generally, the more electrons within the conjugated substituent, the longer the alkene bond and the more contracted the benzene bond becomes. Within the context of previous chapters, these phenomena seem to arise from a similar mechanism as π-back bonding. The significant difference present here as compared to the \([\text{B}_{12}(\text{YH})\_n\text{X}_{12-n}]\) species is the multiple electron shuttle. For these mono-substituted ether species, conjugation may allow for significant electron density to be shuttled into the cage, stabilizing oxidation all the more.
Figure 5.1. Representation of the alkene and benzene bonds being monitored for evidence of the electron shuttled between \( \pi \)-rich substituents and the oxidized cage.

Table 5.4. Alkene Bond Lengthening\(^{[a]}\) and Benzene Contraction\(^{[b]}\) of the Mono-Substituted Ether Derivatives of \( \textit{closo} \)-Dodecahydrododecaborate

<table>
<thead>
<tr>
<th>Species</th>
<th>R</th>
<th>Alkene Lengthening (pm)</th>
<th>Benzene Contraction (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C=CH(_2)</td>
<td>1.08</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>C≡CH</td>
<td>0.32</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>n/a</td>
<td>-1.01</td>
</tr>
<tr>
<td>4</td>
<td>C=CHPh</td>
<td>2.79</td>
<td>-0.80</td>
</tr>
<tr>
<td>5</td>
<td>C=C(Ph)(_2)</td>
<td>4.29</td>
<td>-0.12</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Alkene bond lengthening refers to the calculated increase in the bond length of the alkene bonds between the two species: \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^0\) and \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^{-2}\)

\(^{[b]}\) Benzene contraction refers to the calculated shortening in the bond length depicted in Figure 1 between the two species: \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^0\) and \([\text{B}_{12}(\text{OR})\text{Cl}_{11}]^{-2}\)

\textit{Conclusion}

A computational analysis of a variety of mono-substituted ether derivatives of the perchlorinated dodecaborate cage has been done using density functional theory. It has been shown that electron donating and \( \pi \)-rich substituents stabilize the neutral species affording a more favorable oxidation pathway. Furthermore, it was seen that particularly for \( \pi \)-rich systems the mechanism for this stabilization is not \( \pi \)-back donation, as is common for dodecaborate
derivatives. It appears that \( \pi \)-rich substituents stabilize the cage through a more direct electron shuttle, rather than the indirect back donation.
References

Chapter 6: Conjugation Between Substituents and *closo*-Dodecahydrododecaborate

The two-electron oxidation pathway available to derivatives of *closo*-dodecahydrododecaborate requires some mechanism of electron density support from the substituents into the cage of the neutral species. This is so due to the support the 26 framework electrons supply the stable dianion species. In previous chapters it was elucidated that π-electron density and a direct shuttle from π-rich substituents provide such support to allow for oxidation to occur. In this chapter, the nature of support provided from conjugated substituents, particularly phenyl groups directly bonded to the cage, will be examined.

Furthermore, the potential for conjugation between the cage and phenyl substituents will be investigated. The ability of substituents to conjugate with the dodecaborate cage is of high interest, as this could allow the electrons present in the electronic scaffold to be varied.

*Computational Methods*

All calculations were performed using DFT as found in the Gaussian 09 suite of programs\(^1\). Geometry optimizations and vibrational frequencies were completed at the BPV86/cc-pVTZ level of theory. For validation of the model, the perhalogenated, or B\(_{12}X_{12}\), boron – halogen bond distances and ionization energies were compared to experimental values found in the literature\(^20\). The particular level of theory was chosen, as the literature\(^19\)\textsuperscript{21} found it to be reliable for systems of this type. An aug – cc – pVTZ basis set was also assessed, but was found not to increase the consistency with experimental data for the B\(_{12}Cl_{12}^{2-}\) species.
All values used for trend comparisons were taken as a change between oxidation states. In all cases, the change in the general property, \( P \), may be represented as:

\[
\Delta P = P_{\text{neutral}} - P_{\text{dianion}}
\]

Values taken in this way were substituent support (\( \Delta \text{ BC} \) and \( \Delta \text{ BCC} \)).

Additionally a charge density profile was made for the 1,12 isomer of \([\text{B}_{12}\text{H}_{10}\text{Ph}_2]^{-2/0}\). This was generated and visualized using the program GaussView\(^5\).

**Results and Discussion**

Charge Distribution

The effect of electron movement in an aromatic system may be monitored through charge distribution along the oxidized pathway. This is shown for the stable dianion and two-electron oxidized product of 1,12-[\(\text{B}_{12}\text{H}_{10}\text{Ph}_2\)] in Figure 6.1 below. From these images, it is qualitatively observed that the boron atoms that are bonded to the phenyl substituents become increasingly positive during oxidation. This is quantified in Table 6.1 for the dianion and neutral species.

Starting with the boron atoms, it is observed that though the cage is undergoing a two-electron oxidation the ‘middle’ boron atoms have an increase in electron density. The carbon atoms on the phenyl substituents, particularly those labeled ‘outside’ have lost electron density upon oxidation. This observation in charge density allocation along with the conclusion from the previous chapters that the cage must have an influx of electrons during oxidation suggests that the phenyl substituents are shuttling electrons in upon oxidation.
Figure 6.1. Gaussian generated charge distribution image (red: negative; green: positive) for both $\text{1,12}^{-}[\text{B}_{12}\text{H}_{10}\text{Ph}_{2}]^{2/0}$ species (a: the stable dianion species; b: the oxidized, neutral species).

Table 6.1. Charge Distribution$^\text{[a]}$ of the $\text{1,12}^{-}[\text{B}_{12}\text{H}_{10}\text{Ph}_{2}]^{2/0}$ species

<table>
<thead>
<tr>
<th>Borons</th>
<th>Dianion</th>
<th>Neutral</th>
<th>Carbons</th>
<th>Dianion</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Directly Bonded</td>
<td>0.329</td>
<td>0.412</td>
<td>Directly Bonded</td>
<td>-0.114</td>
<td>-0.109</td>
</tr>
<tr>
<td>Bonded$^\text{[b]}$</td>
<td>-0.086</td>
<td>-0.106</td>
<td>Bonded$^\text{[b]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle$^\text{[c]}$</td>
<td></td>
<td></td>
<td>Outside$^\text{[d]}$</td>
<td>-0.122</td>
<td>-0.084</td>
</tr>
</tbody>
</table>

$^\text{[a]}$Charge distribution is the average Mulliken charge calculated and visualized in the Gaussian program.

$^\text{[b]}$Boron and carbon atoms under the category ‘Directly Bonded’ refers to those atoms directly bonded to the phenyl substituent or dodecaborate cage respectively.

$^\text{[c]}$Boron atoms under the category ‘Middle’ refers to those ten boron atoms unsubstituted.

$^\text{[d]}$Carbon atoms under the category ‘Outside’ refers to those ten carbon atoms on the phenyl rings that are unsubstituted.

Cage-Phenyl Bond Distance Contraction

Electrons shuttled from the substituents into the cage by any mechanism i.e. conjugation or $\pi$-back donation may be monitored via the change in cage-substituent bond distance. This contraction is quantified for all three isomers in Table 6.2 below. Each isomer shows a significant contraction of this bond between -5 and -6 pm, suggesting that there is additional
electron density between the cage and phenyl group upon oxidation. This contraction supports the notion that the phenyl groups are shuttling electron density into the cage to stabilize the neutral species during oxidation.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>1,2</th>
<th>1,7</th>
<th>1,12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta BC$ (pm)</td>
<td>-6.14</td>
<td>-5.24</td>
<td>-5.68</td>
</tr>
</tbody>
</table>

$^a$Cage-Phenyl bond distance contraction refers to the average change in bond distance between the carbon and boron atoms involved in the direct bond between the cage and phenyl group between the two charge states: $[\text{B}_{12}\text{H}_{10}\text{Ph}_2]^0$ and $[\text{B}_{12}\text{H}_{10}\text{Ph}_2]^-$.

Benzene Contraction

In an effort to examine the potential of conjugation between the phenyl substituents and the cage, the bond distances of the phenyl substituents were monitored. In particular it was noticed that the carbon-carbon bond ‘parallel’ to the cage, depicted in Figure 6.2, shortened upon oxidation. The values for this contraction are shown in Table 6.3 for each isomer. A significant shortening of this bond is observed for each isomer, causing the bond order to be closer to 2 than its original 1.5. Such a contraction accompanied with the influx of electron density observed from the charge distribution suggests that the phenyl groups are indeed conjugated with the cage.

![Figure 6.2](image-url)
Table 6.3. Benzene Contraction\(^{[a]}\) of the Diphenyl Derivatives of closo-Dodecahydrododecaborate

<table>
<thead>
<tr>
<th>Isomer</th>
<th>1,2</th>
<th>1,7</th>
<th>1,12</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔBC (pm)</td>
<td>-1.21</td>
<td>-1.29</td>
<td>-1.30</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Benzene contraction refers to the calculated shortening in the bond length depicted in Figure 2 between the two species: \([\text{B}_{12}\text{H}_{10}\text{Ph}_2]^0\) and \([\text{B}_{12}\text{H}_{10}\text{Ph}_2]^2\)

Conclusion

A computational analysis of the three isomers of the diphenyl derivatives of closo-dodecahydrododecaborate, or \([\text{B}_{12}\text{H}_{10}\text{Ph}_2]\), has been performed using density functional theory. It has been shown that the phenyl substituents shuttle electron density into the cage during oxidation, leading to a shortening of the bond distances between the cage and the phenyl groups. In addition, it was seen that the phenyl groups undergo a contraction, such that conjugation of the substituents with the cage seems likely. Furthermore, it has been now seen that the dodecaborate cage may be supported by an influx of electron density afforded due to conjugation.
References

Chapter 7: Use of Substituents as Source and Drain on \textit{closo-}
Dodecahydrododecaborate

For dodecaborate to be utilized as an SMT scaffold, it will need to be shown and understood how a chemical source and drain may be used to shuttle electrons. Further, the redox – gate switch will need to be evaluated. To begin such a foundational understanding, this work computationally evaluates the derivative [B$_{12}$Cl$_{10}$NH$_2$NO$_2$].

\textit{Computational Methods}

All calculations were performed using DFT as found in the Gaussian 09 suite of programs\textsuperscript{1}. Geometry optimizations and vibrational frequencies were completed at the BPV86/cc-pVTZ level of theory. For validation of the model, the perhalogenated, or B$_{12}$X$_{12}$, values were compared to experimental values found in the literature\textsuperscript{2}. The particular level of theory was chosen, as the literature\textsuperscript{2-4} found it to be reliable for systems of this type. An aug – cc – pVTZ basis set used and found not to increase the consistency with experimental data for the B$_{12}$Cl$_{12}$\textsuperscript{2/-0} species.

The three isomers – ortho, meta, and para were each tested. These were generated by functionalizing the previously optimized perchlorinated dodecaborate cage.

All properties examined were taken as a change between oxidation states. In all cases, the change in the general property, P, may be represented as:

\[ \Delta P = P_{\text{neutral}} - P_{\text{dianion}} \]
Values taken in this way were $\Delta \text{BB}$, $\Delta \text{BCl}$, $\Delta \text{BN}$ (nitro and amino), and overall ionization energy.

**Results and Discussion**

Oxidation Pathway Energetics

The energy needed to toggle a redox-gated transistor “on/off” may be quantified by the overall ionization energy. The calculated overall ionization energies are shown in Table 7.1 for the amino, nitro derivatives along with the perchlorinated cage for comparison. The addition of the amino and nitro substituents afforded a significant (more than 100 kJ mol$^{-1}$) decrease in overall ionization energy compared to just the perchlorinated cage. The increase in favorability of the oxidation pathway could be due to the electron donating nature of the amino group. The support given by the amino group may be indirectly monitored through the change in cage-substituent bond distance upon oxidation.

<table>
<thead>
<tr>
<th>Species</th>
<th>Overall Ionization Energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho $[\text{B}<em>{12}\text{Cl}</em>{10}\text{NH}_2\text{NO}_2]$</td>
<td>656.6</td>
</tr>
<tr>
<td>meta $[\text{B}<em>{12}\text{Cl}</em>{10}\text{NH}_2\text{NO}_2]$</td>
<td>667.9</td>
</tr>
<tr>
<td>para $[\text{B}<em>{12}\text{Cl}</em>{10}\text{NH}_2\text{NO}_2]$</td>
<td>673.9</td>
</tr>
<tr>
<td>$[\text{B}<em>{12}\text{Cl}</em>{12}]$</td>
<td>835.8</td>
</tr>
</tbody>
</table>

[a] Overall ionization energy refers to the calculated difference in total energy between the two species: $[\text{B}_{12}\text{Cl}_{10}\text{NH}_2\text{NO}_2]^0$ and $[\text{B}_{12}\text{Cl}_{10}\text{NH}_2\text{NO}_2]^2$

Owing to the fact that oxidation removes framework electrons, the cage expands during oxidation. In general, the greater amount of electron density from the substituents into the cage, the lesser the cage expansion becomes. To monitor the expansion, the change in average boron–boron bond distance was monitored for each amino, nitro derivative and is shown alongside the
perchlorinated cage in Table 7.2. Due to the amino group being electron donating, the cage expansion is less for the amino, nitro derivatives, as compared to just the perchlorinated cage.

<table>
<thead>
<tr>
<th>Table 7.2. Cage Expansion[^a] of the Amino, Nitro Perchlorinated Derivatives of closo-Dodecahydrododecaborate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>ortho [B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}]</td>
</tr>
<tr>
<td>meta [B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}]</td>
</tr>
<tr>
<td>para [B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}]</td>
</tr>
<tr>
<td>[B\textsubscript{12}Cl\textsubscript{12}]</td>
</tr>
</tbody>
</table>

[^a]Cage expansion refers to the calculated difference in the average boron-boron bond distance between the two species: [B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}]\textsuperscript{0} and [B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}]\textsuperscript{2}.

Substituent Support

Upon oxidation, it has been shown the substituents π-back donates with the cage. This occurrence causes a shortening in the bond distance between the cage and the particular substituent atom. Thus, the amount of support, or more precisely electron density, may be conveniently monitored through the bond distance change. For each substituent this is bond distance shortening is shown in the amino, nitro derivatives, alongside the perchlorinated cage for comparison in Table 7.3.

For each isomer of [B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}] the amino – cage bond distance has the greatest bond distance shortening, as follows the electron donating nature of the amino substituent. The nitro – cage bond distance, on the other hand, experiences the least bond distance shortening. This disparity between the amino and nitro support suggests that on a dodecaborate scaffold the two substituents do indeed act as a source and drain. Furthermore, though each isomer functions as a potential transistor, the ortho isomer experiences the greatest difference between support provided by the amino and nitro groups.
Table 7.3. Substituent Support\(^{[a]}\) of the Amino, Nitro Perchlorinated Derivatives of \textit{closo}-Dodecahydrododecaborate

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔBCl (pm)</th>
<th>ΔBN\textsubscript{amino} (pm)</th>
<th>ΔBN\textsubscript{nitro} (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{ortho}</td>
<td>-4.73</td>
<td>-7.22</td>
<td>-0.75</td>
</tr>
<tr>
<td>\textit{meta}</td>
<td>-4.67</td>
<td>-7.13</td>
<td>-1.54</td>
</tr>
<tr>
<td>\textit{para}</td>
<td>-4.54</td>
<td>-7.11</td>
<td>-2.32</td>
</tr>
<tr>
<td>\textit{[B\textsubscript{12}Cl\textsubscript{12}]}</td>
<td>-4.91</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Substituent support refers to the calculated difference in bond distance between the cage and substituent between the two species: \([\text{B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}}]\)\(^0\) and \([\text{B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}}]\)\(^2\)

Conclusion

For \textit{closo}-dodecahydrododecaborate to be used as a scaffold for a molecular transistor, it must be able to be coupled with a chemical source and drain, while maintaining redox-gate functionality. This was tested on the \([\text{B\textsubscript{12}Cl\textsubscript{10}NH\textsubscript{2}NO\textsubscript{2}}]\) derivatives using a DFT model. It was seen that the amino and nitro groups increase the favorability of the oxidation pathway. Additionally, the change in substituent – cage bond distances upon oxidation shows that the amino group acts as a source, while the nitro group acts a drain.
References


From the computational studies in Chapter 3 the utility of the hydroxyl derivative as a π-back donor was observed. Further, the hydroxyl derivatives serve as a synthetic precursor for several other derivatives, including many of the ether derivatives discussed in Chapter 5.1 Thus, synthesizing the hydroxyl derivatives will be useful in allowing further insight into the system by way of spectroscopy and potentially serving as a starting point for further functionalization. The synthesis of the hydroxyl derivatives has already been described in the literature2; however, the conditions therein are not precisely detailed. This section describes the conditions for a controlled and precise hydroxylation of dodecaborane.

**Experimental Methods**

**General Considerations.** Cs₂[B₁₂H₁₂] was obtained from Twelfth Vertex company. All other reagents were purchased from Sigma Aldrich and used without further purification unless otherwise noted. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon unless otherwise noted. NMR data were collected at room temperature on a Bruker DRX 300 MHz NMR spectrometer. ¹H NMR spectra were referenced to the appropriate solvent peak or 7.24 ppm for residual d-chloroform. ¹¹B NMR spectra were given with respect to external Et₂O·BF₃ (δ(¹¹B) 0 ppm).

**Synthesis of Bis(methyltriphenylphosphonium) Hydroxyl-un-decahydro-closo-dodecaborate(2-),[MePPh₃]₂B₁₂H₁₁(OH)₁.** A method similar to that previously reported¹³ was modified as follows: 8 mL of 95.7% sulfuric acid was cautiously added to 12 mL of ultrapure,
deionized water. 0.5 g (1.23mmol) of Cs$_2$B$_{12}$H$_{12}$ was added into this. The mixture was then refluxed at 110°C for 50 minutes ($^{11}$B NMR spectroscopy was used to determine the end of the reaction). Once at room temperature, the solution was neutralized with careful addition of a 20g CaCO$_3$ per 200 mL water slurry. Vacuum filtration was used to remove CaSO$_4$. The volume of the filtration was reduced to approximately 30 mL. 1.50 g (5.04 mmol) of methyltriphenylphosphonium bromide was added to the filtrate. Immediately, white precipitates were observed. The mixture was stored at 4°C overnight. The precipitate was filtered, dried, and recrystallized from acetonitrile/ethanol. The reaction yielded 0.701g (80%). Both the $^1$HNMR and $^{11}$BNMR were consistent with previously reported data. $^{11}$B NMR (300 MHz, CH$_3$CN): δ -23.40 (d, J= 1.32 Hz, 1B), -17.27 (d, J= 1.34 Hz, 5B), -15.04 (d, J= 1.33 Hz, 5B), 6.43 (s, 1B).

This reaction was done on multiple scales. All reagents were scaled proportionally. On the 5 g (12.3mmol) scale, a yield of 7.44 g (85%) was observed. On the 10 g (24.6mmol) scale, a yield of 15.02 g (86%) was observed.

**Synthesis of Bis(methyltriphenylphosphonium)-1,7-Dihydroxyl-decahydro-closo-dodecaborate(2-), [MePPh$_3$]$_2$B$_{12}$H$_{10}$(OH)$_2$.** The method for the above synthesis of bis(methyltriphenylphosphonium) hydroxyl-un-decahydro-closo-dodecaborane(2-) was modified as followed: The mixture was refluxed at 140°C for 12 hours. On the 0.5 g (1.23mmol) scale, a yield of 0.610 g (68%) was observed. Both the $^1$HNMR and $^{11}$BNMR were consistent with previously reported data. $^{11}$B NMR (300 MHz, CH$_3$CN): δ -23.75 (d, J= 1.31 Hz, 2B), -20.03 (d, J= 1.34 Hz, 2B), -17.42 (d, J=1.34 Hz, 4B), -15.28 (d, J= n/a, 2B), 4.23 (s, 2B). On the 5 g (12.3mmol) scale, a yield of 6.01 g (67%) was observed. On the 10 g (24.6mmol) scale, a yield of 15.02 g (86%) was observed.
Synthesis of Bis{bis[(triphenylphosphoranylidene)ammonium]}-1,7,9-Trihydroxy-nonahydro-closo-dodecaborate(2-), [PPN]$_2$B$_{12}$H$_9$(OH)$_3$. A method similar to that previously reported$^6$ was modified as follows: 8 mL of 95.7% sulfuric acid was cautiously added to 12 mL of ultrapure, deionized water. 0.500 g (1.23 mmol) of Cs$_2$B$_{12}$H$_{12}$ was added into this. The mixture was refluxed at 140°C for 24 hours ($^{11}$B NMR spectroscopy was used to determine the end of the reaction). Once at room temperature, the solution was neutralized with careful addition of a 20 g CaCO$_3$ per 200 mL water slurry. Vacuum filtration was used to remove CaSO$_4$. The volume of the filtration as reduced to about 30 mL. 1.41 g (2.46 mmol) of bis(triphenylphosphine)iminium chloride was added to the filtrate. Immediately white precipitates were observed. The mixture was stored at 4°C overnight. The precipitate was filtered, dried, and recrystallized from ethyl acetate. The reaction yielded 1.43 g (92%). Both the $^1$HNMR and $^{11}$BNMR were consistent with previously reported data. 11B NMR (300 MHz, CH$_3$CN): δ -23.94 (d, J=1.29 Hz, 3B), -20.03 (d, J= 1.30 Hz, 3B), -17.43 (d, J= 1.27 Hz, 3B), 1.92 (s, 3B). On the 5 g (12.3 mmol) scale, a yield of 15.23 g (98%) was observed. On the 10 g (24.6 mmol) scale, a yield of 29.49 g (98%) was observed.

Alternative Synthesis of Bis(methyltriphenylphosphonium) Hydroxyl-undecahydro-closo-dodecaborate(2-), [MePPh$_3$]$_2$B$_{12}$H$_{11}$(OH)$_1$ Previously$^2$, the hydroxylation of the cage has been reported to proceed through an acid catalyzed mechanism. This hypothesis was tested by exchanging sulfuric acid with hydrochloric acid keeping all other reaction conditions identical as for the synthesis of [MePPh$_3$]$_2$B$_{12}$H$_{11}$(OH)$_1$.

Results and Discussion

The reaction conditions and average yields for products [MePPh$_3$]$_2$B$_{12}$H$_{11}$(OH)$_1$, [MePPh$_3$]$_2$B$_{12}$H$_{10}$(OH)$_2$, and [PPN]$_2$B$_{12}$H$_9$(OH)$_3$ may be seen in Table 8.1. The $^{11}$B-NMR spectra
for these products may be found in the Supplemental Section. Cs₂B₁₂H₁₂ was heated in a solution of sulfuric acid at 90°C for 5 hours, which yielded crystalline [MePPh₃]₂B₁₂H₁₁(OH)₁ after workup. This reaction was performed multiple times and gave an average yield of 72.5 %. When the temperature was increased to 110°C, the reaction reached completion at 50 minutes with a 72% yield. The temperature could not pragmatically be increased to 140°C, as [MePPh₃]₂B₁₂H₁₀(OH)₂ begins to form.

Heating Cs₂B₁₂H₁₂ for 27 hours at 110°C in a solution of sulfuric acid produced [MePPh₃]₂B₁₂H₁₀(OH)₂ exclusively upon workup. This reaction produced a 51.5 % yield on average. Increasing the temperature to 140°C, gives a reaction time of 12 hours and a better percent yield on average. A reaction temperature of 90°C was not vigorous enough to provide product in a practical amount of time.

Heating Cs₂B₁₂H₁₂ for 23.5 hours at 140°C in a solution of sulfuric acid produced [PPN]₂B₁₂H₉(OH)₃ upon workup. On average this reaction was in 92.0 % yield. The reaction did not go to completion at 110°C after 163 hours.

<table>
<thead>
<tr>
<th>Table 8.1: Reaction Conditions and Yields for Products 2, 3, and 4</th>
</tr>
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<tbody>
<tr>
<td>Product</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>[MePPh₃]₂B₁₂H₁₁(OH)₁</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>[MePPh₃]₂B₁₂H₁₀(OH)₂</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>[PPN]₂B₁₂H₉(OH)₃</td>
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<td></td>
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</tbody>
</table>
Following the alternative synthesis for \([\text{MePPh}_3]_2\text{B}_{12}\text{H}_{11}(\text{OH})_1\) using hydrochloric acid in place of sulfuric acid, no evidence of hydroxylation was present.

**Conclusion**

The precise and controlled synthesis of \([\text{MePPh}_3]_2\text{B}_{12}\text{H}_{11}(\text{OH})\), \([\text{MePPh}_3]_2\text{B}_{12}\text{H}_{10}(\text{OH})_2\), and \([\text{PPN}]_2\text{B}_{12}\text{H}_9(\text{OH})_3\) has been demonstrated at multiple times and temperatures and at higher yields than previously reported. Both the \([\text{MePPh}_3]_2\text{B}_{12}\text{H}_{10}(\text{OH})_2\) and \([\text{PPN}]_2\text{B}_{12}\text{H}_9(\text{OH})_3\) could theoretically exist as a variety of isomers; however, during the course of these studies the 1,7 and 1,7,9 respective isomers were exclusively seen. Continued work will include a synthesis of \([\text{PPN}]_2\text{B}_{12}\text{H}_8(\text{OH})_4\) to see if only one isomer is produced. Furthermore, the previous suggestion that the hydroxylation of the cage proceeds via an acid-catalyzed mechanism has been disproven. When reacted with hydrochloric acid under the same conditions as sulfuric acid, no evidence of hydroxylation was found. Further investigation will be needed to determine the catalyst.
References


Chapter 9: Computational Examination of the Transition Metal Bis(dicarbollide) Sandwich Complex

The dicarbollide ligand, \([\text{C}_2\text{B}_9]^-\), has been shown to form sandwich complexes with transition metals.\(^1\)\(^2\). A model metal bis(dicarbollide) sandwich complex is shown in Figure 9.1. The most stable conformation of the sandwich complex is dependent upon the metal and its oxidation state. Though one conformation is preferable, thermal energy allow for free rotation at room temperature with the metals whose rotation has been studied so far, namely \(\text{Ni}^{3+}\) and \(\text{Co}^{4+}\). The proper transition metal could feasibly have high enough energy barriers to allow only the thermodynamically favorable conformation at room temperature. If this metal then had a different preferred conformation in its other oxidation state, the transition metal bis(dicarbollide) sandwich complex would be a redox-induced molecular rotor.

![Figure 9.1. A representation of a metal bis(dicarbollide) sandwich complex](image)

Herein, an examination of first- and second-row transition metals is performed to determine viability towards a redox-induced molecular rotor.
Computational Methods

All calculations were performed using DFT as found in the Gaussian 09 suite of programs. Geometry optimizations and vibrational frequencies for the first – row transition metal bisdicarbollide sandwich complexes were completed at the BPV86/cc-pVTZ level of theory. Geometry optimizations and vibrational frequencies for the second – row transition metal bisdicarbollide sandwich complexes were completed at the BPV86/SDD level of theory. All atoms in the structure were described using an SDD basis set. The dicarbollide ligand cups were systematically placed around the metal with varying dihedral angles to construct the rotational angle curve. This was done independently for each oxidation state of each metal. The oxidation state of the metal was changed by altering the overall charge of the molecule. The dihedral angle chosen to monitor the system was the C1-B9-B18-C33 dihedral angle from 0 to 180°, as previously used in the literature. The relative energy of each dihedral angle was taken in reference to the energy of the global minimum of the lowest oxidation state, (III), for each metal.

Results and Discussion

Nickel Bis(dicarbollide) Sandwich Complex

To gain some perspective with an experimental comparison the Ni (III)/ (IV) bis(dicarbollide) sandwich complex was studied first. The rotational angle curves for both oxidation states are shown in Figure 9.2. Both curves predict or observe the same minima and maxima for both oxidation states. Furthermore, both the predicted and observed curve have similar rotational energy barriers as seen in the literature. Due to the low energy barriers, these
species would undergo free rotation at room temperature. Thus, other metals should be examined to determine viability for a redox – induced molecular rotor.

![Graph showing dihedral rotational curves for Ni (III)/(IV) bisdicarbollide sandwich complexes](image)

**Figure 9.2.** Dihedral rotational curves for the Ni (III)/(IV) bisdicarbollide sandwich complexes

**Cobalt and Iron Bisdicarbollide Sandwich Complexes**

A dihedral rotational curve was produced for both the Co (III)/(IV) and Fe (III)/(IV) bisdicarbollide sandwich complexes. These are shown in Figures 9.3 and 9.4, respectively. In the lower oxidation state both Co and Fe exhibit a similar global minimum as Ni. Neither,
however, have a large enough energy barrier to warrant a stabilized energy well. In addition, both Co(IV) and Fe(IV) are much higher in energy relative to their lower oxidation state than Ni (IV) was with its lower oxidation state. Thus, neither Co nor Fe is a good candidate for redox– induced molecular rotors under the criteria developed.

Figure 9.3. Dihedral rotational curves for the Co (III)/(IV) bisdicarbollide sandwich complexes
Validating a Basis Set for the Palladium Bisdicarbollide Sandwich Complex

In order to study any second–row metal, including Pd, a new computational method needed to be validated. To do so, the Ni(IV) bisdicarbollide sandwich complex’s dihedral rotational curve was generated under various basis sets that are amenable to second–row metals. The three basis sets chosen were LanL2DZ, LanL2MB, and SDD. These were chosen due to their frequency and reliability for Pd in the literature. The curves generated for Ni(IV) under these basis sets are shown in Figure 9.5, alongside cc-pVTZ for comparison.

Figure 9.4. Dihedral rotational curves for the Fe (III)/(IV) bisdicarbollide sandwich complexes
Each of the new basis sets predicts the same minima and maxima as the cc-pVTZ basis set did. The main difference between the new basis sets and the larger cc-pVTZ basis set is that the new basis sets predict higher energies for every dihedral angle than the cc-pVTZ. In order of increasing similarity with cc-pVTZ, the basis sets are arranged: LanL2MB < LanL2DZ < SDD.

**Figure 9.5.** The dihedral curves for the Ni(IV) bisdicarbollide sandwich complex with four different basis sets to compare accuracy and precision. (orange: cc-pVTZ; blue : LanL2DZ; green : LanL2MB; yellow : SDD)

**Palladium Bisdicarbollide System**

Using the SDD basis set the dihedral rotational curve for the Pd(III)/(IV) bisdicarbollide sandwich complexes were generated. The shapes, minima, and maxima are very similar between the Ni and Pd. A significant difference between the two metals is the increased barrier height observed in the Pd(III)/(IV) complexes. The largest barrier at 180° is about 4 kcal/mol higher in Pd(III)/(IV) than Ni(III)/(IV). This suggests the Pd(III)/(IV) shows the most potential in serving
as a molecular rotor of the metals studied in this work (Ni, Co, Fe, and Pd). A compilation of the data for these metals is shown in Table 9.1.

![Dihedral rotational curves for Pd(III)/(IV) Bisdicarbollide Sandwich Complexes](image)

**Figure 9.6.** Dihedral rotational curves for Pd(III)/(IV) Bisdicarbollide Sandwich Complexes
Table 9.1. Compiled Dihedral Rotational Data for Ni, Co, Fe, and Pd (III)/(IV) Bisdicarbollide Sandwich Complexes

<table>
<thead>
<tr>
<th></th>
<th>Ni(III)</th>
<th>Ni(IV)</th>
<th>Co(III)</th>
<th>Co(IV)</th>
<th>Fe(III)</th>
<th>Fe(IV)</th>
<th>Pd(III)</th>
<th>Pd(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Minimum[a]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(III)</td>
<td>68</td>
<td>145</td>
<td>0</td>
<td>79</td>
<td>10</td>
<td>10</td>
<td>145</td>
<td>145</td>
</tr>
<tr>
<td>Ni(IV)</td>
<td>5-7</td>
<td>14-15</td>
<td>4</td>
<td>4-6</td>
<td>4-5</td>
<td>2-8</td>
<td>10-12</td>
<td>10-12</td>
</tr>
<tr>
<td>Oxidation State Jump[b]</td>
<td>66</td>
<td>105</td>
<td>118</td>
<td>49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] The global minimum refers to the dihedral angle with the lowest total energy taken in the lowest oxidation state, (III).
[b] The rotational energy barriers refer to the energy difference between the global minimum and the local maxima to its immediate right and left.
[c] The oxidation state jump refers to the energy difference between the global minimum and the same angle in the higher oxidation state, (IV).

* Calculations using the basis set: cc-pVTZ.
† Calculations using the basis set: SDD.

Conclusion

A computational methodology to examine the rotational energies of first – row transition metal bisdicarbollide sandwich complexes was described. Ni, Co, and Fe (III) / (IV) were examined and determined to have shallow enough energy wells to allow for constant rotation at room temperature. To study second – row transition metal bisdicarbollide sandwich complexes the LanL2DZ, LanL2MB, and SDD basis sets were studied with the Ni (IV) bisdicarbollide system. It was determined that the SDD basis set provided the most similar values as did the cc-pVTZ basis set, and thus, it was used to calculate the Pd (III) / (IV) rotational curve. From this it was noticed that the rotational barriers are large enough that it is possible that Pd could have a fixed dihedral angle at room temperature. More generally, to screen a transition metal to exist in a metal bisdicarbollide sandwich complex to act as a redox – induced molecular rotor the following properties should be examined: global minima, rotational energy barriers, and the energy difference at the global minimum between the oxidation states.
References

7. Sperger, T.; Sanhueza, I.A.; Kalvet, I.; Schoenebeck, F. Chem. Rev. Article ASAP.
Chapter 10: Shifted Rotation of the Palladium Bisdicarbollide Sandwich Complex Due to Methyl Addition

The transition metal bisdicarbollide sandwich complex, \([\text{M(C}_2\text{B}_9\text{)}_2]^x\), exhibits free rotation at room temperature for several metals, such as Ni, Co, and Fe. Second – row metals, such as Pd, may place specific rotational conformations in an energy well, affording only one conformation at room temperature. The readily available oxidation pathways present to Pd and other second – row metals suggests that a second – row transition metal bisdicarbollide sandwich complex could be used as a redox – induced molecular rotor. In this way, functionalizing the ligand, either on a carbon or a boron atom, would be advantageous. Several groups have begun a synthetic library towards such functionalities on both the carbon\(^{1-3}\) and boron\(^{4-6}\) atoms. Though this has been studied synthetically, the effect on rotation of the addition of an R group has not been examined thoroughly. Herein, the dihedral rotational curve of a Pd (IV) bisdicarbollide sandwich complex with a methyl group attached to one carbon atom, shown in Figure 10.1, is studied.

\[ \text{Figure 10.1. A representation of the Pd (IV) bisdicarbollide sandwich complex with a methyl group attached} \]
Computational Methods

All calculations were performed using DFT as found in the Gaussian 09 suite of programs\(^7\). Geometry optimizations and vibrational frequencies were completed at the BPV86/SDD level of theory for every atom in the structures. The total energies obtained from these calculations were plotted against the dihedral angle, C1-B9-B18-C33 to obtain the dihedral rotational curve.

Results and Discussion

The dihedral rotational curve of the Pd(IV) bisdicarbollide sandwich complex with and without the methyl group is shown in Figure 10.2. The addition of a methyl group does not appear to affect the rotational barriers, keeping the viability of the sandwich complex as a redox – induced molecular rotor. Though the same global minimum and maximum are seen at 145° and 116° respectively, the local minima and maxima have been significantly shifted. These values are shown in Table 10.1.
Conclusion

The effect on rotation of the addition of a methyl group to the Pd(IV) bisdicarbollide sandwich complex was monitored computationally through the dihedral rotational curve. No change in the rotational energy barriers was observed. The local minima and maxima shifted to larger angle values. To examine this effect further these studies should be carried out on the Pd (III) oxidation state as well.

Table 10.1. Dihedral Rotational Data for the Pd(IV) Bisdicarbollide Sandwich Complex with and without an Attached Methyl Group

<table>
<thead>
<tr>
<th></th>
<th>Pd (IV) ; R = CH₃</th>
<th>Pd (IV) ; R = H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Minimum (°)</td>
<td>145</td>
<td>145</td>
</tr>
<tr>
<td>Local Minima (°)</td>
<td>13, 90</td>
<td>5, 74</td>
</tr>
<tr>
<td>Global Maximum (°)</td>
<td>116</td>
<td>116</td>
</tr>
<tr>
<td>Local Maxima (°)</td>
<td>55, 111</td>
<td>40, 111</td>
</tr>
<tr>
<td>Rotational Energy Barriers (kcal / mol)</td>
<td>10 – 12</td>
<td>10 – 12</td>
</tr>
</tbody>
</table>
References:

Chapter 11 : Conclusion

Dodecaborate and the Beginning Puzzle Pieces

This collection of computational and experimental work grew out of an eclectic set of ideas in the literature. The puzzle pieces given described a unique three – dimensional¹, aromatic cluster² that when substituted could follow two, one – electron oxidation pathway³. An important piece of this metaphoric puzzle was that oxidation must be stabilized by some method, which was empirically done through cage substitution.⁴ Though proposed, π-back bonding was not fully elucidated for these species until this work.⁵ Stabilization is needed, in part, due to a loss of two of the 26 delocalized, framework electrons of the cage.⁶ In the first section of this work, Chapters 2 – 4, the intent is to comprehensively and analytically understand the nature of the oxidation pathway, dodecaborate’s response to oxidation, and, perhaps most intriguingly, the method or methods of stabilization in that pathway.

A Novel Computational and Data Processing Methodology to Describe Dodecaborate’s Oxidation Pathway

The work herein describes a systematic approach towards a complete and analytical description of dodecaborate and its derivatives’ oxidation pathway. The approach taken is a density functional theory calculation at the BPV86/cc-pVTZ level. This method is routinely used for calculations of systems of this type.⁵,⁷-⁸ The novel methodology is the large – scale data processing done and the creative approach taken to provide an informative description of the oxidation pathway.

To model the oxidation pathway, the following properties were examined: overall ionization energy, cage expansion, and substituent support. These were all modelled as a change
between the optimized dianion and neutral species. The overall ionization energy was examined, as it provides a direct correlation to experimental cyclic – voltammetry values. \(^8\) It also provides information about the favorability of the oxidation pathway, which shows the impact of the stabilization provided by the substituents. Cage expansion yields insight into the electron density the closomer is losing during oxidation and has been very useful at describing both the electron density given by the substituents and the overall stability of that particular pathway. Substituent support was examined following an empirical observation where the cage – substituent bond distance was seen to contract upon oxidation. This calculation is a direct observation of electron density an individual substituent shuttles into the closomer. It is with this property, that one is able to compare the stabilization provided by different substituents, potentially in a way to optimize a particular pathway.

The above methodology allowed for several predictions in coherence with experimental work found in the literature. \(^8\) It was observed that the neutral species of dodecaborate, \([\text{B}_{12}\text{H}_{12}]^0\), is unstable and does not exist. Furthermore, the cage – halogen bond distances and first ionization energies of the perhalogenated structures were found in agreement with experimental, literature values.

In addition, to a general model to describe the oxidation pathway, a methodology has been outlined to observe and quantify \(\pi\)-back bonding. To this end, a natural bond orbital analysis may be done. The \(\pi\)-back bonds are those bonds that appear in the neutral species, and not the dianion species, are of entirely p-character. These may be quantified both by the number of substituents on a particular closomer engaging in them, as well as the occupancy of each individual \(\pi\)-back bond.
Elucidation and Description of π – Back Donation within Derivatives of Dodecaborate

A major inquiry in this work is in regards to the mechanism of electronic support utilized between the cage and substituents upon oxidation, which had been only previously suggested to be π-back donation.\(^5\) There are several ways this work has supported this claim. Most notably, the natural bond orbital shows the presence of π-back bonds between several substituents and the dodecaborate cage. The effects of π-back donation are seen through the oxidation pathway properties i.e. the overall ionization energy, cage expansion, and substituent support.

As the cage receives more electron density or π-back donation, the neutral species becomes more stable, or more aptly, less unstable, thereby decreasing the overall ionization energy. This correlation is shown in Chapter 4, where the substituents in \([\text{B}_{12}(\text{SH})_n\text{F}_{12-n}]\) species unilaterally provide less π-back donation than the substituents in \([\text{B}_{12}(\text{OH})_n\text{F}_{12-n}]\), generating lower overall ionization energy values for all \(n\)-values of \([\text{B}_{12}(\text{OH})_n\text{F}_{12-n}]\) than \([\text{B}_{12}(\text{SH})_n\text{F}_{12-n}]\). As described earlier, the bond between the cage and substituent will become contracted during oxidation, if the substituent is providing π-back donation. In Chapter 4, it was observed that \([\text{B}_{12}(\text{SH})_n\text{F}_{12-n}]\) receives less π-back donation from its substituents than \([\text{B}_{12}(\text{OH})_n\text{F}_{12-n}]\). This is coupled with the increased cage – substituent bond distance contraction experienced by the \([\text{B}_{12}(\text{OH})_n\text{F}_{12-n}]\) species. Thus, the cage – substituent bond distance contraction will increase with an increase in π – back donation, as the attraction between the two becomes greater.

In addition to providing support for π-back donation, this work has been able to use the collected observations to both rank the donating abilities of the examined substituents, as well as develop a list of indications that a substituent would be a suitable π-back donor. To provide context for how the substituents are compared with regards to their π – back donation abilities,
the preceding logic regarding overall ionization energy, substituent support, and bond occupancy found in the natural bond orbital analysis will be used.

In Chapter 3, the halogens, F, Cl, and Br, were compared. It was found that these halogens increasingly provide \( \pi \) – back donation support as: \( \text{Br} < \text{Cl} < \text{F} \). Within these species, the comparison was quantified by the change in overall ionization energy as a hydroxyl substituent replaced one of the halogens (Table 3.3). In this comparison, it was found that the three examined halogens provided a less favorable oxidation pathway than the hydroxyl group. In Chapter 4, the chalcogens, -OH and -SH, were examined. Here, it was observed that the examined chalcogens provide increasing \( \pi \) – back donation support as: \( \text{SH} < \text{OH} \). Furthermore, one may infer a way to predict the relative \( \pi \) – donation ability a substituent will have from the data and idea presented herein. The closer in proximity the substituent is to the cage, the more \( \pi \) – back donation will occur. This may be rationalized by considering that nearness allows for better orbital overlap between the substituent and the empty \( p \) – orbitals around the cage. Both the halogen and chalcogen substituents examined follow this correlation.

*The Use of Dodecaborate as a Scaffold for a Single – Molecule Transistor*

The insight gained from the first section, Chapters 2 – 4, coupled with the previous information in the literature discussed in the beginning of this conclusion narrowed this work towards functionalizing derivatives for scaffolding molecular electronics. The specific electronic component studied is the single – molecule transistor. Among other reasons, dodecaborate serves as an exceptional candidate for such a component due to its oxidation pathway. Consider the natural bond orbital analyses done in Chapters 3 and 4. These showed \( \pi \) – back donation was only present in the neutral species, and not the dianion species. Thus, electronic communication can be redox – gated for derivatives of dodecaborate. The second section of this work, Chapter 5
– 7, examines various modalities of dodecaborate as a scaffold for a single – molecular transistor. Specifically, of interest is the possibility of conjugation between the substituents and the cage, the elucidation of a chemical source and drain, and a model to describe a wide library of functionalities.

First, in Chapter 5, a variety of ether derivatives were examined to both develop a library of useful derivatives and show the viability of the previously outlined computational model towards that library. In this work it is seen that π – rich substituents, such as phenyl ethers, provide a more favorable oxidation pathway than the hydroxyl group alone. This raises the question of whether or not a substituent could directly and completely conjugate with the dodecaborate cage.

This question of conjugation was addressed in Chapter 6, and is of importance towards electronic scaffolding, when considering the cage’s proclivity to couple with an exterior circuit. Using all regioisomers possible, the biphenyl system studied in Chapter 6 indicated that conjugation could indeed occur between the cage and a substituent. Considering that conjugation could occur, one must then consider the possibility of using a chemical source and drain, as in Chapter 7. The substituents modelled in this way were an -NH₂ and -NO₂ group, as the source and drain, respectively. Drawing primarily from the change in cage – nitrogen bond distances upon oxidation, it was observed that the amino and nitro groups exhibit properties of a source and drain.

These studies on the elucidation and description of π – back donation and the examination of dodecaborate towards electronic scaffolding provide on its basic level a foundation to further understand a complex oxidative relationship between cage and substituent. Moreover, it provides a systematic and analytical way model such a relationship by outlining
both a computational methodology and an intuitive way to process the large amount of data generated. For the field of polyhedral boranes, this work provides the first quantitative description of π–-back bonding within derivatives of dodecaborate. Toward molecular electronic, this work describes a novel scaffolding system to generate a wide library of single–molecule transistors.

**Utility of the Bisdicarbollide Transition Metal Sandwich Complex**

The further exploration of dodecaborate derivatives as a scaffold for molecular machines led to an interesting point in the literature. The bisdicarbollide transition metal sandwich complex is known, and has even been directed towards the use of controlled rotary motion. The goal of such a molecular device is to switch stable conformations based upon oxidation state. In screening candidate molecules, two parameters become pressingly important. The first is that both oxidation states must have a preferred conformation, where the rotational barriers are high enough to prevent significant thermal rotation at room temperature. The second is that the oxidation states must have unique stable conformations. The attempts in the literature have thus far been to functionalize one or both of the dicarbollide ligands to alter rotational barriers and stable conformations. The right conditions have not yet been found in this way. In this work rather than altering the dicarbollide ligands, the transition metals themselves were changed.

**A Computational Approach to the Generation of Rotational Potential Energy Diagrams for First and Second Row Bisdicarbollide Transition Metal Sandwich Complexes**

To computationally assess the effect the transition metals had on the rotation of the complexes, rotational potential energy diagrams were prepared for both oxidation states of the particular metals. Of the first–row transition metals studied, Ni, Co, and Fe, all exhibited free rotation, having rotational barriers less than 10 kcal mol⁻¹. Thus, a computational approach was designed for second–row transition metals.
The computational method outlined used a density functional theory model at the BPV86/SDD level. This was chosen after a comparison of basis sets, including LanL2DZ, LanL2MB, and SDD, on the Ni (IV) bisdicarbollide sandwich complex. For this control complex, the methodology was found to give similar results with the larger cc–pVTZ basis set.

**Viability of the Palladium Bisdicarbollide Sandwich Complex as a Redox – Induced Molecular Rotor**

In Chapter 9, the rotational potential energy diagram of the palladium bisdicarbollide sandwich complex was found using the previously described computational approach. Here, it was seen that palladium has rotational barriers higher than 10 kcal mol\(^{-1}\). Moreover, two, distinct conformations were observed for the two oxidation states of palladium. These were the initial requirements for a candidate transition metal to be considered viable towards a controlled, molecular rotor.

In Chapter 10, an example of how rotation might be affected by functionalizing one of the dicarbollide ligands was examined. The addition of a methyl group was found to shift the rotational maxima and minima quite significantly. Thus, for a thorough examination of a functionalized palladium bisdicarbollide sandwich complex, the rotational potential energy diagram would need to be generated for each individual functionalization.

**Conclusion**

This work began from a few key ideas in the literature, nucleating around π–back bonding and became angled towards building a library and systematic methodology of describing molecular electronic scaffolds. An analytical and comprehensive approach to describe the oxidation properties of dodecaborate derivatives was outlined and employed. The utility of π–back bonding in dodecaborate derivatives was described and used to further suggest paths towards stabilizing oxidation of the cage. Specific calculations to examine the viability of
dodecaborate as scaffold for a single – molecule transition were performed. These included ether functionalities, conjugation with substituents, and chemical sources and drains. To add to the molecular machinery capabilities of dodecaborate derivatives, the transition metal bisdicarbollide sandwich complexes were examined towards use as redox – induced molecular rotors. In this way, palladium was found to be a potential candidate towards that end.
References


Supplemental Information

$^{11}$B-NMR for Chapter 8 products

$[\text{MePPh}_3]_2\text{B}_{12}\text{H}_{11}(\text{OH})_1$

$[\text{MePPh}_3]_2\text{B}_{12}\text{H}_{10}(\text{OH})_2$
$[\text{PPN}]_2\text{B}_{12}\text{H}_6(\text{OH})_3$
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