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QTAIM Study of Bonding in Carboranes

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Abstract

The bonding in carboranes has been a subject of interest for scientists due to the number of atoms in close radial proximity of each other in the molecules despite being deficient of valence electrons[1]. A three-center-two-electron bond has been hypothesized to explain the boron atom's ability to form more than three bonds within a molecule and several papers have been written supporting the existence of this bonding arrangement within carboranes[10-11]. This study utilized computational chemistry techniques including DFT and the QTAIM method, the Laplacian scalars, charge values, basin paths, Poincare-Hopf algebra, and specifically, a B3LYP DFT method with an *ab initio* MP2 level of theory, and a 6-311+G(2d,p) basis set to produce a geometric optimization of two *closo*-carboranes. The computational results determined that there is no three-center-two-electron bonding in these molecules due to the satisfaction of the Poincare-Hopf theorem and because all the structures bond critical points connecting to ring critical points and to atoms. The smaller difference between the bond critical points and their corresponding ring critical points in the two axial positions of both molecules indicates they are the weakest and would break first. The breaking of the first axial bond would lead to the *nido* structure and subsequent breaking of the second the *arachno* structure, which supports Wade's Rules characterizing the cluster tightness of the *closo* structure from the *nido* and *arachno* structures. The structural characterization of carboranes is, therefore, more accurately described by Wade's Rules. The charge values and Laplacian scalars results show electron densities that indicate fragment behavior, like ligand behavior, between the boron and carbon atoms and their corresponding hydrogens. A more accurate theory for describing the bonding in carboranes would include steric proximity and ligand/fragment coordination to overcome the electron deficiency, combined with Wade's Rules for the characterization of structure.

1. Introduction

1.1 The Chemistry of Boron

A traditional drawing of a Lewis structure diagram is not possible with carboranes, due to the lack of electrons to satisfy the structure of the molecule, and when it was discovered that boron can make more than three bonds scientists began to hypothesize exactly how carboranes bond. Recent advances in the technology used for structural determination have established that boron atoms are capable of bonding in quite an unusual way. For example, diborane is structured in such a way that the hydrogen atoms form a bridge between the two boron atoms, which is abnormal considering the number of atoms versus the number of electrons in the molecule[1]. Molecules that consist of boron and hydrogen atoms are named boranes, molecules consisting of boron, carbon, and hydrogen atoms are named carboranes[2]. When two molecules possess the same numbers of valence electrons or the same electronic structure the molecules are referred to as isoelectronic with each other[2]. Particular borane and carborane molecules have certain characteristics in common that lead to similarities in their geometric, bonding, energetic, and reactive properties, and an isoelectronic series is a characteristic that can establish similarities in the properties of the molecules[1,3]. The alikeness in the properties allows for analysis and the development of generalized rules for boranes and carboranes that first started with Wade's rules, a way of counting electrons, and then eventually evolved into the current Jemmis mno rules, a consolidated method for classifying structures in boranes[3,4]. These rules are based on a $(4n + 2)$ formula similar to the Huckel rule for electron counting within organic molecules[5]. Carboranes that have an electron count of $(4n + 2)$ are prefixed with *closo-*, carboranes with an electron count of $(4n + 4)$ are prefixed with *nido-*, and carboranes with an electron count of $(4n + 6)$ are prefixed with *arachno-*. These prefixes also predict the structure of carboranes by indicating the number of vertices, (n) for *closo-*, $(n + 1)$ for *nido-*, and $(n + 2)$ for *arachno-* carboranes[1,5,6]. The *closo-*, *nido-*, and *arachno-* structures are shown in Figure 1 along with the arrows that designate their similarities of properties that first move down and then diagonally. Wade's and Jemmis' rules have been consistently used to rationalize the structure of carboranes by estimating the tightness of clusters that predict the structure of the molecule based on the number of vertices and electrons.

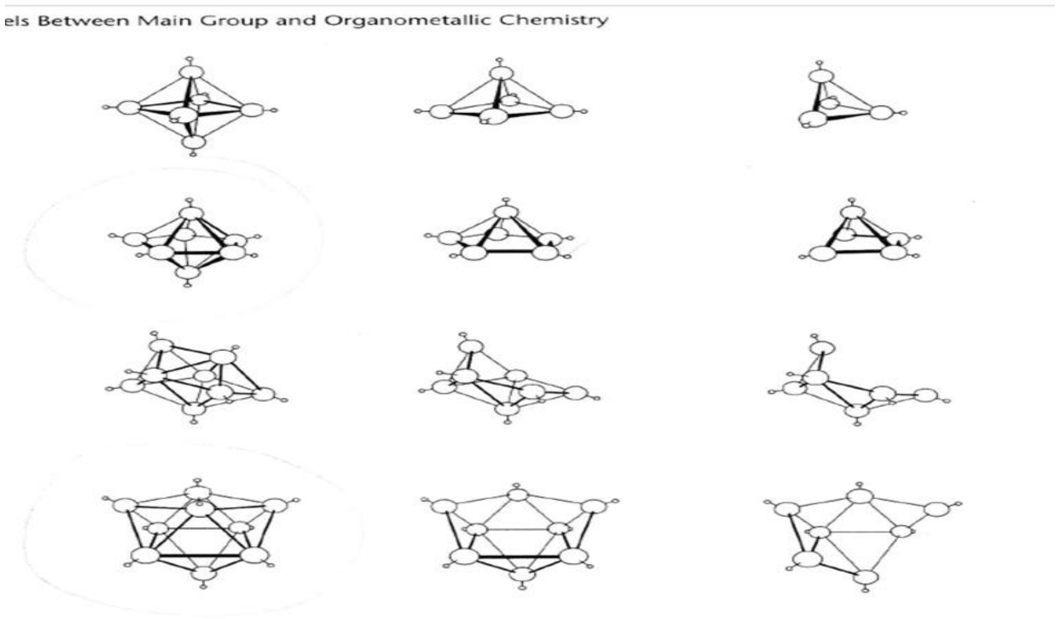

Figure 1- Structural types of carboranes Image from Miessler & Tarr 3rd Eds. 2004®

The methods that are used to analyze, compute, and theorize about the properties of boranes and carboranes can be divided into three groups: the experimental structural determination methods that include amounts of electron density localization between two atoms illustrate a bond physically by mathematically mapping the areas of highest electron probability[3]. A molecular graph of a molecule demonstrates graphically the connections between atoms, and the bond, ring, and cage critical points. A bcp, bond critical point, represents the minimum of electron density in one direction in space and maxima in the other two[3]. A rcp, ring critical point, represents the minimum of electron density in two points in space and maximum in the third[3]. A ccp, cage critical point, represents the minimum of electron density in all three directions of space[3]. A particular bond that consists of a three-center and two-electrons has been hypothesized to explain the deficiency of electrons compared to classical bonding in other boranes and carboranes[9,10,11]. The three-center-two-electron bond reportedly has two electrons in the bonding molecular orbital, and zero electrons in the nonbonding and antibonding orbitals, that are hypothesized to overcome the insufficiency of electrons and bond the three atoms together[9,10,11]. All critical points are stationary points in the electron density (the first derivative of $\rho(r) = 0$) in all three dimensions of space. An atom is the absolute maximum in all three dimensions. In topology, these critical points are categorized as (3,-3) for an atom, (3,-1) for a bond, (3,+1) for a ring and (3,+3) for a cage where the first number is the number of first derivatives that are equal to zero and the second number is the sum of the signs of the second derivatives. A three-center-two-electron bond is where one of the (3,-1) critical point joins three of the (3,-3) critical points instead of only two. DFT stands for density functional theory and is a computational quantum mechanical method that analyzes the structure of a molecule in its ground state using data on the electron density within a molecule. The B3LYP level of theory was chosen because of its previous success in generating electron densities for QTAIM analysis[9]. The Poincare-Hopf algebraic formula is often used to rationalize the configurations of molecules, where the number of bond critical points, ring critical points, and cage critical points are subtracted from the total number of atoms in the molecule[11]. Per the Poincare-Hopf Theorem, the solution to the formula should equal one for a molecule to theoretically exist in a stable configuration. Raman spectroscopy or x-ray crystallography, the computational structural determination methods that include DFT and NBO, and the bonding analysis methods that include QTAIM and Poincare-Hopf algebra. Ligands are ions or molecules that bind to a central atom and form a coordination complex through the donation of electrons[7]. Coordination chemistry theories like the Ligand Close-Packing Theory describe the relationship between ligands and the central atom in the complex[7]. Close-Packing Theory states that the geometry of a molecule allows for the coordinating ligands to be as sterically close together as possible, and that this proximity allows for the complex to be more energetically stable. The boron atom's ability to bond despite an electron deficiency may be explained by this energetic principle of stability based on steric proximity. QTAIM stands for the Quantum Theory of Atoms in Molecules and is a way of classifying crystalline structures mathematically by using the electron density expressions to calculate the molecule number of properties of a molecule based on an atomic view[1,8]. QTAIM treats each atom individually to discern patterns in bonding, energy, partial charge, and electron localization within a molecule. A QTAIM analysis examines the topology of the electron density (ρ) in a molecule and describes bonds and interatomic surfaces based on the gradient of rho leading to bond paths and critical points. Analyzing the Laplacian of the electron density rho values, ($\nabla^2(\rho)$),can reveal information about the electron localization within a molecule[3]. The Laplacian of the electron density results are the physical basis of VSPER, Valence Shell Electron Pair Repulsion Theory, and Lewis Theory of bonding[3]. The areas with the greatest amounts of electron density localization between two atoms illustrate a bond physically by mathematically mapping the areas of highest electron probability[3].

1.2 Previous Theoretical Studies

Molecular orbital calculations were performed on several borides, boranes, and carboranes to hypothesize the formula and geometry of plausible molecules that have yet to be discovered. The data collected from these calculations led to one of the first hypotheses of two- and three-center bonding within boranes and carboranes.[1] Jemmis used the RMP2(fc)/6-31G *ab initio* method and the three-dimensional Huckel method to report the relative energies of four isomers of $C_2B_5H_7$ that consisted of: 2,4-, 2,3-, 1,2-, and 1,7-$C_2B_5H_7$ structures. The reported results showed zero kcal/mol for the relative energies in the 2,4- isomer, as seen in a previously reported study, and the other three isomers varied in energy from 27.2 kcal/mol to 51.3 kcal/mol for the 3-D Huckel method and from 16.58 kcal/mol to 65.78 kcal/mol for the *ab initio* calculations.[2] Studying the geometries of boranes and carboranes can also provide valuable bonding information about these molecules. Using electron density and molecular electrostatic potential calculations, it was reported that the hydrogen atoms of the boron to hydrogen bonds in *closo*-boranes, carboranes, and silaboranes, possess a negative charge and that the electron densities lie majorly on the exterior of these molecules.[3] Since bonding only occurs within areas of electron density, mapping their locations provides a literal picture of how boranes and carboranes bond. The structure was reported to be t-shaped and when bridged, moves the more positive charge from the carbon atom of the C-H bond to the hydrogen atom, which reduces the strength of those bonds.[3] This new information helps to piece together the puzzle of the bonding in boranes and carboranes; however, this theory is one that may prove to be inaccurate due to incorrect calculations or analysis due to its variation from all other theories reports about carboranes. A few studies have collected data about both the geometric and energetic properties of specific boranes and carboranes to analyze how and why they have bonded. Utilizing a three-dimensional Huckel computational method, it was reported that $C_2B_5H_7$ prefers a deltahedral structure opposed to a polyhedral one.[6] This structural information is integral to understanding why $C_2B_5H_7$ bonds in its specific conformation compared to its analogues. By studying the bridging hydrogen atoms, it was reported using molecular orbital calculations that the hydrogens above the B_n plane are angled towards the cap of these molecules.[4] Using geometric optimization and QTAIM calculations of 9-vertex *closo*-boranes, it was reported that the structure of these molecules is not truly deltahedral because they do not possess triangular shaped faces or an even distribution of electron density, which are criteria for a deltahedral classification.[12] Employing *ab initio*, DFT, and geometric optimization calculations of the nine isomers that fit the formula $C_2B_{n-2}H_n$, n= 5-7, revealed similar magnitudes of the carbon to hydrogen bonds and the boron to hydrogen bonds in $C_2B_5H_7$ molecules and larger carboranes.[9] The study also reported that the most stable isomer of $C_2B_5H_7$ concerning energetics, has the carbon atoms in the second and fourth positions of the molecule.[9] The classification of molecules structurally is important to understanding how they bond and boranes and carboranes are still the subject of debate in this area. An in-depth look at the 1,2,4,7-anti-tetramethyl-2-norbornyl cation using the QTAIM analysis method, it was reported that the molecule does not contain a three-center-2-electron bond as previously reported from crystal analysis. A study to broadly describe the κ-deformation of the Poincare-Hopf symmetry quantum group of underlying κ-Minkowski space-time was recently performed and claims an underlying, general space-time structure that does not commute, below the Plank scale using the κ-deformation.[11] The study also presents a deformation of igl(4) Hopf algebra is compatible with the κ-Minkowski space-time as well as the deformation of Heisenberg algebra, which helps to reconstruct space-time at the scale in which the effects of quantum gravity are taking place.[12] In an effort to ascertain why nonmetal hydrides violate the Lewis structure diagram and VSEPR model, it was discovered that charge values of the hydrogen ligands in BX_4, NX_4, and CX_4 compounds become increasingly more positively charged as the electronegativity of the central atom rises, indicating that Period 2 and 3 hydrides exhibit a unique bonding characteristic that is not predicted by the VSEPR model, and that ligand close packing theory explains the repulsion and charge values for these hydride ligands more accurately.[13] The information discovered about these molecules can be correlated to similar boranes and carboranes in the previously performed research and provide more accurate answers as to how and why carboranes bond in their particular constitutions. By correlating the geometry of boranes and carboranes, patterns can be established for determining why these molecules bond in the manner that they do based on their individual characteristics.

1.3 Computational Methods

Closo-carboranes $C_2B_5H_7$ and $C_2B_7H_9$, as well as non-cluster molecules: B_2H_4, C_2BH_7, BCH_5, and B_3CH_7, were optimized under DFT using the B3LYP method with a 6-311+G(2d,p) sized basis set. Geometries were verified as local minimum by calculating vibrational frequencies. All geometry optimizations were performed using the Shiva PQS cluster and Gaussian 09 software to provide data on the bond lengths in Angstroms, and relative energies in atomic units. Zero imaginary frequencies existed in the reported geometries, which indicates a feasible geometric representation because imaginary vibrational frequencies denote an unstable transition state geometry or saddle point. Wave function files were generated using B3LYP/3-311+G(2d,p) and AIMALL calculations were run on these wave function files to produce molecular graphs, partial charges, and analysis of the electron density. The program Aim Studio was used to view the mgpviz files that produced the three-dimensional representations of the molecules.

The structural isomers of closo-carboranes were analyzed using the Poincare-Hopf Theorem algebra, Equation (1) where N = number of atoms, X = number of Bond Critical Points, Y = number of Ring Critical Points, and Z= number of Cage Critical Points, to determine the viability of a three-center-two-electron bond present within the carborane. The simpler, non-clustered molecules were used as classical values for the bond lengths and rho values of the bond critical points, similarly to a control group, for comparison of these known values to the specific experimental data collected for the rho values of the bond and ring critical points of $C_2B_5H_7$ and $C_2B_7H_9$ that were analyzed. A small difference between the B-B and C-B bonds of the non-clustered compounds and the carboranes would indicate the analysis is statistically valid. The Laplacian geometries, charge values, and basin paths were obtained by running the AIMALL program on individual atoms and were also viewed using the AIMStudio program.

$$(N-X+Y-Z=1) \tag{1}$$

2. Results & Discussion

The four structural isomers of $C_2B_5H_7$ that were optimized by the Gaussian software were examined to determine the most thermodynamically stable structure using their relative energies as provided in Table 1. The cis-ring structure has the two carbon atoms of the molecule were arranged next to each other within the ring of the molecule. The axial-ring structure consisted of the two carbon atoms arranged in the two axial positions within the ring. The axial-equatorial structure consisted of one carbon in the axial position and one carbon atom within the ring. The trans-ring structure consisted of the carbon atoms arranged so that they are not next to each other, but both on the molecule's ring. The most energetically favorable isomer of $C_2B_5H_7$ was then determined from the reported results to be the Trans Ring isomer conformation because it possessed the lowest amount of energy in atomic units and was therefore, the isomer that was focused upon for the results and comparisons of this study. The relative energies stated vary by 0.101 atomic units (265 kJ/mol) for all the four isomers of $C_2B_5H_7$.

Table 1- the relative energies of the isomers of $C_2B_5H_7$

Structure	Electronic energy (Atomic Units)	Relative energy (kJ/mol)
Cis Ring	-204.754	+ 70.875
Trans Ring	**-204.781**	0.0
Axial Ring	-204.680	+265.12
Axial-Equatorial Ring	-204.716	+170.62

Table 2 shows the reported experimental ρ(r) values for the bond critical points of the non-cluster molecules containing boron and carbon atoms and the data found in Table 3 is a collection of the ρ(r) values for the bond and ring critical points of $C_2B_5H_7$, and their differences (Δ). Table 4 shows the differences between the classical (simple, non-clustered) ρ(r) values, from Table 2, of the bond critical points and the bond and ring critical points of the experimental data for the carborane reported in Table 3. Table 3 illustrates the differences between the bcp ρ(r) values and the corresponding rcp ρ(r) values where there is attachment, and these results support the findings that the molecule does not exhibit signs of three-center-two-electron bonding. Because the values are not identical, meaning there is a clear distinction between the positions of the bcp's and the rcp's in the structure of $C_2B_5H_7$ and because ρ(r) is a function of position. This distinction indicates there is another bonding pattern within the *closo*-carborane molecules, not one that involves three centers and two electrons. While there is not a largely significant lower ρ(r) value for the rcp's versus the bcp's, the ρ(r) values are lower in almost every bond of the atoms, and every value for both bond and ring critical points is lower than the comparative non-clustered values reported in Table 2. The lower rcp values shows a definite unique gradient vector at the juncture with the bcp and indicates the electron density is not uniform between the bond and its corresponding ring. A three-center-two-electron bond would show no difference between the ρ(r) values of the bcp's and the ρ(r) values of the rcp's to which they are connected to on the ring structure, and the similarity to the classical molecules indicates reasonable experimental values.

The lower values for every bcp and rcp to which they correspond and the classical non-clustered compounds, illustrated in Table 4, provide supporting evidence that three-center-two-electron bonding is not an accurate description of the bonding within the Trans-Ring isomer of $C_2B_5H_7$. The smaller difference between the ρ(r) BCP values of the axial bonds within $C_2B_5H_7$ and $C_2B_7H_9$ indicate they are the weakest and would be the first to break, which corresponds with Wade's Rules for tightness of the cluster where one axial bond breaks to form a *nido* cluster and the second breaks to form an *arachno* clustered compound.

Table 2- simple molecule values in atomic units

Molecule/Atoms	Bond	ρ(r)
B_2H_4	B-B	0.184
CB_3H_7	B-B	0.174
C_2BH_7	C-B	0.189
CBH_5	C-B	0.193

Table 3- $C_2B_5H_7$ values in atomic units

$C_2B_5H_7$	BCP ρ(r)	RCP#1 ρ(r)	**Δ**	RCP#2 ρ(r)	**Δ**
B7(A)-B14(E)	0.115	0.114	**0.00100**	0.114	**0.00100**
B13(E)-B14(E)	0.152	0.115	**0.0370**	0.115	**0.0370**
C1(E)-B12(E)	0.174	0.104	**0.0700**	0.104	**0.0700**
C5(E)-B9(A)	0.126	0.114	**0.0120**	0.104	**0.0220**

Table 4- $C_2B_5H_7$ value comparison to simple (non-cluster) values in atomic units

$C_2B_5H_7$	BCP ρ(r)	Simple BCP ρ(r) B_2H_4	**Δ**	Simple BCP ρ(r) CB_3H_7	**Δ**	Simple BCP ρ(r) C_2BH_7	**Δ**	Simple BCP ρ(r) CBH_5	**Δ**
B9(A)-B13(E)	0.115	0.184	**0.069**	0.174	**0.059**				
B13(E)-B14(E)	0.152	0.184	**0.032**	0.174	**0.022**				
C1(E)-B12(E)	0.174					0.189	**0.015**	0.193	**0.019**
C5(E)-B9(A)	0.126					0.189	**0.063**	0.193	**0.067**

The results seen in Image 1 show bond paths (black lines), bond critical points (green dots) ring critical points (red dots), and cage critical points (blue dot) of the minimum energy structure of $C_2B_5H_7$ where the bcp's and rcp's represent the minima of electron density at which point the bond would be most likely to break. The single cage critical point is seen in the center of the molecule. The bonds on the edges of the molecule exhibit very straight, characteristic bonds but the curvature of the bonds between the atoms of the ring and each other requires further investigation where the gradient vectors and basin path results will likely provide a better understanding of the bonding in the carborane. The proposed three-center-two-electron bond would produce a molecular graph that shows three atoms joined to a single bcp, not to a maximum. Again, the results do not support the proposed theory of three-center-two-electron bonding within $C_2B_5H_7$ and present the question of exactly what kind of bonding is present within the molecule.

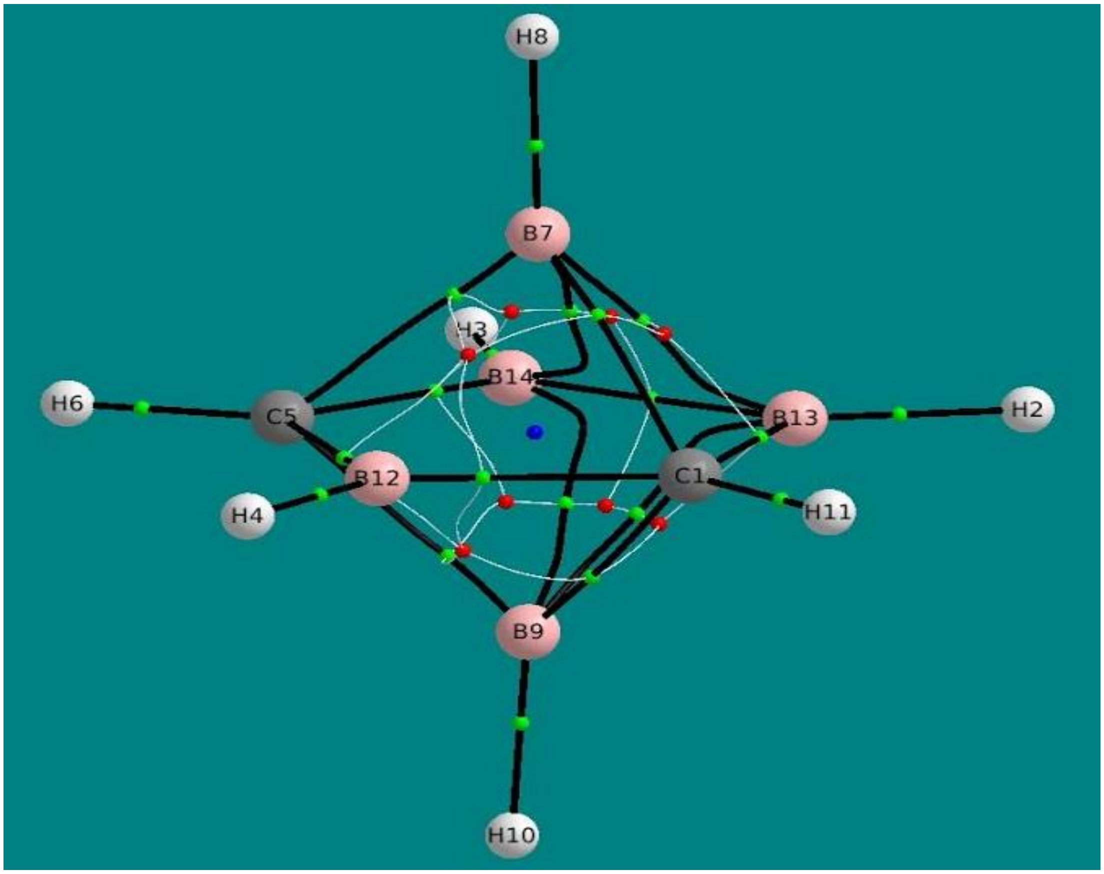

Image 1- Side view of the $C_2B_5H_7$ trans ring molecular graph

Table 5 shows the reported bcp and rcp ρ(r) values for $C_2B_7H_9$ and Table 6 illustrates the differences between the ρ(r) values of the bcp's and rcp's to the simple, classically bonded molecules. Three-center-two-electron bonding in the carborane would be represented by structures in which the bond critical points are connected to other bond critical points in the molecule. The connection between bond critical points structurally would cause the Poincare-Hopf algebra to not equal one and would mathematically represent how the electron deficiency is overcome. The ρ(r) values represented in Table 5 again show the differences between the bcp and the rcp's of which it is attached, illustrating that there is not three-center-two-electron bonding within $C_2B_7H_9$ either. Again, as with $C_2B_5H_7$, the bcp ρ(r) values are comparable to the values from molecules that exhibit classical bonding patterns. The fact that there is any difference between the bond critical points and the ring critical points proves the hypothesis of three-center-two-electron bonding in carboranes to be inaccurate. This is because in a three-center-two-electron bond the bcp and the rcp are mathematically identical, which allows for three atoms to bond with only two electrons. The reported results support Wade's Rules for describing the tightness of the cluster within the molecules and give structural and bonding information about *closo*-carboranes.

Table 5- $C_2B_7H_9$ values in atomic units

$C_2B_7H_9$	BCP ρ(r)	RCP#1 ρ(r)	**Δ**	RCP#2 ρ(r)	**Δ**
B3(A)-B5(E)	0.114	0.0924	**0.0216**	0.112	**0.00200**
B2(E)-B6(E)	0.139	0.116	**0.0230**	0.0489	**0.0901**
C1(E)-B6(E)	0.165	0.116	**0.0490**	0.0489	**0.116**
C1(E)-B3(A)	0.136	0.116	**0.0200**	0.0924	**0.0436**
C8(E)-B5(E)	0.123	0.111	**0.012**	0.112	**0.011**
B5(E)- B7(E)	0.114	0.111	**0.003**	0.092	**0.022**

Table 6- $C_2B_7H_9$ value comparison to simple (non-clustered) values in atomic units

$C_2B_7H_9$	BCP ρ(r)	Simple BCP ρ(r) B_2H_4	**Δ**	Simple BCP ρ(r) CB_3H_7	**Δ**	Simple BCP ρ(r) C_2BH_7	**Δ**	Simple BCP ρ(r) CBH_5	**Δ**
B2(A)-B6(E)	0.139	0.184	**0.045**	0.174	**0.035**				
B5(E)-B7(E)	0.114	0.184	**0.070**	0.174	**0.060**				
C1(E)-B3(E)	0.165					0.189	**0.024**	0.193	**0.028**
C8(E)-B2(A)	0.160					0.189	**0.029**	0.193	**0.033**

The computational results of the electron density of the trans-ring configuration of $C_2B_7H_9$ using the AimStudio program are shown in the molecular graph in Image 2 and again represent the bcp's, rcp's, and ccp of the molecule. The molecular graph of $C_2B_7H_9$ shows a similar structure to a predicted nine-vertex *closo*-carborane and like $C_2B_5H_7$ the proposed three-center-two-electron bond would produce a molecular graph that clearly exhibits a localization of electron density within the center of the molecule because of the sharing of two electrons between three atoms, and again, the bonds represented would not appear directly between two atoms as they do in typical covalent bonding or as they appear in Image 2. Notably, the bcp of the C8 to B5 bond does not connect to the rcp and the difference between the ρ(r) values of the bcp and rcp's are quite small, which indicates an unusual bonding characteristic that supports fragment behavior within the molecule. The C8-B5 bcp value is 0.123 and its corresponding rcp is 0.111, while the B5-B7 bcp value is 0.114 and its corresponding rcp is the same as the C8-B5 rcp value. Since the B5-B7 value is not identical to the rcp value, there is no catastrophic breaking that would open the ring and be very close to a three-center-two-electron bond. The non-identical (ρ) values of the bcp and rcp of the C8-B5 bond and the satisfaction of the Poincare-Hopf Theorem Therefore, the description of a ring within the molecule will need more analysis in future research.

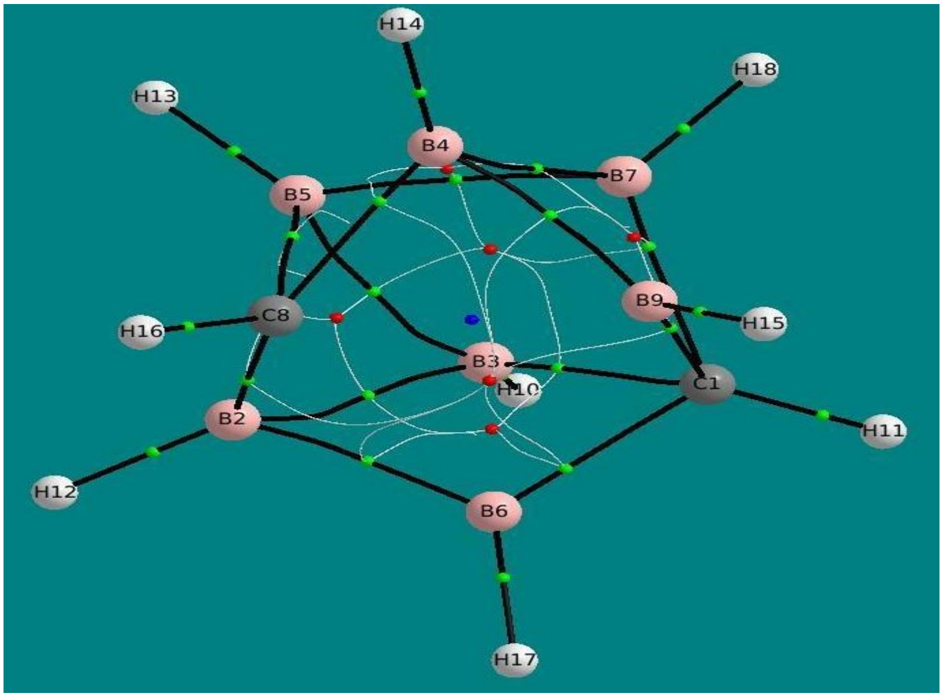

Image 2- Side view of the $C_2B_7H_9$ trans ring molecular graph

The Poincare-Hopf Theorem was applied to all four of the structural isomers of $C_2B_5H_7$ to determine if they would violate the theorem and provide evidence in support of three-center-two-electron bonding or if the isomers would confirm the algebraic theorem and again dispute the proposed three-center-two-electron bond. The results are presented in Table 7 and show that the isomers all confirmed the theorem algebraically and present substantiation to the theory that carboranes do not exhibit three-center-two-electron bonding.

Table 7- the satisfaction of the Poincare-Hopf theorem

Structure	# of Atoms	# of BCP's	# of RCP's	# of CCP's	Total
Cis Ring	14	-18	+6	-1	=1
Trans Ring	**14**	**-32**	**+20**	**-1**	**=1**
Axial Ring	14	-20	+8	-1	=1
AxEq Ring	14	-20	+8	-1	=1
$C_2B_7H_9$	**18**	**22**	**6**	**1**	**=1**

In the Laplacian density results, the scalar 2nd derivative of the gradient vector field of the electron density mapping of the electron pairs are the Laplacian ∇^2 values. The most negative values equal the areas of greatest electron density and the Laplacian critical points are represented geometrically in Image 3 as the yellow spheres, where each carbon atom can be clearly seen as making five bonds each. In $C_2B_5H_7$, both carbon atoms C1 and C5 show a bond between their terminal hydrogen and to four other boron atoms located in the molecule. These Laplacian spheres echo the ring and cage structure also seen in the molecular graph of Image 1. The single spheres seen between the carbon atoms and the boron and hydrogen atoms they bond to indicates polarity within those bonds, the two spheres between bonding boron atoms indicates non-polarity within those bonds, and no spheres between the boron atoms and their corresponding hydrogen atoms demonstrates negligible electron density in those bonds. The Laplacian of the electron density results for $C_2B_7H_9$, shown in Image 4, illustrate the greatest electron densities around the carbon atoms and echo the shape of the ring and cage structure seen in the molecular graph. Again, the negligible electron densities between the boron atoms and their corresponding hydrogen atoms is seen, and the spheres surrounding the C8 atom indicate polarity within its bonding and non-polarity in the C1 atom. The boron atoms in $C_2B_7H_9$ show a mixture of both polar, non-polar bonding, and negligible density between boron atoms in the ring structure of the molecule.

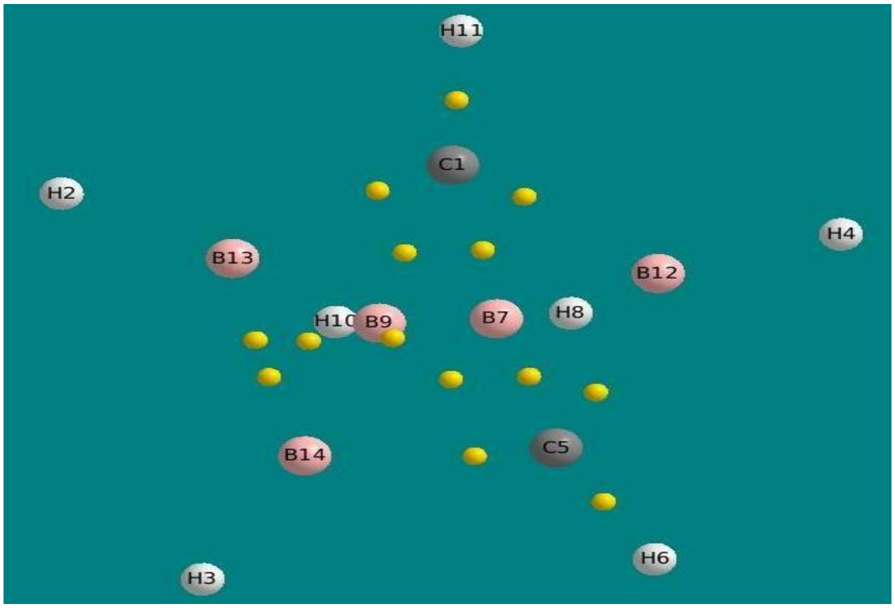

Image 3- Laplacian Critical Points of $C_2B_5H_7$

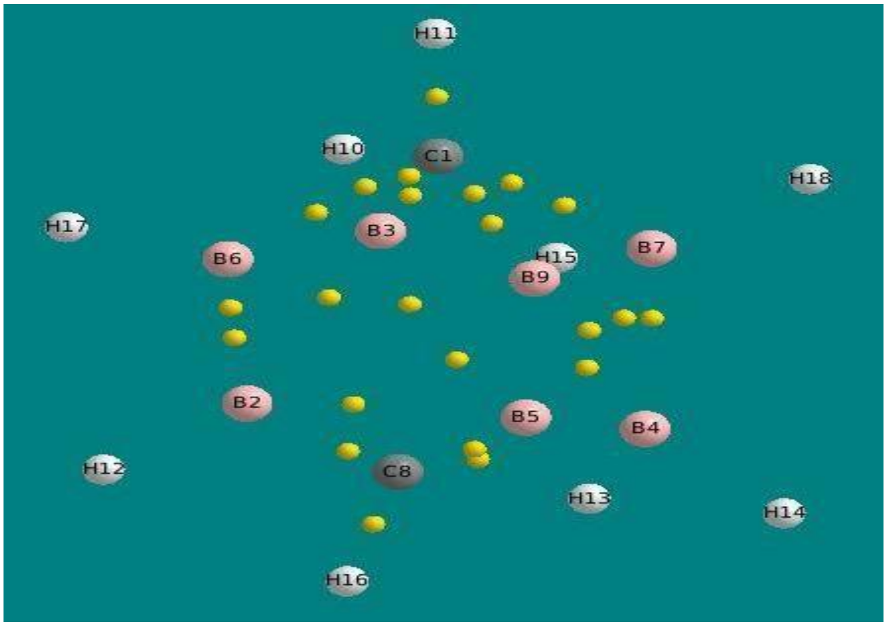

Image 4 - Laplacian critical points of $C_2B_7H_9$

The partial atomic charge values for both carboranes and the simpler molecules were obtained and are represented in Table 9, and reveal several interesting patterns concerning the positive or negative charge character of each atom within a bond. The hydrogen atoms take on a charge relative to the other atom in which it is bonded to, also seen in previous research, and indicate that the atom is easily influenced by the charge character of the other atom in the bond. The hydrogen atom has a slight positive charge when bonded to a carbon atom and relatively consistent negative charge when bonded to a boron atom. The charge value for the carbon atom is also influenced by number, or lack thereof, of boron atoms within the molecule, becoming more negatively charged with higher ratios of boron to carbon atoms, and possessing a negligible charge without the presence of boron atoms. The charge values of the boron atoms become more positive when carbon atoms are present within the molecule, but become less positively charged with the higher numbers boron atoms. The effect of the boron and carbon atoms upon the charge value of the surrounding atoms is highly indicative of fragment behavior exhibited by atoms that constitute functional groups within molecules. The fragment behavior in the varying charge of the atoms may explain overall the molecule's ability to form clustered compounds with limited amounts of electron density.

Table 9- reported charge values

Molecule	Bond(s)	Charge Values Atom / Atom
B_2H_4	2 B-H	**+1.15/ -0.58**
C_2H_6	2 C-H	**-0.0070/ +0.0024**
CB_3H_7	3 B-H	**+1.84/ -0.61**
	C-H	**-1.90/ +0.038**
C_2BH_7	B-H	**+1.88/ -0.63**
	2 C-H	**-0.68/ +0.010**
$C_2B_5H_7$	2 C-H	**-1.87/ +0.093**
	2 B-H	**+1.33/ -0.58**
	2 B-H	**+1.03/ -0.58**
	B-H	**+1.73/ -0.58**
$C_2B_7H_9$	C-H	**-2.00/ +0.10**
	C-H	**-1.47/ +0.10**
	2 B-H	**+0.97/ -0.57**
	2 B-H	**+1.03/ -0.58**
	2 B-H	**+1.20/ -0.57**
	B-H	**+0.86/ -0.56**

3. Conclusions & Acknowledgments

The satisfaction of the Poincare-Hopf algebra, the Laplacian results showing spheres of electron density directly between the two atoms forming the bond and not three, and the bond critical points not equaling mathematically and attaching to the ring critical points, all provide evidence that three-center-two-electron bonding is not occurring. Both closo-carboranes exhibit a pattern of electron localization that produces a network of discrete, weak single bonds, but provides no real evidence for true three-center-two-electron bonding in the molecule. Overall, the reported results provide significant weight to the evidence that there is an adherence to Wade's Rules concerning the tightness of the cluster due to the lower difference in $\rho(r)$ values of the bond critical points at the axial locations, and that the proposed theory of three-center-two-electron bonding is not an accurate description describing the bonding character of carboranes.

The varying charge values of each atom depending upon both the atoms it is bonded to and the overall number of other atoms in the molecule indicate a dependent relationship between the atoms. The dependent relationships between the charge values of the boron and carbon atoms and to their corresponding hydrogen atoms indicates fragment behavior within the carborane molecules that may help to explain the bonding characteristics in an electron deficient system. The resulting conclusion is that the carbon and hydrogen and boron and hydrogen fragments affect and interact with each other possibly due to steric proximity, forming the overall character and structure and overcoming the electron deficiencies of the carborane molecules analogous to the behavior exhibited by close-packed ligands in coordinated complexes. A more accurate theory for describing the bonding in carboranes would include steric proximity and ligand/fragment coordination to overcome the electron deficiency, combined with Wade's Rules for the characterization of structure. Future work in exploring these molecules further would include the addition of hydrogen atoms to explore the potential favorability of the axial bond breakage to form a *nido* or *aracho* structured cluster compound. Optimizing more geometries for more *closo* structures, and several *nido* and *arachno* clustered carboranes to elucidate different bonding patterns and characteristics using the QTAIM analysis method. Special acknowledgements to the Chemistry Department and the Undergraduate Research Program of the University of North Carolina at Asheville, and the National Science Foundation's Major Research Instrumentation Grant.

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