

# The Application of Density Functional Theory to Four Problems in Inorganic Chemistry: A Comparison to Traditional *ab Initio* Methods

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The recent surge in popularity of the density functional theory (DFT) approach to quantum chemistry has resulted in many studies aimed at quantifying the relative accuracy of the various DFT techniques compared to the more traditional *ab initio* quantum chemical methods. In an earlier paper (Derecskei-Kovacs, A.; Marynick, D. S. *Chem. Phys. Lett.* **1994**, 228, 252) we evaluated the performance of various density functionals on the notoriously difficult problem of the structure of gas-phase beryllium borohydride. Here, we extend that work by evaluating the performance of several density functionals on four difficult structural/energetics problems in inorganic chemistry: (1) the structure of bis(cyclopentadienyl)beryllium; (2) the isomerization energies of three carboranes,  $C_2B_3H_5$ ,  $C_2B_4H_6$ , and  $C_2B_5H_7$ ; (3) the structure of  $C_3Li_4$ ; and (4) the dimerization energies of substituted beryllium hydrides.

## Introduction

In recent years, the computational chemistry community has experienced an explosive growth in the application of density functional theory (DFT) to a variety of problems in chemistry.

The best density functional methods achieve greater accuracy than the more traditional Hartree–Fock methods with little or no increase in computational cost.<sup>1,2</sup> As a result, there is an increasing body of evidence<sup>3,4</sup> that DFT offers a viable alternative to conventional *ab initio* approaches.

Unlike traditional wave function based procedures, DFT methods compute electron correlation through functionals of the electron density. While the functional of the density that reproduces exactly the ground-state energy for any molecular system is not known, Hohenberg and Khon showed in 1964 that one does exist.<sup>5</sup> Since then, a variety of approximate forms of this functional have been developed which differ in their treatment of correlation and exchange.<sup>6</sup>

The recent surge in popularity of the density functional approach to quantum chemistry has resulted in many studies aimed at quantifying the relative accuracy of these various functionals.<sup>4,7,8</sup> It is the goal of this study to test the different functionals on a variety of inorganic systems that have proven difficult in the computation of accurate conformational or

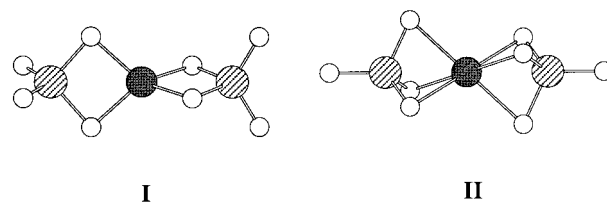
reaction energetics and to compare these results with those from post-Hartree–Fock *ab initio* methods and with experiment, when possible.

A plethora of recent studies on organic<sup>9–11</sup> and transition metal<sup>12</sup> systems by DFT methods have appeared. Perhaps less widely examined is the performance of DFT methods on main-group inorganic systems.<sup>13</sup> It is for this reason that we turn our attention to the behavior of density functional methods on these systems. There are many classic structural problems in this area. One such problem is the structure of beryllium borohydride. It has long been known that in the gas phase, beryllium borohydride consists of more than one structure. The two most stable isomers are shown in Figure 1. While a number of theoretical investigations of this system have been carried out,<sup>14,15</sup> very high level *ab initio* calculations<sup>14</sup> were required to definitively assign the ground-state structure as the  $D_{3d}$  isomer. In a previous paper,<sup>15</sup> we examined the performance of a variety of density functionals on this problem, and we found that nonlocal functionals performed very well.

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In this paper, we extend our previous work by evaluating the performance of a variety of density functionals on other related systems. The common features of most of these systems are that they possess multiple minima on their potential energy surfaces and that the valence structures of these various minima are radically different from one another. Most contain 3-center 2-electron bonding, which is indicative of a high degree of electron delocalization and is a consequence of the electron deficiencies of these systems. The highly delocalized bonding



**Figure 1.** Beryllium borohydride isomers **I** and **II**.

implies large electron–electron interactions within the molecule and thus strong electron correlation effects. They should, therefore, prove to be a significant test of density functional theory.

### The Four Computational Problems

**Bis(cyclopentadienyl)beryllium.** Since the discovery of bis(cyclopentadienyl)beryllium in 1959,<sup>16</sup> its structure has been greatly debated. A number of experimental<sup>17</sup> and theoretical<sup>18</sup> investigations have led to the proposal of several conformations with varying degrees of coordination of the Cp rings to the beryllium atom. The three most important of these proposed structures are shown in Figure 2. At one extreme, a Cp ring may be coordinated monohapto ( $\eta^1$ ) to the beryllium, and at the other extreme, it is coordinated pentahapto ( $\eta^5$ ).<sup>18d</sup> Pentahapto binding is associated with increased delocalization along the cyclopentadienyl ring.<sup>19</sup>

While the gas-phase structure is not known with certainty, there is considerable indirect experimental evidence<sup>17</sup> pointing

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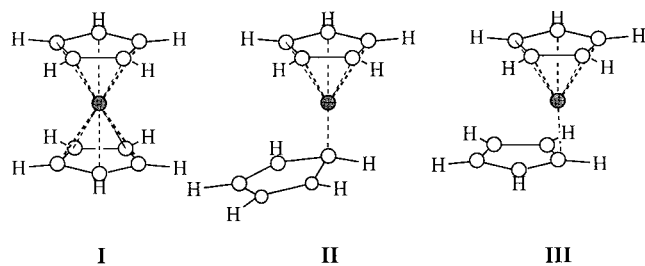


Figure 2. Some possible structures for bis(cyclopentadienyl)beryllium.

to the  $C_s$  structure (2-II) as the absolute minimum. X-ray diffraction data<sup>17d,f</sup> indicate that in the crystal a "slip sandwich" structure (Cp rings remain parallel but are offset) is the most stable (2-III). The  $C_s$  structure has been observed by NMR<sup>17b,p</sup> and confirmed by theory<sup>18</sup> for the isoelectronic bis(pentamethylcyclopentadienyl)boron cation.<sup>17b,p</sup>

In this study we examine the  $D_{5d}$  isomer (2-I) and the  $C_s$  structure with the nonparallel Cp rings (2-II). The  $D_{5d}$  isomer exhibits six 3-center 2-electron Be-C-C bonds.<sup>18d</sup> The  $C_s$  structure possesses one  $\eta^1$ -coordinated Cp ring with one classical 2-center 2-electron  $\sigma$  bond between the Be atom and the ring and one  $\eta^5$ -coordinated Cp ring with two 3-center 2-electron Be-C-C bonds and a very delocalized Be-C 2-center bond.<sup>18d</sup> Because the coordination number of the metal and the degree of delocalization of the Cp rings are different for these two isomers, one would expect correlation energy to be important in determining the relative energies of these species.

**$C_2B_3H_5$ ,  $C_2B_4H_6$ , and  $C_2B_5H_7$ .** The next set of molecules that we examine are members of a family of *closo*-carboranes which have electronic structures that can be described by combinations of 2- and 3-center bonds.<sup>20</sup> We studied two isomers of  $C_2B_3H_5$ , three isomers of  $C_2B_4H_6$ , and two isomers

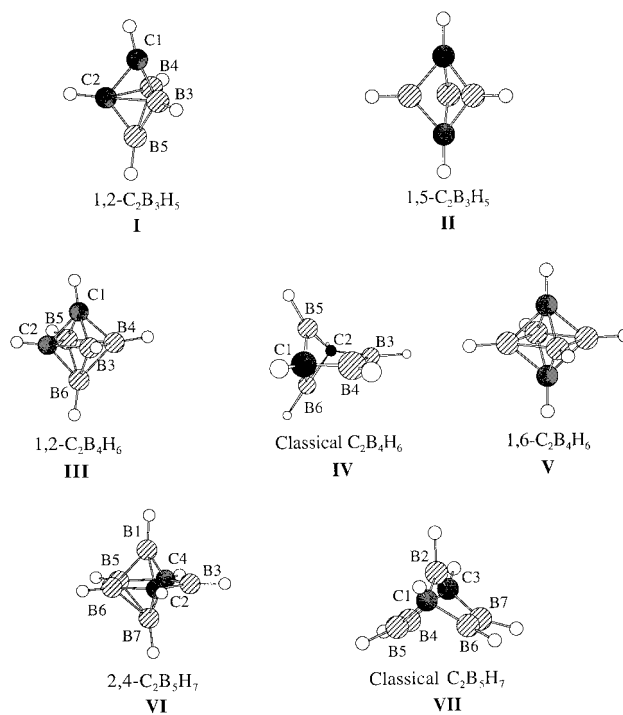


Figure 3. The carborane systems investigated.

of  $C_2B_5H_7$ , shown in Figure 3. These molecules all have one common feature: the various isomers all have differing degrees of delocalization associated with their valence structures, and thus electron correlation effects should be significant.

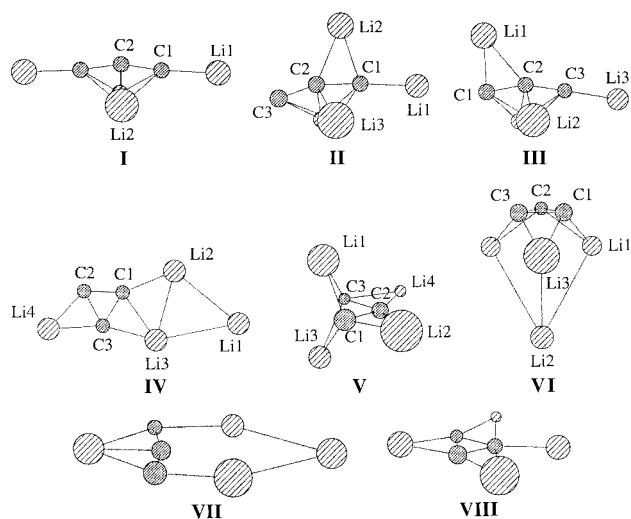
The valence structure of 1,2- $C_2B_3H_5$  (3-I) consists of three 2-center C-B bonds and three 3-center B-C-B bonds,<sup>20c</sup> while the 1,5- isomer (3-II) has six 2-center C-B bonds.<sup>20c</sup> The  $C_2B_4H_6$  isomers also have varying numbers of 3-center bonds.<sup>20c</sup> Structure 3-V has the most delocalization, with seven 3-center bonds.<sup>20b,c</sup> 1,2- $C_2B_4H_6$  (3-III) has five 3-center bonds, two 2-center C-B bonds, and one 2-center C-C bond.<sup>20c</sup> The classical structure (3-IV) has the least delocalization, with seven 2-center bonds.<sup>20c</sup> 2,4- $C_2B_5H_7$  (3-VI) has six 3-center bonds and two 2-center bonds<sup>20b,c</sup> while the classical structure (3-VII) has eight 2-center bonds.<sup>20c</sup>

**$C_3Li_4$ .** The nonclassical bonding nature of lithium compounds has long been accepted,<sup>21</sup> and the ground-state structure of  $C_3Li_4$  is a good example of this. An early theoretical work<sup>22</sup> found the ground state to be an unusual  $C_{2v}$  structure, with several other conformations close in energy to this minimum. In a recent paper,<sup>23</sup> we confirmed the  $C_{2v}$  structure to have the lowest energy and located seven other energetically competitive minima on the potential energy surface at the MP2/6-311G\* level. These structures are shown in Figure 4. Here, we test the ability of DFT to reproduce the high-level ab initio energetics for these very unusual structures.

**Substituted Beryllium Hydride Dimers.** The final systems that we investigate are substituted beryllium hydrides and their

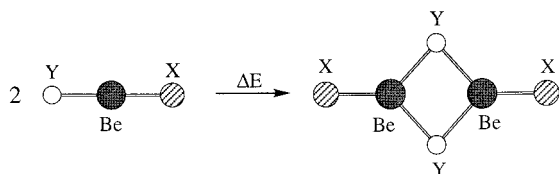
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**Figure 4.** The eight local minima on the  $C_3Li_4$  potential energy surface at the MP2/6-311G\* level.

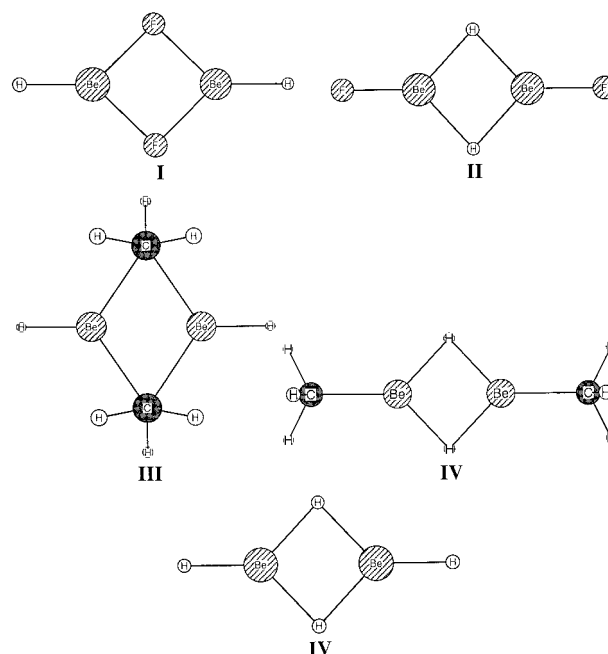
dimers. Specifically, we examine the dimerization energy of the reaction



where X and Y = H,  $CH_3$ , and F. Many related systems have been studied,<sup>24–27</sup> and electron correlation has been shown to contribute significantly to the dimerization energies. Earlier computational studies on  $Be_2H_4$ <sup>25,26,28</sup> found that the dimer exhibits  $D_{2h}$  symmetry and the dimerization energies are  $\sim 32$  kcal/mol. We explore structurally analogous systems with  $C_{2v}$  and  $D_{2h}$  symmetry for the beryllium hydrides and their dimers, shown in Figure 5.

### Computational Details

Most of the calculations were performed using the Gaussian 92<sup>29</sup> suite of programs. In order to provide a basis for comparison with traditional ab initio methods, we optimized the geometries of all the species at at least the MP2/6-31G\* level. We then reevaluated the energetics of all the species at the MP4 level. All DFT calculations were restricted to nonlocal methods, since it is commonly accepted that only these approaches yielded quantitative accuracy. In all cases, we examined the B-LYP,<sup>30,31</sup> B-P86,<sup>30,32</sup> B3-LYP<sup>31,33</sup> and B3-P86<sup>32,33</sup>



**Figure 5.** The substituted beryllium hydrides examined.

functionals and compared these results to the ab initio results and to experiment, when available. In all systems except  $Cp_2Be$ , stationary points were characterized by analytic force constant evaluations.

For bis(cyclopentadienyl)beryllium, we optimized the geometries at the MP2/6-31G\* level and then reevaluated the energetics at the MP2/6-311G\*\*//MP2/6-31G\* level. It should be noted that, at the MP2 level, the  $C_s$  structure is not a minimum on the potential energy surface: it collapses smoothly to the  $D_{5d}$  structure. DFT geometry optimizations were performed using all four functionals and the 6-31G\* basis set. The energetics were reevaluated at the DFT/6-311G\*\*//DFT/6-31G\* level. Unlike the MP2 case, at this level of theory, the low-energy  $C_s$  isomer is a minimum on the potential energy surface. We also calculated MP4 energetics using the B3-LYP/6-31G\* optimized structures.

In the carborane systems, the ab initio geometry optimizations were performed at the MP2/6-311G\* level and the energies were recalculated at the MP4/6-311G\*\*//MP2/6-311G\* level. The density functional geometry optimizations and energetics evaluations were performed at the DFT/6-311G\*\*//DFT/6-311G\* level.

For  $C_3Li_4$  (Figure 4), we used the geometries previously calculated at the MP2/6-311G\* level and the energetics previously calculated at the MP4/6-311G\*\*//MP2/6-311G\* level.<sup>23</sup> We then examined the energetics using a slight modification of the G2MP2<sup>39</sup> method. This method optimizes the geometry of a molecule at the MP2/6-31G\* level and then uses this geometry for subsequent basis set extension

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**Table 1.**  $\text{Cp}_2\text{Be}$  Internuclear Distances (Å) and Average Absolute Deviations (Å) for the  $D_{5d}$  Isomer

	MP2 <sup>a</sup>	B-P86 <sup>a</sup>	B3-P86 <sup>a</sup>	B-LYP <sup>a</sup>	B3-LYP <sup>a</sup>
Internuclear Distances <sup>b</sup>					
Be—C	2.023	2.058	2.040	2.070	2.055
C—C	1.419	1.427	1.415	1.430	1.419
C—H	1.084	1.091	1.082	1.090	1.083
Average Absolute Deviations <sup>c</sup>					
	0.017	0.008	0.021	0.011	

<sup>a</sup> A basis set of 6-31G\* was employed for all geometry optimizations.

<sup>b</sup> The  $C_s$  structure was not a minimum on the potential energy surface: it collapsed smoothly to the  $D_{5d}$  structure. <sup>c</sup> Average absolute deviation in distances relative to MP2 (for  $D_{5d}$  only).

corrections through QCISD(T) and MP2 single-point calculations. We found that the 6-31G\* basis set is not adequate to describe the geometries of several of the isomers of  $\text{C}_3\text{Li}_4$ ; therefore, we manually performed the basis set extension calculations using our MP2/6-311G\* optimized geometries. We then examined the G2MP2 energetics at 0 K, with and without vibrational zero point energy corrections, in order to ensure the validity of comparisons of these energies to the other energetic data in the study. We denote this modified G2MP2 approach as G2MP2'. We also reoptimized the geometries of all of the isomers at the DFT/6-311G\* level. We were not able to obtain convergence for the two highest energy isomers, Structures 4-VII and 4-VIII, with all of the density functionals evaluated; therefore, we will not include these two isomers in our discussion of this system.

For the substituted beryllium hydrides, the geometries were calculated at the MP2/6-311G\*\* level and the energetics were evaluated at the MP4/6-311G\*\*/MP2/6-311G\*\* level. Here polarization functions were added to the hydrogens because dimerization occurs through the hydrogens in some cases. For this system, we decided to examine the ab initio energetics at an even higher level than we did with the other systems studied. We employed the Gaussian-2<sup>34</sup> or G2 method in the Gaussian 94<sup>35</sup> suite of programs. This method uses a series of component calculations to approximate a much higher level calculation (QCISD(T) and MP4 basis set extension corrections) with a very large basis set. In order to ensure valid comparisons with both our MP4 and density functional results, we utilized G2 energetics only at 0 K, with no vibrational zero point corrections included. The density functional optimizations were performed at the DFT/6-311G\*\* level, and the same level was employed for energetics. In order to examine DFT energetics more comparable to the G2 calculations, we then reevaluated the energetics using the B3-LYP functional and a 6-311+G(3df,2p) basis set.

## Results and Discussion

**Bis(cyclopentadienyl)beryllium.** Table 1 presents the optimized internuclear distances for the  $D_{5d}$  isomer, with deviations calculated relative to the MP2 optimized structure. The corresponding bond lengths for the  $C_s$  isomer are not available, since this is not a stable structure on the potential energy surface at the MP2 level. B3-P86 comes very close to reproducing the MP2 geometry of the  $D_{5d}$  structure, but the average absolute deviations in bond distances for the other three functionals do not compare as well. As was the case in our earlier work on beryllium borohydride,<sup>15</sup> the choice of exchange functional is more important than the choice of correlation functional.

The relative energetics of the  $D_{5d}$  and  $C_s$  isomers of bis(cyclopentadienyl)beryllium are presented in Table 2. In agreement with the indirect experimental evidence, HF/6-311G\*\*/HF/6-31G\* predicts the  $C_s$  structure to be lower in energy than the  $D_{5d}$  by 7.44 kcal/mol. Notably, MP2 optimizations fail to even show the  $C_s$  structure on the potential energy surface. Here the  $C_s$  isomer collapses smoothly to the  $D_{5d}$  structure. This represents a significant failure for MP2 theory and a corresponding success for DFT, since optimizations and

**Table 2.** Relative Energies of the  $D_{5d}$  and  $C_s$  Isomers of  $\text{Cp}_2\text{Be}$  (kcal/mol) Calculated with Different ab Initio and Density Functional Methods and with Different Basis Sets

method and basis set	$-\Delta E^a$
HF/6-31G**/HF/6-31G*	6.34
HF/6-311G**/HF/6-31G*	7.44
MP2/6-31G**/MP2/6-31G*	<i>b</i>
MP2/6-311G**/HF/6-31G*	5.43
MP4/6-31G**/B3-LYP/6-31G*	-1.04
B-P86/6-31G**/B-P86/6-31G*	-0.06
B-P86/6-311G**/B-P86/6-31G*	1.42
B3-P86/6-31G**/B3-P86/6-31G*	-0.49
B3-P86/6-311G**/B3-P86/6-31G*	0.85
B-LYP/6-31G**/B-LYP/6-31G*	3.40
B-LYP/6-311G**/B-LYP/6-31G*	5.33
B3-LYP/6-31G**/B3-LYP/6-31G*	2.57
B3-LYP/6-311G**/B3-LYP/6-31G*	4.27

<sup>a</sup> The energy of the  $C_s$  structure was taken as 0.00 kcal/mol. <sup>b</sup> The  $C_s$  structure was not a minimum on the potential energy surface: it collapsed smoothly to the  $D_{5d}$  structure.

energy calculations using all four functionals at the DFT/6-311G\*\*/DFT/6-31G\* level correctly predict the  $C_s$  isomer to be the ground-state structure. Also, we reevaluated the energetics of the B3-LYP/6-31G\* optimized structures at the MP4/6-31G\* level, since we did not have an MP2 optimized structure for the  $C_s$  isomer. These calculations incorrectly predict the  $D_{5d}$  isomer to be the low-energy structure by 1.04 kcal/mol, even though the B3-LYP/6-31G\* optimizations yield the correct trend. B-P86/6-31G\* and B3-P86/6-31G\* optimizations also incorrectly predict the  $D_{5d}$  structure to have a lower energy, but subsequent energy reevaluations using the larger 6-311G\*\* basis set yield the correct result.

**$\text{C}_2\text{B}_3\text{H}_5$ ,  $\text{C}_2\text{B}_4\text{H}_6$ , and  $\text{C}_2\text{B}_5\text{H}_7$ .** The internuclear distances for the optimized structures of all the carborane systems are found in Table 3. In this system, we have experimental data to which we may compare our computational results. Both the ab initio and DFT methods produce geometries that are in quite good agreement with experiment, with MP2 producing the smallest average absolute deviations in bond distances. For the 15 experimentally known unique internuclear distances between heavy atoms, we find that the theoretical models yield the following deviations: MP2, 0.009 Å; B-P86, 0.012 Å; B3-P86, 0.010 Å; B-LYP, 0.014 Å; B3-LYP, 0.010 Å. Taking the MP2 geometries as reference points, the overall average absolute deviations for the 29 distances (Å) calculated are B-P86, 0.002; B3-P86, 0.011; B-LYP, 0.007; and B3-LYP, 0.008. All of the density functionals, most notably B-P86, perform well on these systems when compared to MP2.

In the case of the  $\text{C}_2\text{B}_3\text{H}_5$  isomers, all calculations correctly predict the well-known  $D_{3h}$  isomer to be the low-energy structure (see Table 4 for the relative energetics of the carborane systems). Since the MP series appears converged for this isomer (see Table 4), MP4 is a suitable ab initio standard for the DFT energetics. All of the density functionals compare well to the MP4 energetics. The Hartree-Fock/6-311G\* optimizations predict a 44.9 kcal/mol difference in energy between the isomers. When electron correlation is included via MP2 or MP4 corrections or directly as in the case of the density functionals, the energy difference falls, on average, by 9.5 kcal/mol. We expect this since the 3-center bonds in the 1,2-isomer should be stabilized relative to the more localized 2-center bonds in the 1,5-isomer when electron correlation is explicitly considered.

**Table 3.** C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, and C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> Internuclear Distances (Å) and Average Absolute Deviations (Å)

	MP2 <sup>a</sup>	B-P86 <sup>a</sup>	B3-P86 <sup>a</sup>	B-LYP <sup>a</sup>	B3-LYP <sup>a</sup>	exptl
Internuclear Distances						
1,5-C <sub>2</sub> B <sub>3</sub> H <sub>5</sub>						
C-B	1.560	1.562	1.551	1.563	1.554	1.556 <sup>b</sup>
B-B	1.855	1.855	1.847	1.864	1.857	1.853
1,2-C <sub>2</sub> B <sub>3</sub> H <sub>5</sub>						
C1-C2	1.517	1.516	1.505	1.527	1.516	
C2-B3	1.740	1.742	1.732	1.754	1.744	
C1-B3	1.533	1.538	1.524	1.534	1.524	
B3-B4	1.839	1.842	1.833	1.851	1.844	
C2-B5	1.519	1.522	1.507	1.515	1.504	
B3-B5	1.704	1.700	1.691	1.707	1.700	
1,6-C <sub>2</sub> B <sub>4</sub> H <sub>6</sub>						
C-B	1.631	1.633	1.620	1.635	1.624	1.634 <sup>c</sup>
B-B	1.720	1.720	1.707	1.722	1.711	1.724
Classical C <sub>2</sub> B <sub>4</sub> H <sub>6</sub>						
B3-B4	1.721	1.721	1.713	1.720	1.715	
C1-B4	1.514	1.514	1.506	1.523	1.516	
C1-B6	1.585	1.587	1.575	1.587	1.578	
1,2-C <sub>2</sub> B <sub>4</sub> H <sub>6</sub>						
C1-B4	1.634	1.639	1.626	1.641	1.630	1.621 <sup>c</sup>
B4-B5	1.739	1.739	1.727	1.743	1.733	1.723
C1-C2	1.542	1.549	1.536	1.556	1.544	1.535
C1-B5	1.628	1.630	1.616	1.631	1.619	1.618
B5-B6	1.721	1.719	1.706	1.717	1.707	1.745
2,4-C <sub>2</sub> B <sub>5</sub> H <sub>7</sub>						
C2-B3	1.551	1.552	1.540	1.551	1.542	1.546 <sup>d</sup>
C2-B4	1.571	1.572	1.559	1.573	1.564	1.565
B4-B5	1.657	1.660	1.649	1.659	1.651	1.651
C2-B6	1.717	1.723	1.710	1.730	1.717	1.708
B4-B6	1.808	1.807	1.794	1.809	1.798	1.816
B3-B6	1.841	1.846	1.832	1.856	1.843	1.818
Classical C <sub>2</sub> B <sub>5</sub> H <sub>7</sub>						
C1-B2	1.632	1.634	1.612	1.619	1.605	
C1-B4	1.517	1.518	1.514	1.534	1.531	
B4-B6	2.172	2.174	2.189	2.256	2.267	
B4-B5	2.773	2.773	2.778	2.835	2.842	
B2-B4	2.054	2.048	2.084	2.142	2.164	
Average Absolute Deviations <sup>e</sup>						
	0.002	0.011	0.007	0.008		

<sup>a</sup> A basis set of 6-311G\* was employed for all geometry optimizations. <sup>b</sup> Reference 36. <sup>c</sup> Reference 37. <sup>d</sup> Reference 38. <sup>e</sup> Average absolute deviation in distances relative to MP2.

In the case of the C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> systems, again all calculations at all levels of theory correctly predict the high-symmetry 1,6-isomer (*D*<sub>4h</sub>) to be the most stable structure. The 1,6-isomer possesses the most 3-center bonding; therefore, it should be most stabilized with the inclusion of electron correlation, as is evidenced in the higher energy differences of the MP4 and DFT calculations. However, the MP series does not appear converged for these three isomers (see Table 4); therefore, no comparisons can be made between the MP2 or MP4 energetics and those obtained with the density functionals.

As is the case with the other carboranes, all calculations predict the classical structure of C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> to be much higher in energy than the 2,4-isomer. The inclusion of electron correlation increases this energy difference by an average of 50%, with the more highly delocalized 2,4-structure more stabilized upon inclusion of electron correlation. However, once again the MP series does not appear converged for these isomers (see Table 4) and therefore no comment can be made about the performance of DFT based on MP2 or MP4 results.

**C<sub>3</sub>Li<sub>4</sub>.** Table 5 presents the optimized internuclear distances for the six lowest energy isomers of C<sub>3</sub>Li<sub>4</sub>. In all cases, the carbon atoms are arranged either quasi-linearly or as three-membered rings. The lithium atoms either are singularly bound to one carbon atom (terminating) or form a bridge between two carbon atoms. In two cases (Figure 4, structures **4-IV** and **4-VI**),

the lithium atoms are also bound directly to one another. Since there are no experimental geometries for any of these structures, we will somewhat arbitrarily take MP2 as our standard. Given this, the average absolute deviations in bond distances compared to the MP2 optimized structures are much larger in this system than in the systems discussed so far. Nonetheless, B-P86 gives the smallest average absolute deviation in internuclear bond distances. Once again, the choice of exchange functional is more crucial than the choice of correlation functional.

Table 6 lists the relative energetics of the six isomers of C<sub>3</sub>-Li<sub>4</sub>. We must be careful in our choice of MP4 as the standard for this system. For structure **6-V**, the MP series appears converged (see Table 6) and can be used with confidence as a standard, but the MP4 energetics cannot be trusted for the other structures due to oscillations in the MP series. However, using structure **6-V** as a basis for comparison, DFT seems to overestimate the instabilities of all of the structures. Unlike the ab initio findings, DFT calculations predict that structure **6-III** is not a minimum on the potential energy surface but collapses smoothly to structure **6-I**. Like the MP4 results, the G2MP2' relative energetics are much lower than those predicted by DFT. Most notably, G2MP2' (at 0 K) predicts that structure **6-II** is degenerate to structure **6-I**, the commonly accepted ground-state structure.<sup>22,23</sup> The G2MP2' energetics indicate that structure **6-I** is lower in energy than structure **6-II** by 0.2 kcal/mol when no zero point energy corrections are included. Upon the inclusion of zero point corrections, G2MP2' calculations indicate that structure **6-II** is more stable than structure **6-I** by 0.2 kcal/mol. This is the first report of an isomer energetically competitive with structure **6-I**.

**Substituted Beryllium Hydride Dimers.** Table 7 presents the optimized geometries of the substituted beryllium hydride dimers that we investigated; Be<sub>2</sub>H<sub>4</sub> (*D*<sub>2h</sub>), H-bridged and F-bridged Be<sub>2</sub>F<sub>2</sub>H<sub>2</sub> (*D*<sub>2h</sub>), and CH<sub>3</sub>-bridged and H-bridged Be<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>H<sub>2</sub> (*C*<sub>2v</sub>). An examination of these optimized geometries reveals that most of the calculated structures are of *D*<sub>2h</sub> symmetry and have the bridging units in the same plane as the beryllium atoms and the terminal units. In the optimized Be<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>H<sub>2</sub> structures, the symmetry is lowered to *C*<sub>2v</sub> and the molecules are no longer planar but have the methyl groups tilted to one side and the hydrogens tilted toward the opposite side of the molecule. The methyl groups are eclipsed with one another. Again, we take MP2 as our standard and see that all of the density functionals reproduce the MP2 geometries very well for all of the dimers. B-LYP yields the smallest average absolute deviations in internuclear bond distances compared to MP2, but the deviations for all of the functionals are quite small.

Table 8 presents the dimerization energies of the substituted beryllium hydride systems. Because these systems are significantly smaller than the other systems studied in this paper, we were able to investigate the energetics at the G2 level (at 0 K and with no vibrational zero point energy correction), which is likely to be more accurate than any other level employed here. Both our MP4 and DFT calculated values for the dimerization energy for Be<sub>2</sub>H<sub>4</sub> (31.4–35.8 kcal/mol) agree quite well with those already in the literature.<sup>25,26,28</sup> However, for half of the functionals examined, DFT reproduces the G2 energetics better than MP4. In particular, B-P86/6-311G\*\* and B3-P86/6-311G\*\* come to within an average of 1.6 and 1.8 kcal/mol, respectively, of reproducing the G2 energetics, while the MP4 calculations have an average absolute deviation of 2.3 kcal/mol. The B3-LYP/6-311G\*\* calculations are also quite close to the G2 results, with an average absolute deviation of 2.3 kcal/mol, while B-LYP/6-311G\*\* does not compare as favorably,

**Table 4.** Relative Energies (kcal/mol) of the 1,2- and 1,5-Isomers of C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, the 1,2-, 1,6-, and Classical Bicyclic Isomers of C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, and the 2,4- and Classical Structures of C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> Calculated with Different ab Initio and Density Functional Methods

method and basis set	-ΔE						
	C <sub>2</sub> B <sub>3</sub> H <sub>5</sub>		C <sub>2</sub> B <sub>4</sub> H <sub>6</sub>			C <sub>2</sub> B <sub>5</sub> H <sub>7</sub>	
	1,2	1,5	1,2	classical	1,6	classical	2,4
HF/6-311G**/HF/6-311G*	44.9	0.0	5.8	8.7	0.0	45.8	0.0
MP2/6-311G**/MP2/6-311G*	35.9	0.0	9.3	38.5	0.0	81.8	0.0
MP3/6-311G**/MP2/6-311G*	37.8	0.0	8.3	30.0	0.0	73.5	0.0
MP4/6-311G**/MP2/6-311G*	36.1	0.0	8.4	32.7	0.0	75.1	0.0
B-P86/6-311G**/B-P86/6-311G*	33.4	0.0	10.8	33.2	0.0	65.7	0.0
B3-P86/6-311G**/B3-P86/6-311G*	35.5	0.0	10.4	33.5	0.0	70.0	0.0
B-LYP/6-311G**/B-LYP/6-311G*	34.8	0.0	11.0	25.9	0.0	57.3	0.0
B3-LYP/6-311G**/B3-LYP/6-311G*	36.6	0.0	10.4	26.7	0.0	61.6	0.0

**Table 5.** C<sub>3</sub>Li<sub>4</sub> Internuclear Distances (Å) and Average Absolute Deviations (Å)

	MP2 <sup>a</sup>	B-P86 <sup>a</sup>	B3-P86 <sup>a</sup>	B-LYP <sup>a</sup>	B3-LYP <sup>a</sup>
Internuclear Distances					
<b>4-I</b>					
C1-Li1	1.852	1.836	1.823	1.830	1.821
C1-Li2	2.224	2.211	2.186	2.214	2.195
C1-C2	1.335	1.330	1.318	1.328	1.319
C2-Li2	1.903	1.894	1.878	1.895	1.883
<b>4-II</b>					
C1-Li1	1.832	1.818	1.798	1.811	1.797
C1-Li2	1.978	1.967	1.955	1.955	1.949
C1-Li3	2.151	2.154	2.112	2.158	2.119
C1-C2	1.421	1.409	1.402	1.410	1.405
C2-Li2	2.057	2.047	2.002	2.056	2.017
C2-Li3	1.917	1.902	1.886	1.904	1.893
C2-C3	1.298	1.297	1.280	1.295	1.279
C3-Li3	2.310	2.263	2.306	2.235	2.288
<b>4-III<sup>b</sup></b>					
C1-Li1	1.926	1.836	1.823	1.830	1.821
C2-Li2	1.904	1.894	1.877	1.895	1.883
C1-C2	1.347	1.330	1.318	1.328	1.318
C1-Li2	2.215	2.212	2.186	2.214	2.195
<b>4-IV</b>					
Li1-Li2	3.048	3.007	2.993	2.972	2.976
Li1-Li3	3.091	3.074	3.058	3.048	3.050
Li2-Li3	2.649	2.633	2.603	2.613	2.596
C1-Li2	2.066	2.061	2.046	2.053	2.045
C1-Li3	2.148	2.137	2.118	2.137	2.122
C2-Li3	2.022	2.020	2.002	2.015	2.001
C1-C2	1.445	1.441	1.425	1.442	1.428
C1-C3	1.410	1.408	1.394	1.407	1.395
C2-C3	1.456	1.453	1.436	1.452	1.437
C2-Li4	1.996	1.983	1.968	1.978	1.968
C3-Li4	1.927	1.916	1.900	1.909	1.898
<b>4-V</b>					
C1-Li1	1.967	1.948	1.926	1.952	1.933
C1-Li2	1.909	1.884	1.855	1.888	1.863
C2-Li2	1.935	1.930	1.926	1.919	1.921
C1-C2	1.445	1.439	1.424	1.438	1.425
C1-C3	1.936	1.880	1.789	1.938	1.826
<b>4-VI</b>					
C1-Li1	2.028	2.023	2.005	2.016	2.004
Li1-Li2	3.393	3.330	3.322	3.326	3.337
C1-C2	1.436	1.432	1.416	1.431	1.418
C1-Li3	2.028	2.024	2.006	2.019	2.005
C1-C3	1.436	1.431	1.415	1.430	1.417
C2-Li1	2.028	2.025	2.007	2.019	2.006
Li2-Li3	3.393	3.314	3.307	3.304	3.320
Average Absolute Deviations <sup>c</sup>					
	0.016	0.034	0.020	0.032	

<sup>a</sup> A basis set of 6-311G\* was employed for all geometry optimizations. <sup>b</sup> Structure **4-III** is not a minimum on the potential energy surface at the density functional level; it collapses smoothly to structure **4-I**. <sup>c</sup> Average absolute deviation in distances relative to MP2.

with an average absolute deviation from G2 energetics of 3.6 kcal/mol. Because G2 approximates a high-level calculation

**Table 6.** Relative Energies of the Different Isomers of C<sub>3</sub>Li<sub>4</sub> (kcal/mol) Calculated with Different ab Initio and Density Functional Methods and with the 6-311G\* Basis Set

method	-ΔE					
	4-I	4-II	4-III	4-IV	4-V	4-VI
MP2/6-311G**/MP2/6-311G* <sup>a</sup>	0.0	2.8	3.9	17.4	21.8	27.9
MP3/6-311G**/MP2/6-311G* <sup>a</sup>	0.0	0.8	4.5	0.8	22.6	12.4
MP4/6-311G**/MP2/6-311G* <sup>a</sup>	0.0	1.7	3.8	11.5	20.7	21.9
G2MP2' <sup>b</sup>	0.0	0.2	3.7	7.0	22.1	17.2
B-LYP/6-311G**/B-LYP/6-311G*	0.0	5.6	<sup>c</sup>	20.5	26.3	33.9
B3-LYP/6-311G**/B3-LYP/6-311G*	0.0	5.0	<sup>c</sup>	15.6	26.4	29.3
B-P86/6-311G**/B-P86/6-311G*	0.0	4.8	<sup>c</sup>	19.9	24.1	31.3
B3-P86/6-311G**/B3-P86/6-311G*	0.0	4.2	<sup>c</sup>	16.3	24.6	28.4

<sup>a</sup> Reference 23. <sup>b</sup> These relative energetics are from G2MP2 calculations with a basis set modification in the geometry optimization step (see text) at 0 K and with no vibrational zero point energy corrections included. When the zero point corrections are included, the relative order of structure **4-I** and **4-II** reverses, with structure **4-II** now 0.2 kcal/mol more stable than structure **4-I**. <sup>c</sup> Structure **4-III** is not a minimum on the potential energy surface at the DFT level; it collapses smoothly to structure **4-I**.

**Table 7.** Substituted Beryllium Hydride Dimer Internuclear Distances (Å) and Average Absolute Deviations (Å)

	MP2 <sup>a</sup>	B-P86 <sup>a</sup>	B3-P86 <sup>a</sup>	B-LYP <sup>a</sup>	B3-LYP <sup>a</sup>
Internuclear Distances					
Be <sub>2</sub> F <sub>2</sub> H <sub>2</sub> (F-bridged)					
Be-F	1.582	1.588	1.572	1.588	1.575
Be-H	1.324	1.336	1.325	1.329	1.323
Be <sub>2</sub> F <sub>2</sub> H <sub>2</sub> (H-bridged)					
Be-H	1.478	1.486	1.475	1.477	1.472
Be-F	1.398	1.399	1.387	1.399	1.388
Be <sub>2</sub> Me <sub>2</sub> H <sub>2</sub> (Me-bridged)					
Be-C	1.827	1.834	1.831	1.839	1.828
Be-H	1.345	1.351	1.340	1.343	1.338
Be <sub>2</sub> Me <sub>2</sub> H <sub>2</sub> (H-bridged)					
Be-H	1.474	1.485	1.474	1.476	1.471
Be-C	1.694	1.690	1.681	1.690	1.684
Be <sub>2</sub> H <sub>4</sub>					
Be-H <sub>br</sub>	1.481	1.481	1.470	1.471	1.466
Be-H <sub>t</sub>	1.332	1.337	1.328	1.329	1.325
Average Absolute Deviations <sup>b</sup>					
	0.006	0.006	0.005	0.007	

<sup>a</sup> A basis set of 6-311G\* was employed for all geometry optimizations. <sup>b</sup> Average absolute deviation in bond distances relative to MP2.

with a very large basis set, we also examined all of the systems using B3-LYP and a triple- $\zeta$  basis set with diffuse and polarization functions. Except for F-bridged and H-bridged Be<sub>2</sub>F<sub>2</sub>H<sub>2</sub>, these calculations produce energetics which are even closer to the G2 results than the corresponding calculations with the smaller basis set. For this system of substituted beryllium hydrides, DFT generally produces estimates of the dimerization energies that are on a par with those predicted with ab initio MP4 calculations. Unlike the other systems in this investigation,

**Table 8.** Dimerization Energy of the Substituted Beryllium Hydrides (kcal/mol) Calculated with Different ab Initio and Density Functional Methods

method and basis set	$-\Delta E$				
	Be <sub>2</sub> H <sub>4</sub>	Be <sub>2</sub> F <sub>2</sub> H <sub>2</sub>		Be <sub>2</sub> Me <sub>2</sub> H <sub>2</sub>	
		F-br	H-br	Me-br	H-br
MP4/6-311G**//MP2/6-311G**	33.8	36.2	28.0	22.7	30.9
G2 <sup>a</sup>	33.4	31.5	23.6	21.3	30.5
B-P86/6-311G**//B-P86/6-311G**	34.7	29.9	26.6	19.7	30.1
B3-P86/6-311G**//B3-P86/6-311G**	35.8	32.9	27.7	21.2	31.5
B-LYP/6-311G**//B-LYP/6-311G**	31.4	27.6	23.6	13.3	26.5
B3-LYP/6-311G**//B3-LYP/6-311G**	32.4	30.6	24.8	15.4	27.9
B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311G**	32.6	27.4	22.3	16.4	28.2

<sup>a</sup> The relative energetics are at 0 K with no vibrational zero point energy correction included.

the choice of correlation functional appears more important than the choice of exchange functional.

### Conclusions

We apply a variety of nonlocal density functionals to four difficult energetic/structural problems in main-group inorganic chemistry. We then compare these results to those from ab initio MP2 and MP4 (and G2 and G2MP2', in some cases) calculations and to experiment, where available. We find that all of the functionals under investigation perform quite well compared to MP2 calculated geometries, with B-P86 achieving the overall smallest average absolute deviations in bond distances relative to MP2. In general, for the 81 unique bond distances calculated in this study, B-P86 has the smallest average absolute deviation in bond distances relative to MP2 of 0.009 Å, B-LYP produces an average deviation of 0.015 Å, B3-P86 has an average deviation of 0.020 Å, and B3-LYP differs from MP2 by an average of 0.021 Å. In particular, B-P86 gives the smallest average absolute deviation in bond distances relative to MP2 for two of our systems: the carboranes and C<sub>3</sub>Li<sub>4</sub>. B3-P86 performs most favorably (compared to MP2) for Cp<sub>2</sub>Be, but is the worst performer for the carboranes and for C<sub>3</sub>Li<sub>4</sub>. B-LYP produces the smallest average absolute deviation in bond distances for the substituted beryllium hydride dimer systems.

In one case (Cp<sub>2</sub>Be), we find that MP2 fails spectacularly while all the density functionals with sufficiently large basis sets are able to determine the correct ground-state structure. We also find that the choice of the exchange functional is much more important than the choice of correlation functional for most of the systems we examined. In the case of the substituted beryllium hydride dimers, we are able to compare our ab initio and DFT results to G2<sup>34</sup> calculations and discover that DFT calculations with a large basis set generally reproduce the G2 energetics at least as well as MP4 calculations do. For the C<sub>3</sub>-Li<sub>4</sub> isomers, we calculate relative energetics at the G2MP2' <sup>39</sup> level and find that, like MP4, G2MP2' predicts relative energetics that are much lower than the DFT results. The G2MP2' calculations also reveal for the first time an isomer which is energetically competitive with the commonly accepted ground-state structure.

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