Octacoordinate Carbons Encaged Inside Carborane Clusters: A Density Functional Theory Investigation

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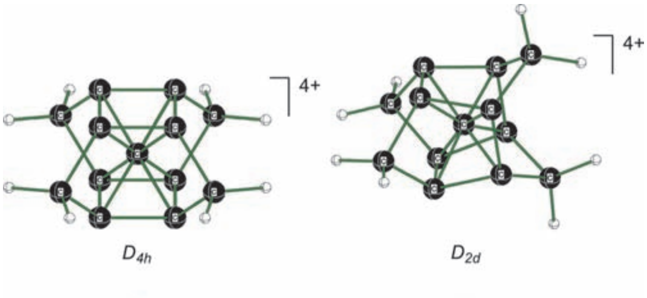
This work focuses on the computational design and characterization of a novel series of endohedral carborane clusters containing octacoordinate carbon centers. The structural and bonding features and the thermodynamic and kinetic stabilities are discussed extensively based on density functional theory calculations. These nonclassical carboranes are fascinating in structure not only for the octacoordinate carbon center but also for the surrounding carbon and boron ligands with inverted bonding configuration. These endohedral carboranes are higher in energy than the corresponding exohedral isomers due to the high strain in the system. A new stability rule based on the donor−acceptor model is proposed to predict the stability ordering for these carborane isomers. In addition, some of these octacoordinate carboranes might have relatively high kinetic stabilities, which is rather hopeful for the experimental syntheses.

1. Introduction

With the challenge to van't Hoff's tetrahedral carbon concept,[1] nonclassical carbons are attracting more and more theoretical and experimental attention during the last years.[2] Despite the importance of the classical tetrahedral carbon to life, the nonclassical forms of carbon are also fascinating and important from the fundamental point of view. On one hand, the tetracoordinate carbons with nontetrahedral configurations have been extensively studied. Especially, the planar tetracoordinate carbon (ptC) has been a topic of considerable interest in recent decades.[2–12] On the other hand, both experimentalists and theoreticians are endeavoring to search for the carbons with the coordination number of more than four, the so-called hypercoordinate carbons.[2] The coordination number of carbon has reached from five up to eight both theoretically[13–27] and experimentally.[28–39] Higher coordination numbers (from 9 to 12) of carbon have also been predicted by quantum chemistry computations.[40,41]

The search for more new structures containing highly coordinated carbons is still of great interest. Furthermore, from the theoretical point of view, it would be very helpful if some general strategies[26,27,42] are proposed for discovering possible hypercoordinate carbon structures. It is also interesting to see that many hypercoordinate carbons are obtained in boroncarbon[14,15,19–21,25,43,44] or carborane[22,23,40,45] compounds. The reasons may be as follows. The hypercoordinate carbons generally still obey the eight-electron rule.[17,26,40,41,46,47] Therefore, the central carbon atom needs only four ligands providing the extra four electrons and the other ligands should give no more electrons to the central carbon. Since boron is electron-deficient, it is possible to attach boron atoms to the saturated central carbon to achieve a higher coordination number. Meanwhile, the structural varieties of carboranes[45] can provide more possibilities for building a hypercoordinate carbon structure. Hypercoordinate carbons can be obtained in various structures, such as polyhedral, endohedral, planar, and wheel-like structures.[45] Since the carborane chemistry has been well-developed, the theoretical investigation of carborane compounds containing hypercoordinate carbons should be more meaningful not only to the concepts in the carborane chemistry but also to the experimental syntheses.



1a **1b**

Figure 1. Hydrocarbon tetracations containing octacoordinate carbons.

Here we present our density functional theory (DFT) studies on a series of carborane isomers containing octacoordinate carbon centers. These neutral carborane clusters are derived from the hydrocarbon tetracations **1a** and **1b** (see Figure 1) which have been computationally studied recently.[26] Among the carboranes studied here (**2a**, **2b**, **3a**−**3j**, and **4a**−**4m**, see Figure 2), the compounds **3a** and **3i** have been proposed in our previous work,[26] and **2a**, **2b**, and **3a** have also been computationally studied recently.[48,49] The structural and bonding characteristics of these novel carborane compounds are extensively described. On the basis of the calculated energies, thermodynamic stabilities are discussed and several stability rules are proposed. Moreover, kinetic stabilities are also investigated for some isomers.

2. Computational Methods

The geometry optimizations and the total energy computations were performed with the Gaussian03 package[50] in the

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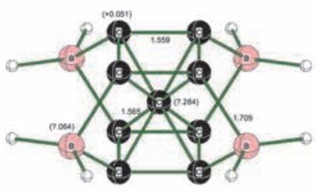
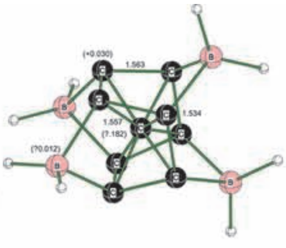


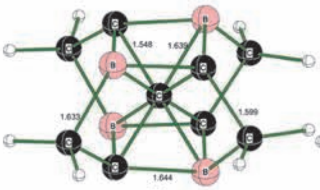
D_{4h}

2a



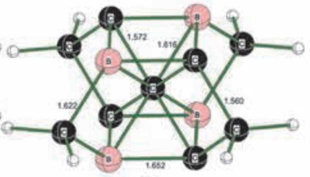
D_{2d}

2b



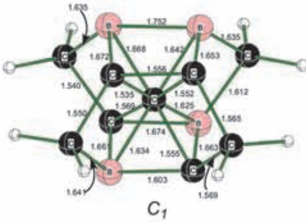
D_{2d}

3a



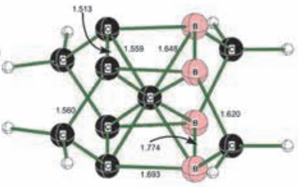
D_{2h}

3b



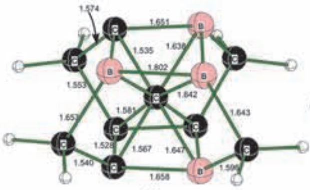
C_1

3c



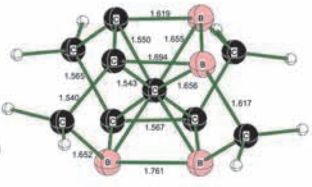
C_{2v}

3d



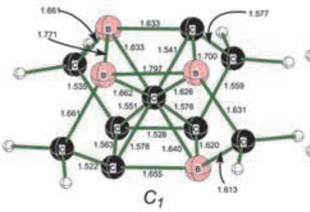
C_s

3e



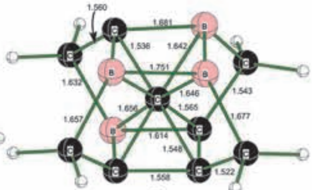
C_2

3f



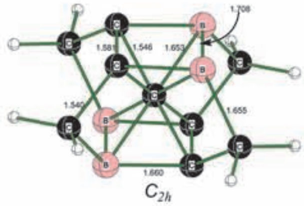
C_1

3g



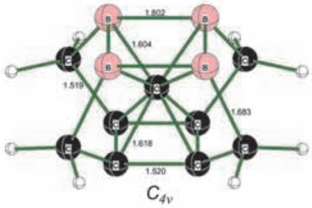
C_s

3h



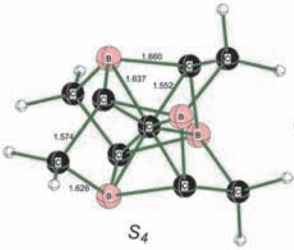
C_{2h}

3i



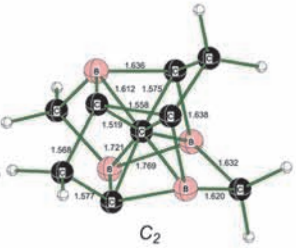
C_{4v}

3j



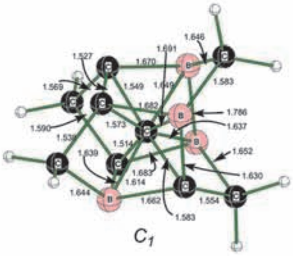
S_4

4a



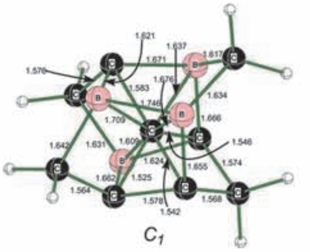
C_2

4b



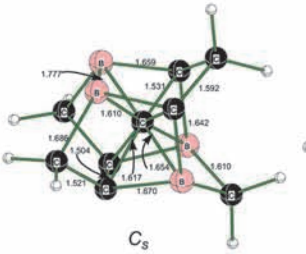
C_1

4c



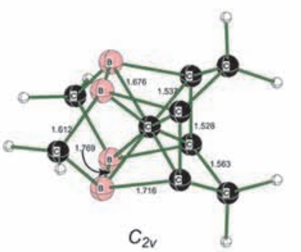
C_1

4d



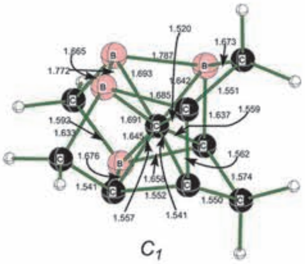
C_s

4e



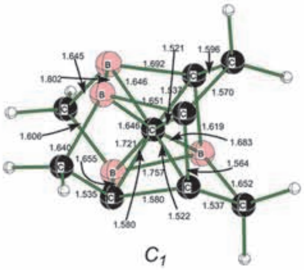
C_{2v}

4f



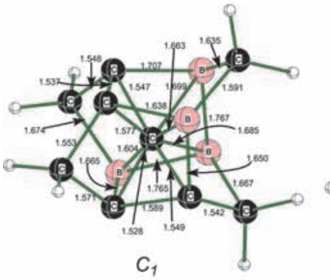
C_1

4g



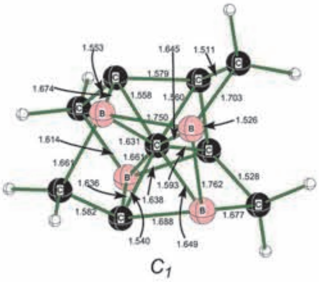
C_1

4h



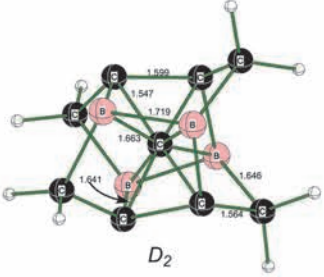
C_1

4i



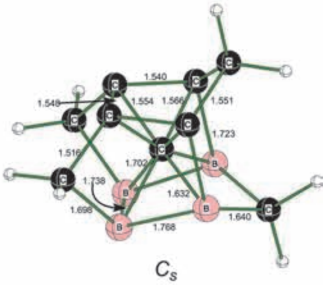
C_1

4j



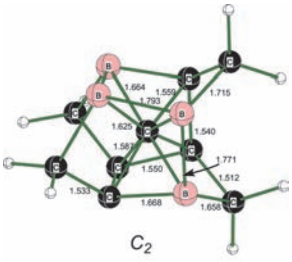
D_2

4k



C_s

4l



4m

Figure 2. Carborane isomers containing octacoordinate carbons which are derived from the hydrocarbon tetracations **1a** and **1b** (unit of bond lengths: Å).

framework of DFT. The Becke−Lee−Yang−Parr three-parameter (B3LYP)[51–55] functional was employed for exchange and correlation. All the computations were carried out with the 6-311+G(d,p) basis set.[18,23,26,47,48,56–58] Once the fully optimized geometry was obtained, vibration frequency analyses were performed at the same level of theory to characterize the stationary points and to evaluate the zero-point energy correction (ZPE). Topological analyses of the electron density were done based on Bader's atoms in molecules (AIM) theory[59–62] by using the AIM2000 program[63,64] in order to verify the bond critical points (BCPs). Natural bond orbital (NBO) analyses[65] were done to compute the natural charge[65] on atoms and the Wiberg bond indices (WBIs[66]) by using the NBO subroutine implemented in the Gaussian03 package.[50] In order to further confirm the transition states that were initially found, the intrinsic reaction coordinate (IRC)[67] was traced from the transition states to the reactants and products.

3. Results and Discussion

3.1. Structural and Bonding Features. We replace four carbon atoms by four boron atoms in the hydrocarbon tetracations **1a** and **1b** (see Figure 1)[26] and get the neutral carborane clusters **2a**, **2b**, **3a**−**3j**, and **4a**−**4m** (see Figure 2) without taking into account the enantiomers. These neutral carboranes are isoelectronic with the hydrocarbon tetracations **1a** and **1b** and therefore also obey the eight-electron rule.[2,25,26,42] All these carborane isomers can be classified into two general groups, the ones derived from **1a** (**2a** and **3a**−**3j**, hereafter called "A-type isomers"), and those derived from **1b** (**2b** and **4a**−**4m**, hereafter called "B-type isomers"). For each general group (A-type or B-type), there are different positional isomers depending on the arrangement of the four boron atoms (see Figure 2). These positional isomers of carboranes can be classified into three groups: (1) B-bridged isomers in which the four borons are all in the bridging positions (i.e., **2a** and **2b**); (2) B-liganded isomers in which the four borons are all in the positions bonding to the central carbon atom (i.e., **3a**−**3j** and **4a**−**4m**); (3) other cases in which the four borons are in both the bridging and the ligand positions. The B-liganded isomers are much lower in energy than the B-bridged isomers, since there are more C−H bonds and less B−H bonds in the former isomers than in the latter and the C−H bond energy is much larger than the B−H bond energy. For example, **2a** and **2b** are 180.1 and 236.5 kcal mol^{-1} higher in energy than **3a**, respectively. Therefore, in this paper we only investigate the B-liganded isomers which are more energetically stable.

In all these carborane cages, a multicenter bond is formed among the central carbon (C_{cen}) and the eight surrounding ligand carbon (C_{lig}) and boron (B_{lig}) atoms. The C_{cen}−C_{lig} and C_{cen}−B_{lig} bond lengths are about 1.51−1.62 and 1.60−1.77 Å, respectively. The WBI values can be used as a measure of the bond strength.[66] The WBIs of the C_{cen}−C_{lig} bonds are about 0.44−0.74, whereas the WBIs of C_{cen}−B_{lig} bonds are generally much smaller, about 0.24−0.49. This indicates that the bonding interaction of the central carbon with the carbon ligands is generally much stronger than that with the boron ligands. This conclusion is also confirmed by the electron density topological analyses based on the AIM theory. As shown in Figure 3, in all these carborane isomers studied here, the BCP always exists for the C_{cen}−C_{lig} bond, whereas there is not always a BCP for the C_{cen}−B_{lig} bond. As for the A-type isomers, it is found that a BCP exists only if the WBI value of the C_{cen}−B_{lig} bond is larger than 0.33. It is necessary to point out that, although in some isomers there is no bond path going through the central carbon and the boron ligand in the framework of the AIM theory, we cannot definitely claim that there is no bonding interaction at all between the central carbon and the boron ligand. For instance, on the basis of the AIM analysis, no bond paths exist between the central carbon and the four boron atoms in carborane **3b**, and the central carbon is thus a ptC. However, like other ptCs, this ptC in **3b** is undoubtedly stabilized through the donor−acceptor interaction between the lone pair of the ptC and the empty p orbitals of the boron atoms. Therefore, it seems unreasonable to claim that no bonding interaction exists at all between the central carbon and the boron atoms in **3b**. Further discussion will be presented below. Moreover, it is still quite a debating issue whether the existence of a bond path based on the AIM theory is the sufficient and necessary condition for the existence of a chemical bond.[68–75] Please note that the confirmation of the existence of chemical bonds between the central carbon and the surrounding boron atoms is beyond the scope of this work. Therefore, for sake of simplicity and convenience, in all these carborane isomers the central carbon atoms are still called "octacoordinate" in this paper.

In all these carborane cages, the central carbon atom and the surrounding carbon and boron ligands are supposed to form multicenter bonds. Like the case for boroncarbon cluster $C@C_4B_4$,[43] the formation of the multicenter bonds can be understood as follows. First, the central carbon forms C_{cen}−C_{lig} covalent bonds with the four carbon ligands since the C_{cen}−C_{lig} bonding interaction is generally much stronger than the C_{cen}−B_{lig} interaction as we have shown above. Then, the system is further stabilized through the electron donor−acceptor interaction between these C_{cen}−C_{lig} bonds and the vacant p orbitals on the boron atoms (see Figure 4.)

Such electron donor−acceptor interaction can be confirmed in the following analysis. By replacing the boron atom with a −CH group in carboranes **3a** and **3b**, we get the corresponding hydrocarbons **5a** and **5b**. There is no bonding interaction between the central carbon and the surrounding −CH groups in both hydrocarbons as all the carbons are saturated and satisfy the Lewis structure rule. After the full geometry optimizations and the frequency analyses, **5a** is confirmed to be still a minimum on the potential energy surface (PES), whereas **5b** is found to be a third-order saddle point (with three negative force constants). Please note that the central carbon atom in **5b** is a ptC, which induces high strain energy and can be stabilized by attaching to electron acceptors.[2,3,9] Indeed, as we can see, the three imaginary vibration frequencies of **5b** disappear after replacing the −CH group by a boron atom as in **3b**. This implies that the boron

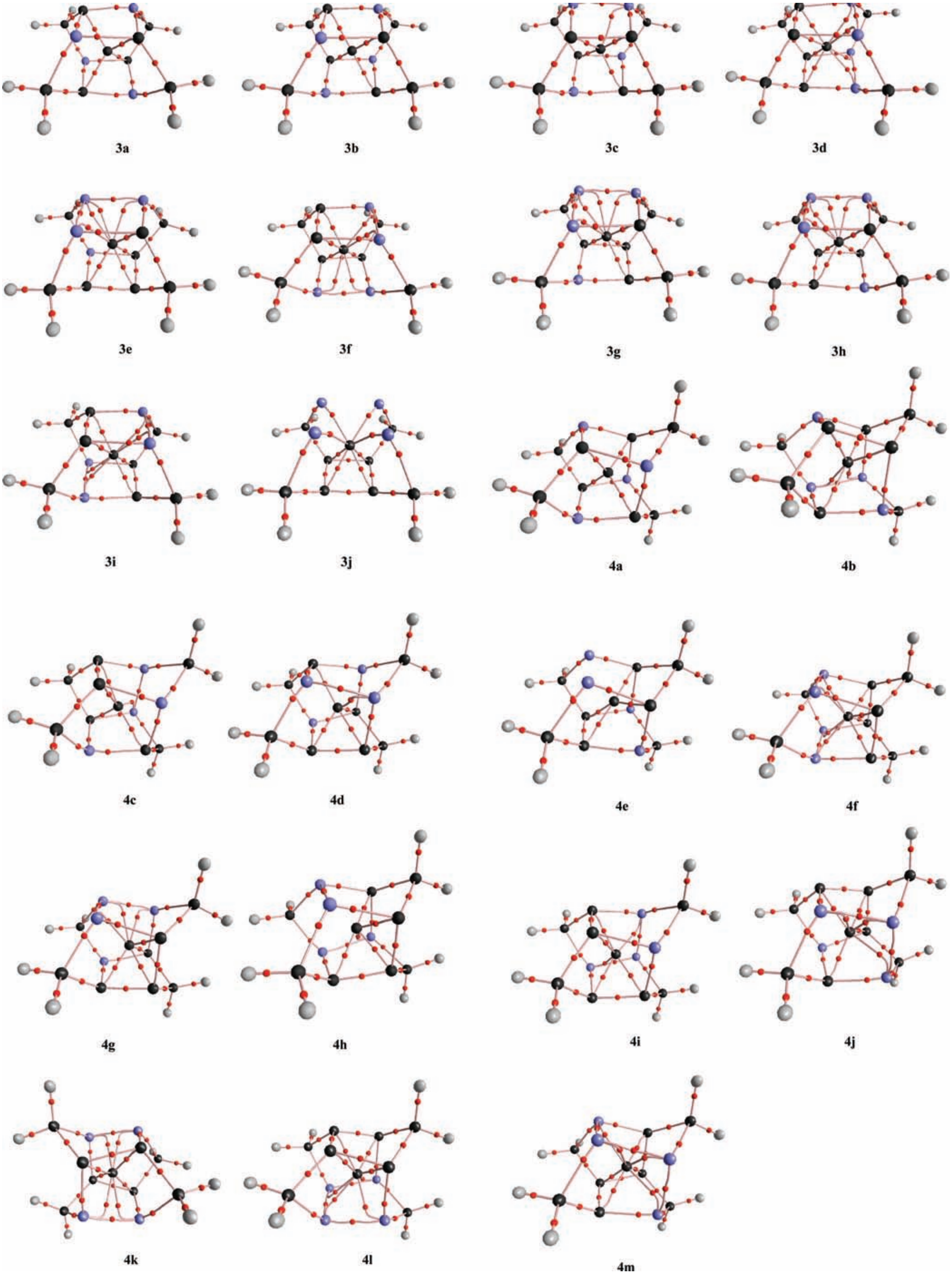


Figure 3. Molecular graphs for the carborane isomers **3a**−**3j** and **4a**−**4m**. Dark, gray, and blue balls are carbon, hydrogen, and boron atoms, respectively. The red balls are the BCPs, and the pink lines represent the bond paths.

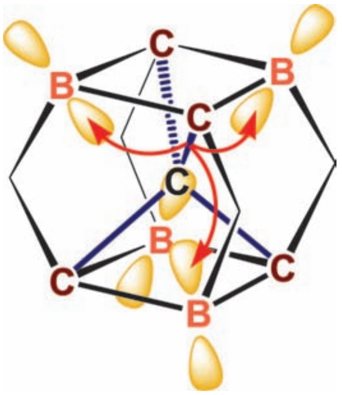
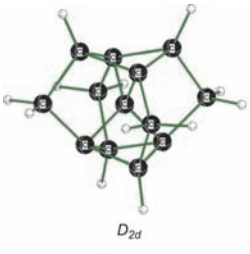


Figure 4. Electron donor−acceptor interaction between the preformed $C_{cen}-C_{lig}$ bonds and the vacant p orbitals on the boron ligands.

atoms indeed stabilize the central ptC since they provide empty p orbitals and act as electron acceptors.



5a

5b

It is also worthy to mention that the carbon and boron ligands have an inverted umbrella-like configuration[2,76] as in the case of the hydrocarbon cations **1a** and **1b**.[26] The four atoms attached to the inverted C or B atom have an umbrella-like arrangement, instead of a tetrahedral classical arrangement. As we can see in Figure 5, the inverted umbrella-like C or B atom is located on the tip of the "umbrella". Among the four attached atoms, we can always find one of them as the "umbrella handle" (see Figure 5). The line joining this "handle" atom and the "tip" atom makes the "umbrella stick", which intersects the plane defined by the other three attached atoms, as shown in Figure 5. We define the "inverted distance"[26] of the inverted C or B atom as the distance from that intersection point to the "tip" atom (see Figure 5). The inverted distance can be used as a measure for determining how much the "tip" atom is "inverted". Following this definition, the inverted distance of the bridgehead carbon in the 8,8-dichlorotricyclo[3.2.1.0.^{1,5}]octane is about 0.1 Å, according to the X-ray crystallography measurement.[76,77] As a comparison, the eight carbon ligands in hydrocarbons **1a** and **1b** have the inverted distance of 0.51 and 0.58, respectively.[26]

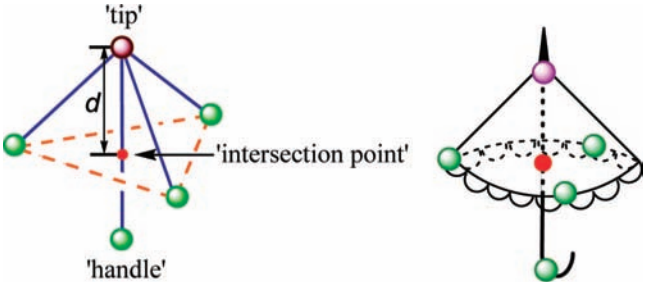
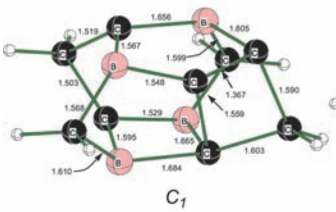


Figure 5. Definition of the inverted distance *d* for an inverted umbrella-like atom.

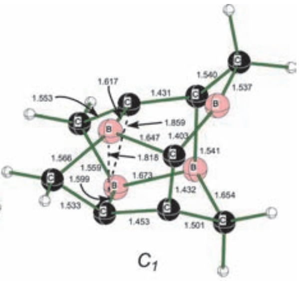
For the A-type carborane isomers (**3a**−**3j**), the inverted distances are 0.40−0.54 Å for the carbon ligands and 0.54−0.68 Å for the boron ligands. For the B-type isomers (**4a**−**4m**), the inverted distances are 0.50−0.61 and 0.63−0.74 Å for the carbon and boron ligands, respectively. As we can see, the boron ligands are in general more "inverted" than the carbon ligands, and the carbon (boron) ligands in the B-type isomers are more "inverted" than those in the A-type isomers.

3.2. Thermodynamic Stabilities. ***3.2.1. Relative Energies.*** The relative energy differs among the carborane isomers, and the maximum energy difference is 78 kcal mol^{-1}, as listed in Table 1.

Similar to the case of the hydrocarbons **1a** and **1b**,[26] these endohedral carborane isomers with octacoordinate carbons are higher in energy than the corresponding exohedral carborane isomers. For instance, the endohedral isomer **4k** is energetically higher by 106.10 kcal mol^{-1} than the corresponding exohedral isomer **6b**. However, the endohedral isomer **3b** is only 7.44 kcal mol^{-1} higher in energy than the corresponding exohedral isomer **6a**.



6a



6b

In analogy to the hydrocarbons **1a** and **1b**,[26] the high relative energy of these octacoordinate carborane cages comes from the nonclassical bonding features and the high strain energy in the system. By comparing the energies to many different isomers and using homodesmotic reactions, the hydrocarbons **1a** and **1b** have been convincingly shown to possess rather high strain energy, because of the eight greatly inverted umbrella-like carbons.[26] Due to the structural similarity to **1a** and **1b**, these octacoordinate carborane clusters may also have high strain energy, which is induced by the inverted carbon and boron ligands in these nonclassical structures.

3.2.2. Stability Rules. In analogy to other carboranes,[78–81] we found that there are several stability rules for these octacoordinate carborane isomers.

First, from Table 2, one can find that isomers with a larger number of C−B bonds are energetically more stable. This rule has been shown valid also for other carboranes.[78,80] This general rule can be understood by the fact that the C−B bond is stronger than the C−C and the B−B bond (the bond energies of C−B, C−C, and B−B bond are 89.0, 82.6, and 70 ± 5 kcal mol^{-1}, respectively).[80,82]

As shown in Table 2, however, the first rule is not able to distinguish the relative stabilities of the isomers which have exactly the same numbers of C−B, C−C, and B−B bonds. Thus, another rule is proposed to predict the relative stabilities of the isomers with the same number of C−B bonds. This rule suggests that the isomer with more $B\cdots C_{cen}\cdots B$ contacts is energetically more stable. To explain it clearly, let us examine the relative positions of the boron ligands surrounding the central carbon atom. As shown in Figure 6, there are three kinds of

TABLE 1: Calculated Results at the B3LYP/6-311+G(d,p) Level for the A-Type and B-Type Carborane Isomers

structure	PG[a]	ZPE[b]	E_{rel}[c]	ω_{min}[d]	q[e]	WBI[f]	gap[g]
3a	D_{2d}	96.27	0.00	252.21	−0.552	3.91	6.23
3b	D_{2h}	95.60	12.58	240.81	−0.671	3.83	4.34
3c	C_1	95.80	18.29	246.38	−0.618	3.86	4.99
3d	C_{2v}	95.43	24.53	239.95	−0.660	3.84	5.55
3e	C_s	95.59	28.30	238.22	−0.622	3.87	4.90
3f	C_2	95.60	30.26	241.39	−0.628	3.84	5.16
3g	C_1	95.43	34.55	245.77	−0.639	3.85	4.69
3h	C_s	95.49	36.51	255.17	−0.613	3.85	4.73
3i	C_{2h}	95.42	39.45	247.51	−0.646	3.81	4.42
3j	C_{4v}	94.56	66.85	253.26	−0.725	3.85	4.44
4a	S_4	96.74	26.00	303.37	−0.520	3.96	5.08
4b	C_2	96.32	37.99	313.24	−0.525	3.95	4.91
4c	C_1	96.07	40.64	286.18	−0.571	3.89	4.14
4d	C_1	96.41	41.35	315.67	−0.532	3.94	4.46
4e	C_s	96.04	43.79	304.91	−0.591	3.88	3.98
4f	C_{2v}	95.51	49.24	267.95	−0.600	3.85	4.47
4g	C_1	95.75	55.46	286.10	−0.556	3.91	4.13
4h	C_1	95.75	56.64	284.04	−0.553	3.89	4.05
4i	C_1	95.69	57.00	288.23	−0.582	3.88	4.01
4j	C_1	95.74	61.76	300.68	−0.581	3.88	3.82
4k	D_2	96.16	63.84	322.42	−0.554	3.89	3.62
4l	C_s	95.21	73.61	298.15	−0.598	3.89	4.06
4m	C_2	95.08	78.02	306.17	−0.618	3.85	4.02

[a] Point group for the optimized structures. [b] Zero-point energy (in kcal mol^{-1}). [c] Relative energy with respect to the most stable isomer which has included the ZPE correction (in kcal mol^{-1}). [d] Smallest vibration frequency (in cm^{-1}). [e] Natural charge on the central carbon atom (in $|e|$). [f] Sum of WBIs for the central carbon atom. [g] HOMO−LUMO gap (in eV).

TABLE 2: Structural Parameters for A-Type and B-Type Carborane Isomers

structure	$n_{\text{C-B}}$[a]	$n_{\text{C-C}}$[b]	$n_{\text{B-B}}$[c]	N_1[d]	N_2[e]	N_3[f]
3a	12	4	0	0	6	0
3b	12	4	0	2	2	2
3c	10	5	1	2	3	1
3d	8	6	2	4	2	0
3e	8	6	2	3	3	0
3f	8	6	2	3	2	1
3g	8	6	2	3	2	1
3h	8	6	2	2	3	1
3i	8	6	2	2	2	2
3j	4	8	4	4	0	0
4a	12	4	0	0	6	0
4b	10	5	1	3	2	1
4c	10	5	1	2	3	1
4d	10	5	1	2	3	1
4e	10	5	1	2	2	2
4f	8	6	2	4	2	0
4g	8	6	2	3	3	0
4h	8	6	2	3	2	1
4i	8	6	2	3	2	1
4j	8	6	2	2	3	1
4k	8	6	2	2	2	2
4l	6	7	3	4	0	0
4m	6	7	3	3	2	1

[a] Number of C−B bonds. [b] Number of C−C bonds. [c] Number of B−B bonds. [d] Number of the nearest B•••C_{cen}•••B contacts. [e] Number of the second nearest B•••C_{cen}•••B contacts. [f] Number of the farthest B•••C_{cen}•••B contacts.

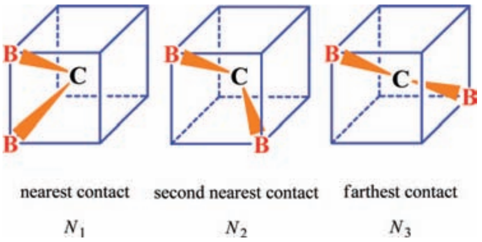


Figure 6. Three kinds of B•••C_{cen}•••B contacts.

relative positions for two boron ligands: the nearest, the second nearest, and the farthest B•••C_{cen}•••B contacts depending on the B•••C_{cen}•••B angle. Let the number of the three contacts be N_1, N_2, and N_3, respectively, for the nearest, the second nearest, and the farthest contact. Then, it is shown in Table 2 that the isomer with the smaller N_3 value has lower energy, and when the N_3 value is same the isomer with the smaller N_2 value is lower in energy.

This rule works very well for all the A-type and the B-type isomers without any exception. This rule can be explained on the basis of the topological charge stabilization (TCS) rule.[83] The TCS rule has been rationalized based on the first-order perturbation theory[84] and is quite successful for predicting and understanding the relative stability of carborane positional isomers.[85–88] To apply the TCS rule to our neutral 4B-carborane isomers, we need to consider the corresponding isoelectric 3B-carborane cation from which the 4B-carboranes can be derived by replacing one of the C_{lig} atoms with a B^+. Then, the relative stability of the derived 4B-carborane isomers can be predicted by investigating the charge distribution of the isoelectric 3B-carborane counterpart. According to the TCS rule, the 4B-carborane isomer generated by the replacement of more positively charged C_{lig} position is energetically more favorable. For example, isomers **3f** and **3i** can be derived from a common 3B-isomer, **7**, by replacing the α- and β-C atom, respectively (see Figure 7). Since the natural charge on α-C is relatively more positive (or less negative) than that on β-C (see Figure 7), the TCS rule predicts that **3f** is more energetically stable than **3i**, which is consistent with our B3LYP/6-311+G(d,p) results. On the other hand, the relative charges on α- and β-C atoms can be predicted qualitatively by comparing the positional arrangements of the B atoms and the α- or β-C atom. For the example of **7**, both α- and β-C atoms are bonded to one boron and three carbon atoms. Therefore, in order to compare the charges, we need to consider the secondary bonding interaction, i.e., the electron donor−acceptor interaction between the C_{cen}−C_{lig} bond and the vacant p orbitals on the B atoms (see

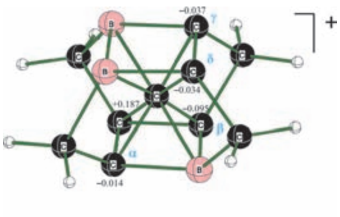


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Figure 7. Structures and charge distributions of two 3B-carborane cations.

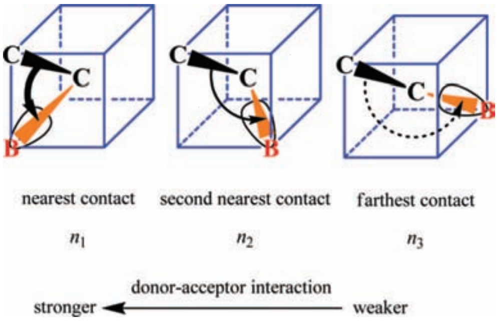


Figure 8. Three kinds of contacts between $C_{cen}-C_{lig}$ and $C_{cen}\cdots B_{lig}$ bonds.

Figures 4 and 8). There are three kinds of such donor−acceptor interactions, depending on the relative distance between the donor ($C_{cen}-C_{lig}$ bond) and the acceptor (boron vacant orbital), as shown in Figure 8.

In **7**, there are two nearest and one second nearest $B\cdots C_{cen}-\alpha$-C contacts ($n_1 = 2$, $n_2 = 1$, and $n_3 = 0$), while there is one nearest, one second nearest, and one farthest of $B\cdots C_{cen}-\beta$-C contact ($n_1 = 1$, $n_2 = 1$, and $n_3 = 1$). Therefore, the total donor−acceptor interaction between the B orbitals and the $C_{cen}-\alpha$-C bond is stronger than that between the B orbitals and the $C_{cen}-\beta$-C bond. This explains why the charge on the α-C is relatively more positive than that on the β-C, as more such donor−acceptor interaction leads to more electron transfer from the $C_{cen}-C_{lig}$ bond to B atoms. Similar analysis can be done for other carborane isomers. For instance, by counting the numbers of three kinds of $B\cdots C_{cen}-C$ motifs for α-C contacts ($n_1 = 2$, $n_2 = 1$, and $n_3 = 0$) and γ-C contacts ($n_1 = 1$, $n_2 = 2$, and $n_3 = 0$), α-C is expected to carry relatively more positive charge than γ-C. According to the TCS rule, therefore, isomer **3f** (derived by the replacement on the α position) is predicted to be energetically more stable than isomer **3h** (derived by the replacement on the γ position), in agreement with our B3LYP/6-311+G(d,p) results.

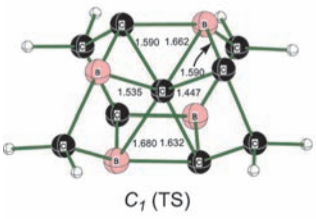
In this way, we can naturally explain our second stability rule, as well as the first rule. Imagine that all the 4B-carborane isomers are obtained consecutively from the isoelectric 1B-, 2B-, and 3B-carboranes, by replacing a C with a B^+ each time. According to the TCS rule, each time the new B atom prefers to replace the more positively (or less negatively) charged C atom. In other words, the more favorable position to introduce the new boron is the more positively or less negatively charged carbon. Obviously, the first preferred position is the C atom forming fewer bonds with the existing B atoms, as the C atom withdraws electrons from the B atoms bonded to it. As a result, the introduction of the new boron prefers to give more C−B bonds, which is exactly what the first rule says. To be the secondary preference, the replaced C atom needs to have more contacts with the surrounding nonbonded B atoms so that more electrons are transferred away due to the donor−acceptor interaction. This explains our second stability rule.

The two stability rules are also supported by the good correlation between the relative energy and the total natural charges on the boron atoms. Figure 9 demonstrates that the isomers with more positive natural charges on the borons are energetically more stable. First, according to the first rule, the more stable isomer has more C−B polarized bonds, giving rise to more positive charge distribution on the B atoms. Second, for the isomers with the same number of C−B polarized bonds, the more stable isomer has more $B\cdots C_{cen}\cdots B$ contacts and thus fewer contacts between $C_{cen}-C_{lig}$ bonds and B atoms, leading to weaker donor−acceptor interaction between the $C_{cen}-C_{lig}$ bonds and the B vacant orbitals (see Figures 4 and 8). If such donor−acceptor interaction is weaker, fewer electrons will be transferred to the boron atoms, and thus the borons will carry more positive charges.

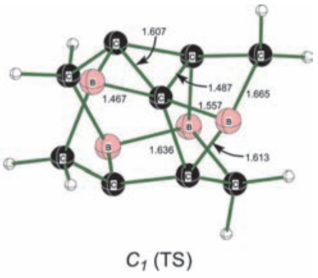
3.3. Kinetic Stabilities.

All these octacoordinate carborane isomers have relatively high values of the vibration frequencies (231−322 cm^{-1}), indicating that these structures correspond to relatively deep local minima on the PES, similar to the hydrocarbon cations **1a** and **1b**[26] and prismanes.[89] Hence, these nonclassical endohedral carboranes are expected to possess relatively high kinetic stabilities, although they have been shown energetically unfavorable compared to the exohedral isomers.

We examined first the HOMO−LUMO gap which is often used to evaluate the chemical reactivity. The isomers **3a** and **4a** give the maximum HOMO−LUMO gaps (6.23 and 5.08 eV, respectively) for the A-type and the B-type carborane isomers. In addition, the HOMO−LUMO gaps of the other A-type isomers are generally larger than those of the other B-type isomers.



8a



8b

Like the octacoordinate hydrocarbon cages **1a** and **1b**,[26] these octacoordinate carborane endohedral isomers can also undergo isomerization into exohedral isomers. For example, isomer **3b** can be rearranged into **6a** through the transition state **8a** with an energy barrier of 22.9 kcal mol^{-1}. This energy barrier is obviously higher than the barriers for the rearrangements of hydrocarbons **1a** and **1b** (15 and 6 to 7 kcal mol^{-1}, respectively)[26] and much higher than the barrier for the rearrangements of the octacoordinate boroncarbon $C@C_4B_4$[43] (1.2 and 1.4 kcal mol^{-1} at the B3LYP/6-311+G** and MP2/6-311+G** level, respectively). For the hydrocarbons **1a** and **1b**, the rearrangements lead to the exohedral isomers with much lower energy (120−140 kcal mol^{-1} lower), indicating that these rearrangements are almost irreversible.[26] In comparison, the carborane **3b** rearranges to an exohedral isomer **6a**, which is only 7.4 kcal mol^{-1} lower in energy than **3b**. Therefore, the rearrangement of **3b** is more reversible. The B-type carborane isomer **4k** can rearrange to **6b** through the transition state **8b** with an energy barrier of 51.1 kcal mol^{-1}. Such a high barrier prevents **4k** from being easily rearranged although the exohedral isomer **6b** is

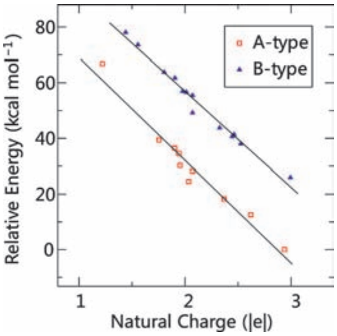


Figure 9. Relative energy vs the sum of the natural charges on the boron atoms for A-type (empty squares) and B-type (solid triangles) carborane isomers.

much lower in energy by 106 kcal mol^{-1}. Hence, we can expect that some of the octacoordinate carborane isomers can probably have relatively high kinetic stabilities, which makes it feasible to synthesize them. We would like to point out that the IRC[67] was traced from the transition states to the reactants and products, in order to further confirm the transition states.

4. Conclusions

Following the same construction strategy for the hydrocarbons **1a** and **1b**,[26] octacoordinate carbons are obtained by encaging them inside carborane clusters. These endohedral carborane isomers are stabilized by forming multicenter bonds among the central carbon and the surrounding carbon and boron ligands. This nonclassical bonding can be understood by supposing the electron donor−acceptor interaction between the $C_{cen}-C_{lig}$ bond and the boron vacant p orbitals. It is also interesting to see that all the carbon and boron ligands have an abnormal inverted umbrella-like configuration.

These octacoordinate carborane isomers are higher in energy than the corresponding exohedral carborane isomers due to the nonclassical bonding features and the high strains induced by the inverted carbon and boron ligands. On the basis of the relative energies of these carborane isomers, two stability rules are proposed to predict the order of stability among these positional isomers. The first rule is that the isomers with more C−B bonds are more stable energetically, which has been proved to be valid also for other kinds of carboranes. The second rule suggests that the isomer with more $B\cdots C_{cen}\cdots B$ contacts is energetically more stable. Both rules can be understood on the basis of the TCS rule.

Kinetic stabilities are also discussed by investigating the isomerization rearrangement for some isomers. Although the exohedral isomer may be more stable in energy, the energy barrier of the rearrangement can be rather large (e.g., 51.1 kcal mol^{-1}), indicating the relatively high kinetic stabilities of the nonclassical carborane clusters. We hope our present study is helpful for the syntheses of this new family of carborane clusters and for the extension of the carborane chemistry.

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