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The Conversion among Various B_4C Clusters: A Density Functional Theoretical Study

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Geometry optimizations and vibration frequencies of B_4C clusters were performed with Becke-3LYP method using 6-31G(d) basis set. We have found 14 stable isomers, and the most stable structure among them is the five-member ring containing two three-member boron rings. We also analyzed these stable isomers in detail, and the results show that the structures containing three-member boron rings are predominant in energy for B_4C clusters. In terms of MO and NBO analysis, the three-centered bond and the π-electron delocalization play an important role in stabilizing the planar five-member rings of these B_4C clusters. Our calculations suggest that isomer4 can be converted into isomer7 with only an energy barrier of 0.31 kJ mol^{-1} at the B3LYP/6-311G+(3df) level. Although the planar structures of the five-member rings (isomers12−14) can be converted with each other, the conversions of isomer14 to isomer13 and isomer13 to isomer12 have high-energy barriers of 70.99 and 68.51 kJ mol^{-1} at the B3LYP/6-31G(d) level, respectively.

Introduction

A compound of boron and carbon has potential applications in diverse aspects, such as control rods in nuclear fission reactors,[1] target tiles in nuclear fusion reactions,[2,3] protective coating of carbon fiber materials, against atomic materials oxygen in spacecraft,[4] and extra hardness material. Especially, boron carbide (B_4C), a high-performance abrasive material with chemical and physical properties similar to diamonds, is the third hardest material known behind diamond and cubic boron nitride.[5] Although the boron carbide was discovered in the 19th century as a byproduct of reactions involving metal borides, until the 1930s it was not studied as the material. Boron carbide is produced from boric acid or B_2O_3 (boron oxide) and carbon-containing materials in electric arc furnaces, and the equation of the reaction is $2B_2O_3 + 7C = B_4C + 6CO$. Because of good resistance to high temperature and acids, high strength, high chemical stability, and low density, the boron carbide becomes one of the perfect raw materials of producing fire-resistant, grinding materials and ceramic production. The low density but a high elastic modulus and compressive strength lead to its being used as a ballistic material. So, boron and carbon compounds have aroused much interest and have been intensively studied by scientists.

For example, in 1995, Wang et al.[6] generated C_nB^- clusters by laser vaporization and studied their structural properties by ab initio calculations. The calculated results show that the C_nB^- ($n = 1-13$) should be linear chains and clusters with even n much more stable than those with odd n. In 1996, Zhan and Iwata[7] reported the new results obtained from ab initio calculation at higher levels on the ground states of the C_nB^- cluster. From these results, we know that the linear structures of C_nB^- ($n = 1-4$) are stable and those of other C_nB^- clusters ($n = 5-7$) are not linear and are very floppy. Simultaneously, Zhan and Iwata[8] also reported the new results for the ground states of the C_nN^- clusters.

Since ab inito methods such as HF, MP2, and MP4 are deficient in computing systems with spin-contaminations in their HF reference wave functions, recently boron and carbon clusters were investigated using density functional theory (DFT) method mostly. In 2003, McAnoy et al.[9] studied C_4B isomers at the CCSD(T)/aug-cc-pvtz//B3LYP/6-31G* level of theory. The theoretical studies suggest that CCBCC will be rearranged to planar cyclo-C_4B if the excess energy of 1 is $\geq$67.4 kJ mol^{-1}. On the other hand, the ring may open to form line CCCCB when cyclo-C_4B has an excess energy $\geq$102.1 kJ mol^{-1}. The following year, McAnoy et al. also studied the rearrangement of NCCCHO to NCCHCO[10] and the rearrangement of energized CCCCBO to OCCCCB[11] as well. Recently, Chuchev and BelBruno[12] studied C_nB and C_nB_2 at the B3LYP/6-311G** level of theory, which predicted that linear and cyclic forms will coexist for smaller cluster sizes but that monocyclic forms will be the exclusive product as n increases. Chuchev and BelBruno[13] also studied the linear C_nN_2 and C_nP_2 in the lowest energy singlet and triplet states using the B3LYP/6-311G** theoretical method for $n = 5-10$ and the B3LYP/aug-cc-pVTZ method for $n = 5-8$.

Though B_4C has been applied widely,[14−23] academic research about it has not been reported. Studying its geometry configurations is very necessary for understanding its properties on different aspects further. In this paper, we reported its various stable isomers and performed a systematic theoretical study for those isomers with density functional theory (DFT) method.

Computational Details

At first, preliminary optimizations were carried out at HF/STO-3G level on the basis of 31 possible isomers designed. To obtain accurate results, optimizations were completely calculated again at B3LYP[24,25]/6-31G(d)[26] level. For each optimized structure, harmonic frequencies and force constants were obtained at the same level of theory to determine the nature of the stationary points, which proved that all reported structures were local minima. To gain more information of the electronic properties, the natural bond orbital population analysis (NBO)[27,28] was carried out at the B3LYP/6-31G(d) level. The calculations for nucleus-independent chemical shifts (NICS)[29] have also been performed to provide aromaticity of these clusters using the

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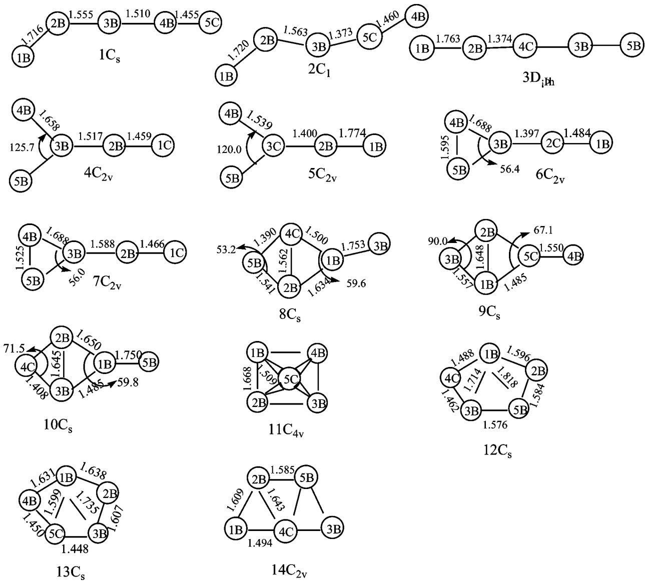

Figure 1. Stable structures, symmetry, and geometrical parameters (bond lengths in Å, bond angles in degrees) of the B_4C isomers optimized at the B3LYP/6-31G* level.

TABLE 1: Electronic Ground State, Total Energy (E_T/au), and Energy Relative to the Lowest Energy (E_r/kJ mol^{-1}) of the B_4C Isomers

isomer	ES[a]	E_T	E_r	isomer	ES[a]	E_T	E_r
1	$^1A'$	−137.0360	458.94	8	$^1A'$	−137.1541	148.87
2	^1A	−137.0884	321.36	9	$^1A_1$	−137.1584	137.58
3	^1SG_G	−137.1162	248.37	10	$^1A_1$	−137.1543	148.34
4	$^1A_1$	−137.0062	537.18	11	$^1A_1$	−137.1079	270.16
5	$^1A_1$	−137.0901	316.90	12	^1A	−137.2108	0.0000
6	$^1A_1$	−137.0808	341.32	13	$^1A'$	−137.2035	19.170
7	$^1A_1$	−137.0650	382.80	14	$^1A'$	−137.2001	28.090

[a] ES, electronic ground state.

optimized structures in the clusters. The conversion between isomer4 and isomer7 was computed at the B3LYP/6-311G+-(3df) level, whereas the conversions of isomer12, isomer13, and isomer14 were carried out at the B3LYP/6-31G(d) level. Vibration frequency analysis had been performed to confirm their identities as transition states, and the intrinsic reaction coordinate (IRC) method had also been performed to search the minimum energy path (MEP). All computations were carried out using the Gaussian03[30] package.

Results and Discussion

Stability Analysis The stable structures of B_4C clusters are presented in Figure 1. There is no imaginary vibration frequency for all these isomers, which shows that all these isomers are the stationary points on the potential energy surface (PES). The most stable structure is isomer12 with C_s symmetry in its $^1A'$ ground state, which is a planar five-member ring shape containing two three-member boron rings.

Combining Figure 1 with Table 1, among three linear (or quasi-linear) isomers, the most stable structure is isomer3 (BBCBB complex) with a rectilinear structure. However, isomer1 and isomer2 are nonbeeline. For the former, the five atoms are in a plane but are not in a beeline; the terminated boron atom is away from the beeline. For the latter, the linear structure is curved, and five atoms are not in a plane.

Among all the stable structures of B_4C clusters presented in Figure 1, isomer4 has a similar structure with isomer7. Isomer4 can be converted into isomer7 when the B4−B5 bond is formed.

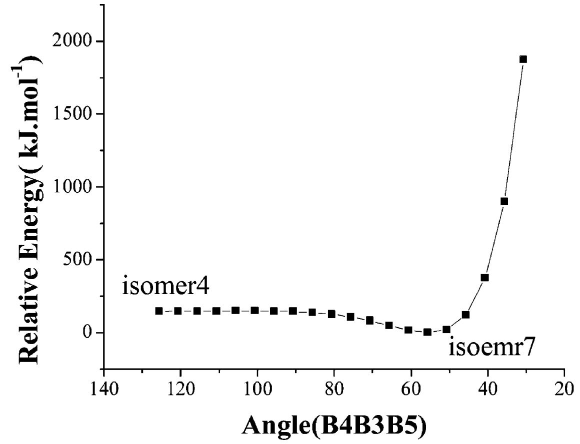

Figure 2. Potential energy surface scan of isomer4 at the B3LYP/6-31G(d) level.

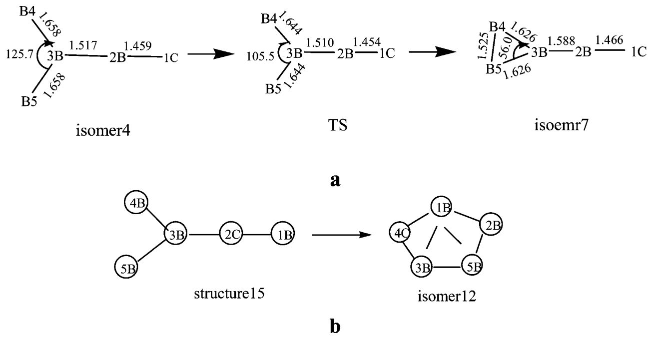

Figure 3. (a) The conversion process from isomer4 to isomer7 at the B3LYP/6-311G+(3df) level of theory. (b) The rearrangement from isomer15 to isomer12.

Figure 2 shows the PES scanning for the forming bond process of B4−B5 bond in isomer4. At first, the energy rose only a little with the decrease of the angle of B4B3B5 till it reached a minimum point (isomer7). Then, with the reducing of the angle sequentially (see Figure 2), the energy would rise quickly. In Table 1, isomer7 has lower energy than isomer4, which is in good agreement with the PES scan. According to the analysis above, we know that both isomer4 and isomer7 are stationary points on the PES and that there is a small potential barrier between them. So, we supposed that there should be a transition state between isomer4 and isomer7. Unfortunately, we optimized transition state and found that it has two imaginary frequencies at the B3LYP/6-31G(d) level. However, when the higher B3LYP/6-311G+(3df) method was used in this calculation, there is only one imaginary frequency with −127.973 cm^{-1} in this transition state, and the corresponding vibration directed isomer4 and isomer7, respectively. In terms of transition theory, at the B3LYP/6-311G+(3df) level, transition state connecting isomer4 and isomer7 is a real one, which was also proved by the IRC analysis calculated. Figure 3a shows the conversion process between isomer4 and isomer7. From Figure 3a, we can find that a three-member boron ring was gradually formed with B4 and B5 atoms being close to each other.

Although isomer4 was optimized with no imaginary frequency shown in Figure 4, the energy differences between isomer4 and TS is so low (only 0.31 kJ mol^{-1}) that isomer4 is easily converted into isomer7. Moreover, the energy difference between isomer7 and TS is 153.80 kJ mol^{-1}, which is obviously large enough that the conversion from isomer7 to isomer4 is very difficult. Therefore, isomer4 would not be created successfully.

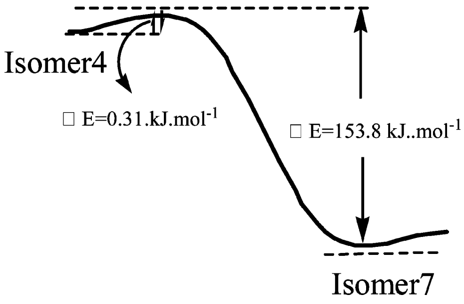

Figure 4. Energy profile for the conversion between isomer4 to isomer7 at the B3LYP/6-311G+(3df) level.

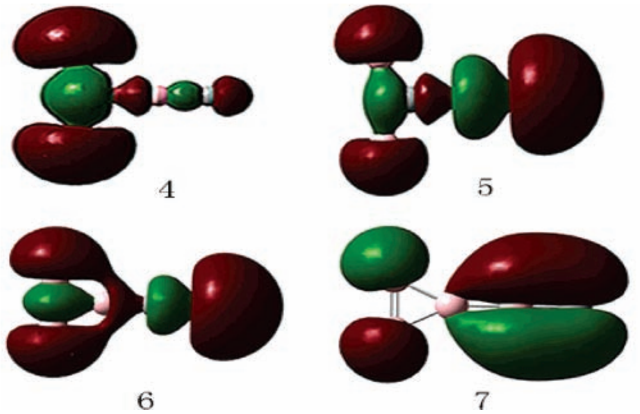

Figure 5. The highest occupied molecular orbital (HOMO) of isomers4−7 in B_4C clusters.

TABLE 2: Atomic Orbital Contributions to HOMOs (the Highest Occupied Molecular Orbital) of Isomers4−7 in B_4C Clusters

isomer	atom	HOMO	isomer	atom	HOMO
4	C1	2.65%	6	B1	53.67%
	B2	2.66%		C2	14.40%
	B3	12.38%		B3	7.83%
	B4	41.16%		B4	12.05%
	B5	41.16%		B5	12.05%
5	B1	65.68%	7	C1	48.44%
	B2	16.43%		B2	37.32%
	C3	3.37%		B3	0.83%
	B4	7.26%		B4	6.70%
	B5	7.26%		B5	6.70%

By analyzing the vibration frequencies of isomer4 and isomer5, we found that the frequencies corresponding to the opening and closing of the B4 and B5 atoms in isomer4 and isomer5 are 137.37 cm^{-1} and 237.91 cm^{-1}, respectively. Because the value of vibration frequency in isomer5 is larger than that in isomer4, there is a higher thermal stability for isomer5 than that for isomer4, which conforms to the order of energies in Table 1.

On the basis of the above discussion, isomer4 can be converted easily into isomer7, however, for isomer5, the ring-closed structure is not in existence. Similarly, we cannot locate structure 15 (the ring-opened structure of isomer6) (see Figure 3b). To solve these interesting questions, the frontier molecular orbitals are given and analyzed as well. Combining Figure 5 with Table 2, for the highest occupied molecular orbital (HOMO), orbital contributions of the B4 and B5 atoms in isomer4 both are 41.16%, and the electron densities of them are so large that the interaction of the B4 and B5 atoms is very strong, which leads to the fact that the B4 and B5 atoms are easy to form a bond. Thereby, isomer4 is easy to convert into isomer7. Whereas for the HOMO of isomer5, the orbital contributions of B4 and B5 atoms (both only 7.26%) are smaller compared with that of isomer4, therefore the interaction of B4 and B5 atoms is weak, which leads to the B4 and B5 atoms not being able to form a bond. For isomer6, orbital contributions of the B3, B4, and B5 atoms in the HOMO are small with 7.83%, 12.05%, and 12.05%, respectively. However, shown in Figure 5, the electron densities over B3−B5 atoms are delocalized in isomer6. The interactions of the B3−B5 atoms are so strong that three-member ring structure is very stable. It is more interesting that isomer12 can be easily attained from isomer6 by optimizing the structure 15 (ring-opened structure of iosmer6) (Figure 3b). From Figure 5 (isomer6), there are the same orbital signs in HOMO for B1 and B4 atoms. According to the principle of orbital symmetry matching, there is a strong interaction between B4 and B1 atoms which results in forming a bond between them. So, the structure15 can easily convert into isomer12 (Figure 3b). For isomer7, orbital contributions of the B3, B4, and B5 atoms of the HOMO are very small with 0.83%, 6.70%, and 6.70%, respectively, and the electron densities over them are localized. There is no overlap between the B3−B5 atoms, and the interactions among them are very weak. So, the three-member ring in isomer7 can be opened.

Figure 6. Delocalized π orbital (MOs) for the planar five-member ring structures of B_4C clusters.

TABLE 3: Nucleus-Independent Chemical Shifts (NICS) for Some B_4C Isomers (in ppm)

isomer	11	12	13	14
PG	C_{4v}	C_s	C_s	C_s
ES	$^1A_1$	$^1A'$	$^1A'$	$^1A'$
NICS[a]	−6.72	−11.85	−21.57	−17.23

[a] NICS at the geometric centers, calculated at the B3LYP/6-31G* level.

Because the three-member boron ring is the most stable structure in all B_3[31] clusters, we assumed that various configurations of B_4C clusters containing three-member boron rings are predominant in energy. On the basis of the above analysis, we know isomer7 is more stable than isomer4 because of isomer7 containing a three-member boron ring; this conforms to the discussion above. Combining Figure 1 with Table 1, we can find that isomer8 and isomer9 hold the analogous structures with isomer10. Because isomer9 and isomer10 both contain a three-member boron ring, they are more stable than isomer8. The difference between isomer9 and isomer10 is that a boron atom was linked to the boron-terminated or to the carbon-terminated four-member ring. From the *Lange's Handbook of Chemistry*,[32] dissociation energy of B−C (448 kJ mol^{-1}) is larger than B−B (297 kJ mol^{-1}), and B−C is more stable than B−B. So, linking a boron atom to the carbon-terminated four-member ring structure is more stable than linking to the boron-terminated, namely, isomer9 is more stable than isomer10. Similarly, comparing isomer7 with isomer6, since there are more B−C bonds in isomer6 (two B−C bonds) than that in isomer7 (only one B−C bond), isomer6 is more stable than isomer7.

Among the isomers12−14 of five-member ring, isomer12 is the most stable structure because of containing two three-member boron rings. The second most stable structure is

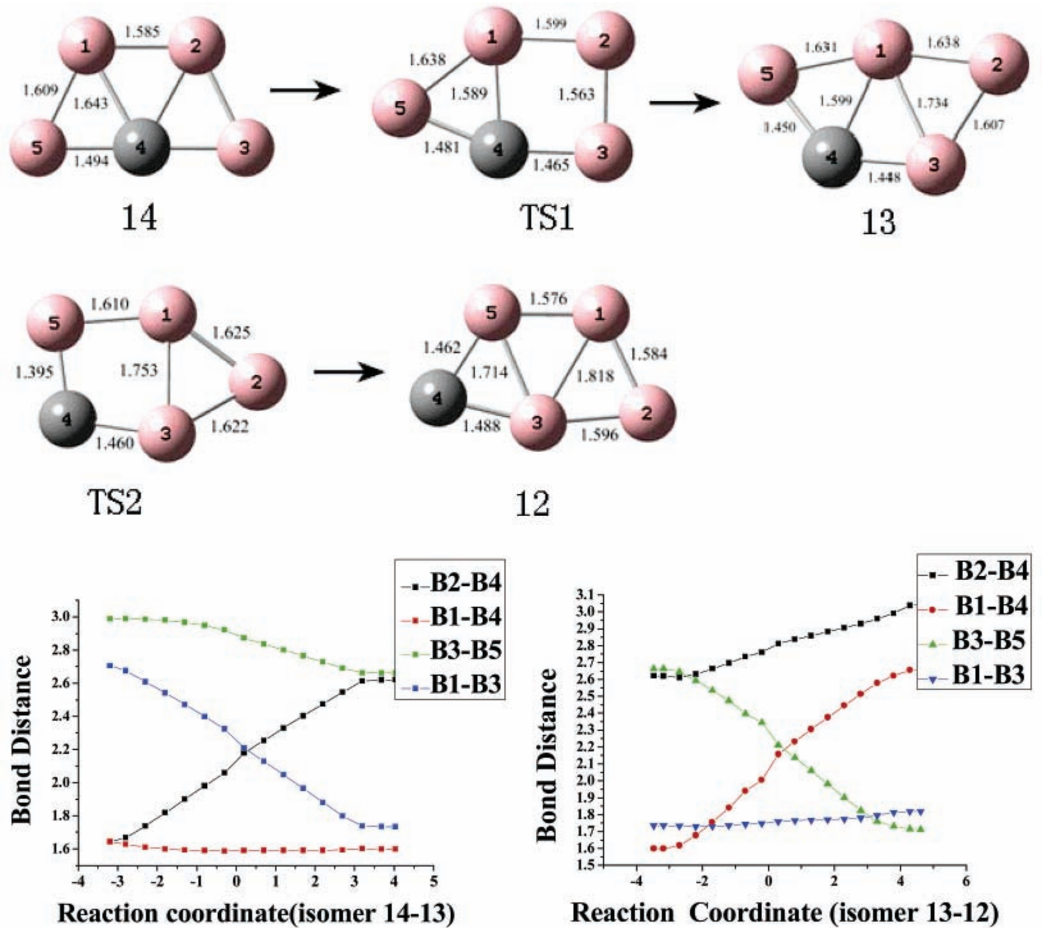

Figure 7. The conversion process from isomer14 to isomer13 and from isomer13 to isomer12 at the B3LYP/6-31G(d) level of theory.

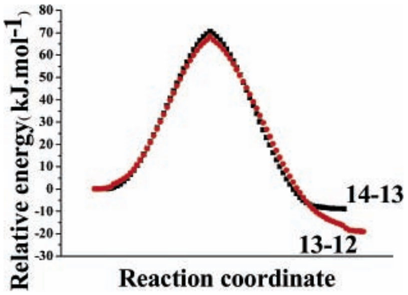

Figure 8. The variety of energy and some bonds (Å) along with the reaction coordinate.

isomer13 containing only a three-member boron ring. While there is no three-member boron rings in isomer14, this isomer has the least stability in three isomers. We can conclude that the stable order of the three isomers is isomer12 > isomer13 > isomer14, which is accordant to the result of energy analysis from Table 1. So, the assumption that the structures containing three-member boron rings are predominant in energy is reasonable.

It has been proposed that the π electrons delocalization play a significant role in stabilizing the planar five-member ring for B_5 neutral species[33] and six-member ring for B_6 neutral clusters.[34] From Figure 6, we notice that the planar five-member ring structures of B_4C clusters all have delocalized π orbital, which shows that the π electrons are highly delocalized among the planar five-member ring of B_4C clusters. In terms of NBO analysis, except for the five σ bonds in isomer12, there is a B1B3B5 three-centered bond, which formed using three hybrid orbitals provided by B1, B3, and B5. The Wiberg bond indices (WBI)[35] of B1B3 and B1B5 are 0.60 and 0.63, respectively, supporting the existence of this three-centered bond. Isomer12 is the most stable structure in B_4C clusters, which might be due to the three-centered bond enhancing its stability with π electrons delocalization, which is similar to the planar five-member ring for B_5 cluster.[33] From Figure 1, we notice isomer11 with a three-dimensional one is less stable than planar five-member ring structures, which is partially because the planar structures are stabilized by π delocalization.

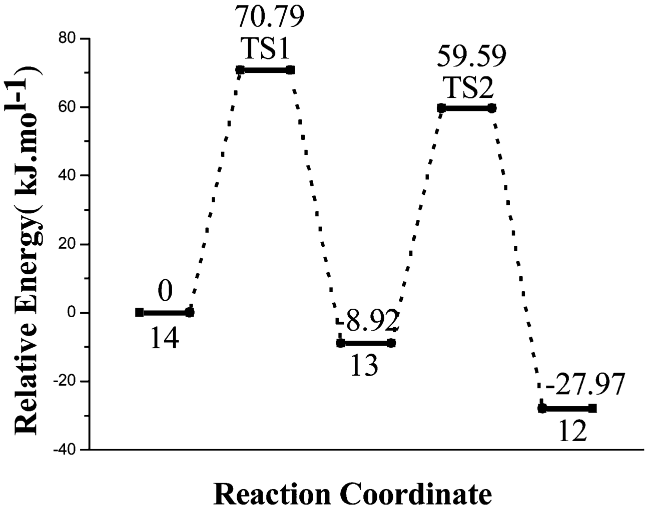

Figure 9. Energy profile (in kJ mol^{-1}) for the conversion from isomer14 to isomer13 and from isomer13 to isomer12 at the B3LYP/6-31G(d) level of theory.

Nucleus independent chemical shifts (NICS) proposed by Hofmann and Schleyer[36] are defined as the negative value of the absolute magnetic shielding, which adapt to inorganic compound, organic compound, and cluster. Reference point which computes NICS is at or 1 Å above the geometrical centers of rings or clusters. Aromaticity is characterized by negative NICS values, antiaromaticity by positive NICS, and nonaromatic compounds by values close to zero. The success of NICS as a measure of the aromaticity is highly conspicuous and NICS has been employed as an effective index of aromaticity. Recently, the relevance of NICS in understanding the aromaticity in benzene and related compounds has been studied.[37] So, we computed NICS values for isomers12−14 of the planar five-member ring and isomer11 of the three-dimensional structure at the GIAO-B3LYP/6-31G(d) level using the optimized geometries in the clusters (Figure 1) to study their aromaticity. Table 3 shows that the NICS values of isomers11−14 are all negative. According to the NICS criterion, they all have aromatic properties. The NICS value for isomer13 is −21.57 ppm, which has the higher degree of aromaticity than that for the others. The three-dimensional structure of isomer11 with the NICS value of −6.72 ppm has the lower degree of aromaticity relatively.

Theoretical investigation for the Conversion of Isomers12−14. From the analysis above, the planar five-member ring structures of isomers12−14 are all stationary points on the neutral B_4C potential surface. So, we attempted to search the conversion processes of isomers12−14.

As shown in Figure 7, isomer14 has C_{2v} symmetry. The angles of B1B2B3 and B2B1B5 both are 115.9°, and the B3, C4, and B5 atoms are almost in a line with the angle of 179.4°. The bond length of B1−C4 and B2−C4 bonds (both are 1.643 Å) is slightly larger than that of B5−C4 (1.494 Å), which indicates that the interaction between C4 and B1 (or B2) is weaker than that between C4 and B5. As shown in Figure 7, a transition-state TS1 in this process was located. In the conversion process from isomer14 to TS1 (shown in Figures 7 and 8), the distance between B2 and C4 would be increased and a similar square ring structure would be formed among B1, B2, B3, and C4 atoms at TS1 point. The distance of B2−C4 is 2.127 Å at TS1 point, which is very larger than that in isomer14, while the distance between B1 and B3 would be decreased in this process. When the distance between B2 and C4 keeps on increasing, the isomer13 with C_s symmetry would be attained. For isomer13, the angles of B3C4B5 and B1B2B3 are 133.6° and 64.6°, respectively, which is smaller than that of isomer14 and TS1, while the angles of B2B1B5 are 161.5°, which is larger than that of isomer14 and TS1. The distance of B2−C4 (2.621 Å) is so large that the interaction of them is very weak in isomer13. However, the distance of B1−B3 is 1.734 Å, which formed the stable chemical bond.

In the conversion process of isomer13 and 12 (shown in Figures 7 and 8), a transition state TS2 was located. In this process, the distance of B1−C4 would be increased with decreasing of B3−B5 bond length. When the distance between B3 and B5 atoms increase continuously, the most stable structure of isomer12 would be formed. For isomer12, the distance of B3−B5 is 1.714 Å, which is shorter than that in isomer13 (2.664 Å) and TS2 (2.287 Å), while the distance of B1−C4 is 2.659 Å, which is very longer than that in isomer13 (1.599 Å) and TS2 (2.075 Å). From Figure 7, it is easy to find that the five-member ring did not vary much in the interconversion processes of isomers12−14.

From Figure 9, we find that TS1 has energy of 70.79 kJ mol^{-1} above isomer14, which indicates that isomer14 can be easily converted into isomer13. Moreover, the energy of isomer13 is lower by 8.92 kJ.mol^{-1} than that of isomer14, suggesting that isomer13 is more stable in thermodynamics than isomer14. The TS2 lies 68.51 kJ mol^{-1} in energy above isomer13, while it lies 87.56 kJ mol^{-1} above isomer12, therefore, isomer13 is easily converted into isomer12. The energy barrier of TS2 is less than TS1 (70.79 kJ mol^{-1}); it shows that the first step (TS1) is faster than the second step (TS2). Comparing the energy of the three isomers, we find that isomer12 is the most thermodynamically stable product.

Conclusions

We have analyzed 14 stable isomers in detail, and the results show that the structures containing three-member boron rings are predominant in energy for B_4C clusters. In terms of MO and NBO analysis, the π electrons are highly delocalized in the planar five-member ring of B_4C clusters, and the three-centered bond enhances the stability of isomer12 with π electrons delocalization. The calculated nucleus-independent chemical shifts (NICS) of the structures of isomers11−14 are all negative values, which indicate their aromatic characters. Our calculations suggest that isomer4 can be converted into isomer7 with only an energy barrier of 0.31 kJ mol^{-1} at the B3LYP/6-311G+(3df) level. Planar five-member ring structures (isomers12−14) can be converted with each other. The conversions of isomer14 to isomer13 and of isomer13 to isomer12 have energy barriers of 70.99 and 68.51 kJ mol^{-1} at the B3LYP/6-31G(d) level, respectively.

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