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Geometric and electronic structures of $B_{12}C_6N_6$ fullerene

Fei Li, Yan Zhang, Hongshan Chen*

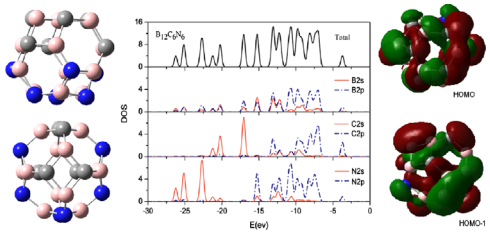
Key Laboratory of Atomic and Molecular Physics & Functional Materials of Gansu Province, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China

HIGHLIGHTS

- All the isomers of $B_{12}C_6N_6$ are optimized and the low energy structures are decided.
- C and N atoms in this cage are inclined to segregate and form B_2C_2 and B_2N_2 squares.
- B–N bonds are identical in $B_{12}C_xN_{12-x}$ (x=0,6) and the B–C bonds possess stronger covalent character.
- The natural charge on N is about −1.17 in both $B_{12}N_{12}$ and $B_{12}C_6N_6$ and the charge on C ranges from −0.60 to −0.72.
- The energy gaps of C_{24}, $B_{12}N_{12}$ and $B_{12}C_6N_6$ are 2.52, 6.84 and 3.22 eV, respectively.

GRAPHICAL ABSTRACT

The low energy isomers of $B_{12}C_6N_6$ are optimized using density functional method. The electronic structure and bonding character in this electron deficient cage are investigated.



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ABSTRACT

An electron deficient fullerene $B_{12}C_6N_6$ is studied by using *ab initio* calculations. The structure is generated by replacing N with C in the $B_{12}N_{12}$ cage to ensure only B–C and B–N bonds are formed. All the possible isomers are optimized and the low energy structures are determined. C and N atoms in the low energy isomers are inclined to segregate and form B_2C_2 and B_2N_2 squares. Natural bond analysis shows that the atomic orbitals of B, C and N in this cage hybrid approximately in $sp^{2.3}$ and then form B–C and B–N bonds. The 2p orbitals perpendicular to the cage surface are partially occupied and the molecular orbitals formed by these orbitals are highly delocalized. The natural charge on N is about −1.17 in both $B_{12}N_{12}$ and $B_{12}C_6N_6$, and the charge on C is −0.72 to −0.60. The molecular orbital compositions show that the B–N bonds are the same in $B_{12}N_{12}$ and $B_{12}C_6N_6$, and the B–C bonds possess stronger covalent character. The HOMO of $B_{12}C_6N_6$ is formed by 2p of B and C, and the LUMO is formed by 2p of C. The energy gap of C_{24}, $B_{12}N_{12}$ and $B_{12}C_6N_6$ is 2.52, 6.84 and 3.22 eV, respectively.

1. Introduction

The discovery of carbon nanomaterials such as fullerenes, nanotubes and graphene triggered wide interest in nanoscale science and technology because of their unusual physical and chemical properties. Boron nitrides are isoelectronic compounds to carbon analogs, and they also attracted intense attention in the past score. BN nanomaterials such as nanotubes and clusters were first predicted theoretically [1–3] and then successfully synthesized [4–7]. Although there are strong similarities in the structures of BN and corresponding carbon compounds, their physical, chemical, and electronic properties differ significantly. For example, carbon nanotubes can be metallic or semiconductors depending on the helicity, radius, and wall-wall interactions, but BN

* Corresponding author. Tel./fax: +86 931 7971277.
E-mail address: chenhs@nwnu.edu.cn (H. Chen).

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nanotubes are wide-gap semiconductors with a gap value around 6.0 eV which is independent of the morphology [2].

Hybrid BCN nanomaterials have also received considerable attention as the potential materials to tune the electronic behavior of pure C and BN systems. It is generally expected that the hybrid materials inherit properties from both of the parent materials. From the very beginning, special interest was paid to the BC_xN stoichiometry which was formed by the substitution of BN atomic pairs by isoelectronic CC pairs to satisfy the charge neutrality condition. Some hybrid materials such as fullerenes, nanotubes and nanofibers have been successfully synthesized [8–16]. The effect of carbon incorporation on the structure and properties of BC_xN ($x=0.25$, 1, and 4) [17] is quite sensitive to the C concentration. In theory, $C_{0.5}(BN)_{0.5}$ single-walled nanotubes [18] and $C_x(BN)_y$ [19] compounds are studied using density functional theory, and the result suggests possible routes for band-gap tuning of these hybrid $C_x(BN)_y$ nanomaterials. A comparative study in terms of experimental and DFT investigation was performed to understand the individual effect of atoms in the bonding structures and the possible phase segregation in BCN materials [20]. The B- and N-doped $(4,4)_i$ and $(8,0)_i$ ($i=3$–5) carbon nanotubes, BC_yN ($y=1$–4,6 and 8), $B_3C_yN_3$ ($y=2$ and 4), B_2CN_2, as well as BN nanotubes were investigated by using B3LYP/6-31G* [21]. Wurtzite BC_2N [22] and $(BC_2N)_n$ ($n=1,2,3,6$) clusters [23–26] have been studied using different theoretical models. The results show that the structures with adjacent B and N atoms and maximum C–C and B–N bonds are more stable. The BN-substituted fullerenes $C_{60-2x}(BN)_x$($x=1$–3 [27], $x=1$–7 [28] and $x=1$–24 [29]) and $C_{70-2x}(BN)_x$ [30] have been investigated, it is also found that the stability is enhanced by keeping BN together. Recently, Zhao et al. [31,32] studied the cubic BC_xN ($0.21<x<19.28$) crystals. The results show that the bandgap of the alloys becomes obvious narrow and it is tunable by controlling the carbon content. Higher carbon content leads to better stability and higher elastic moduli, making these compounds as potential superhard materials.

The above studies, both in experiment and theory, focus on the hybrid B–C–N systems with the B/N ratio of 1. The study for the nonstoichiometric systems is very scarce. There exist boron-rich bulk phases [33] of boron carbonitrides and they possess special physical and chemical properties. Especially at high pressure and temperature, the boron-rich B–C–N powders [34] and crystalline orthorhombic B_2CN [35] were synthesized. Possible diamond-structured configurations of t-B_2CN [36] were studied and a t-B_2CN containing only B–N and B–C bonds in a tetragonal cell was shown having the lowest total energy. Due to the intraband transition in this electron-deficiency structure, the t-B_2CN is predicted to be a large anisotropic crystal with special optical properties [37]. The stability and electronic structures of $C_{60-n}B_n$ and $C_{60-m}N_m$ were studied by DFT calculations [38,39]. By connecting the acceptor $C_{48}B_{12}$ and donor $C_{48}N_{12}$ or putting them into a carbon nanotube, a molecular rectifier or a heterojuction was obtained. B_2CN sheet and single-walled B_2CN nanotubes were also studied using density functional calculations; the results indicate that zigzag and armchair B_2CN nanotubes are optically anisotropic with respect to light polarization [40]. In this paper, the nonstoichiometric $B_{12}C_6N_6$ cage is studied. The structure is generated by substituting N with C in $B_{12}N_{12}$. All the different isomers are optimized and the low energy structures are determined. The electronic structures of C, BN and BCN cages are compared.

2. Computation methods

The calculations are performed using the DFT model B3LYP. The exchange-correlation energy is calculated using gradient corrected hybrid functionals in Becke's three-parameter expression [41,42], which includes a mixture of Hartree–Fock exchange with VWN functional III [43] for local correlation and the non-local correlation given by the LYP term [44]. The basis set uses double-ζ split basis augmented by polarization functions 6-31G(d). For the low energy isomers, we also performed calculation using configuration interaction method CISD/6-31G(d). All the calculations are carried out using the Gaussian 03 package [45].

3. Results and discussion

3.1. Low energy isomers of $B_{12}C_6N_6$

There are two stable cage structures for C_{24} [25]. One consists of 12 pentagonal rings and two hexagonal rings in D_6 symmetry (denoted as C_{24}-$5^{12}6^2$), the other consists of six tetragonal rings and eight hexagonal rings with O_h symmetry (denoted as C_{24}-4^66^8). The isomer $5^{12}6^2$ is a little lower in energy. $B_{12}N_{12}$ [25] is isoelectronic with C_{24} and also has these two structures. Since the isomer $5^{12}6^2$ contains pentagonal rings, it will form weak B–B and N–N bonds in this structure. The isomer $B_{12}N_{12}-4^66^8$ is obviously preferable in energy. This structure is shown in Fig. 1. For the convenience of discussion in the following section, two views of the structure are illustrated.

The structure of $B_{12}C_6N_6$ is generated by substituting six nitrogen atoms with carbon in $B_{12}N_{12}$-4^66^8. The isomers generated in this way contain only B–N and B–C bonds. The number of substituting six of the 12 nitrogen atoms by carbon is very large. As the cage of $B_{12}N_{12}$-4^66^8 has symmetry T_h, most of the substitutions are identical. The structure in Fig. 1 can be thought containing four layers, and each layer has three N atoms. The substitution can be labeled using the index (n_1 n_2 n_3 and n_4) with the restriction $0\le n_i\le 3$ and $n_1+n_2+n_3+n_4=6$ (n_i is the number of carbon atoms in each layer). The number of the substitutions can be calculated by

$$\frac{1}{2}(C_2^1A_4^1+C_3^1A_4^4+C_3^1C_3^1A_4^1+C_3^2C_3^2A_4^1+C_3^2C_3^1C_3^1C_2^1A_4^1)=184$$

As the eight hexagonal rings can be divided into four pairs (top and bottom), not all these isomers are different. By using another index, i.e., the number of carbon atoms in the eight hexagonal rings, the chemically distinct isomers can be easily screened out. Among these chemically distinct isomers, many of them are enantiomers, i.e., a pair of isomers are mirror images of each other. A pair of enantiomers have identical energy and they can be picked out by the help of view software. Totally there exist 50 different isomers after excluding the chiral symmetry.

The 50 different isomers are optimized at the theory level B3LYP/6-31G(d). The distribution of the binding energies of all the isomers is presented in Fig. 2. Although all the isomers contain only B–N and B–C bonds, the local environment of the chemical

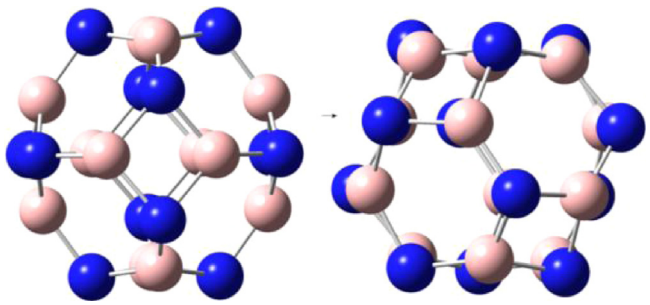

Fig. 1. The structure of $B_{12}N_{12}$–4^66^8 cage (pink for B blue for N). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)