Theoretical study on the structural, electronic, and optical properties of B\textsubscript{n}C\textsubscript{n} (n = 1–13) clusters

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Abstract

We applied density functional theory (DFT) calculations to investigate the low-energy geometries and electronic characteristics of stoichiometric B\textsubscript{n}C\textsubscript{n} (n = 1–13) clusters. We performed harmonic vibration frequency analysis to ensure that the ground-state isomers are the real local minima. B\textsubscript{n}C\textsubscript{n} clusters tend to evolve from planar and annular structures to quasiplanar bowl structures to maintain the lowest structural energy as cluster size n increases. The clusters with even n have large HOMO–LUMO gaps and high stability. We used the time-dependent DFT (TDDFT) calculations to acquire the optical absorption spectra for the lowest-energy B\textsubscript{n}C\textsubscript{n} (n = 4, 6, 8, 10, 12) clusters. The clusters exhibit strong absorption in the ultraviolet region. With the increase of n, the absorption of clusters, particularly that of the B\textsubscript{8}C\textsubscript{8} cluster, intensifies in the visible region. Therefore, the clusters investigated in this work can be used to fabricate novel two-dimensional materials for visible-light absorption and have potential applications in various fields, such as catalysis.

1. Introduction

Boron carbides are a class of ceramic materials with complex atomic structures and high carbon concentrations [1]. They have attracted considerable attention because of their superhardness, low density, high-temperature stability, high neutron absorption cross section, and excellent thermoelectric characteristics [2]. Given these properties, boron carbides are fascinating materials that can be used in high-temperature semiconductors, wear-resistant components, light-weight armor, neutron radiation absorbers in nuclear reactors, and electrode materials for batteries and fuel cells [1, 3–5]. Boron–carbon nanostructures, including nanosprings [6], nanowires [7, 8], and clusters [9], have become major research topics in recent years because of their potential applications in nanoelectronics, nanomechanics, and flat-panel displays. The novel features of bulk boron carbides are also reflected by limited boron–carbon nanostructures.

Research on the cluster phase, a boron carbide nanostructure, remains lacking. Different B\textsubscript{n}C\textsubscript{m} clusters can be produced through experimental methods, such as laser–induced plasma deposition [10], pulsed laser evaporation [11], direct laser vaporization [12], cluster beam laser vaporization [13], and reactive molecular ion irradiation [14]. The vaporization behaviors of small BC, BC\textsubscript{2}, and B\textsubscript{2}C clusters have been studied through mass spectrometry [15]. Furthermore, the vibrational spectra for BC [16, 17], BC\textsubscript{2} [18], linear BC\textsubscript{3}, and linear B\textsubscript{2}C\textsubscript{2} [19] have been acquired through Fourier–transform infrared spectroscopy and electron spin resonance spectroscopy. The ground states, certain excited electronic states, and absorption spectra of BC and BC\textsubscript{2} have also been investigated [11, 20]. Some theoretical studies have elucidated the energy, structure, and stability of small nonstoichiometric boron–carbon clusters, such as B\textsubscript{4}C [21], C\textsubscript{6}B [22], B\textsubscript{n}C (n = 1–7) [23], C\textsubscript{m}B\textsubscript{3} (n = 1–8) [24], C\textsubscript{n}B\textsubscript{2} (n = 1–7) [25], B\textsubscript{m}C\textsubscript{n} (n = 1–5, m = 1–5) [9], and B\textsubscript{n}C\textsubscript{2} (n = 3–8) [26] via density functional theory (DFT) calculations. B\textsubscript{n}C\textsubscript{m} clusters present various stabilities and reactive activities given their different bonding modes. Information about boron–carbon clusters is useful because we can effectively grow
material surfaces desired for photocatalysis and nanoelectronics applications by using small BₙCₙ clusters as sources and different processing techniques and processing conditions. Moreover, the electronic, optical, and magnetic characteristics of the BₙCₙ clusters are different from those of corresponding bulk materials given the quantum confinement effect and new topological structures of the clusters. Stable clusters with new properties can be used as structural units for synthesizing cluster-assembled materials [27–30], which are novel nanomaterials with potentially far-reaching technological applications in the future. Time-dependent DFT (TDDFT) calculations have shown that semiconductor clusters, such as stoichiometric ZnₙOₙ (n = 1–16, 24, 36) [31], SiₙCₙ (n = 12, 16, 20, 30, 35, 60) [32, 33], and Bₙ (n = 2–20, 38, 40) [34] clusters, have unique optical properties. Nagare et al. [31] systematically investigated the optical and electronic characteristics of ZnₙOₙ (n = 1–16, 24, 36) clusters via TDDFT calculations. They found that the optical properties of the clusters are dependent on their sizes, shapes, and dimensionalities. Absorption spectra show that the intensity of spectral lines increases and blueshift occurs with increments of cluster size. The optical excitations of planar and annular clusters lie in the low side of the ultraviolet region, whereas the optically active transitions of three-dimensional ZnₙOₙ clusters occur in the visible region. Duan and Burggraf [33] acquired the absorption spectrum of the most stable Si₁₂C₁₂ isomer through TDDFT calculations and found that optical oscillators have high intensity in the visible blue region. Malloci et al. [35] experimentally investigated the photoelectric characteristics of unsaturated hexagonal ZnO prism clusters and found that the redshift of spectral lines increases as cluster size increases.

In this work, we first systematically calculated the structural and electronic characteristics of stoichiometric BₙCₙ (n = 1–13) clusters by applying DFT calculations. Moreover, we studied the equilibrium geometry, bonding nature, and stability of the clusters. We obtained the absorption spectra of the lowest-energy BₙCₙ (n = 4, 6, 8, 10, 12) clusters through TDDFT calculations and discussed the source of the electronic excitations of the clusters. To our knowledge, the optical characteristics and origins of stable BₙCₙ clusters have remained unreported. We introduce the calculation methods used in this work in the following section. We then present the results and discussion.

2. Computational methods

We performed spin-unrestricted calculations by using the DMol³ program [36, 37] in the DFT framework. The exchange–correlation interaction was expressed through the generalized gradient approximation (GGA) method [38] proposed by Perdew, Burke, and Ernzerhof [39]. All-electron potentials and double numerical basis set plus polarization (DNP) functions were selected. The SCF convergence was 10⁻⁶ hartree and global orbital cutoff was 5.1 Å. All clusters were optimized without symmetry restrictions. The energy tolerance of 10⁻⁵ hartree was selected, and the force on atoms was set to be less than 0.002 hartree/A to obtain reliable results. It is to be noted here that calculations were not performed for each spin state of the given cluster, but the Aufbau principle as implemented in the DMol³ program was used to obtain the optimal spin state of the cluster. Van der Waals dispersion effects were also considered in calculations with Grimme’s DFT-D method [40]. The charge transfer on each atom in the clusters was determined through electrostatic potential (ESP) analysis. The correctness of ESP charges has been verified by recent literatures [41–43]. Normal-mode vibrational analysis in DMol³ code shows that BₙCₙ clusters with the lowest energy have no imaginary frequencies.

We performed full-potential linear-muffin-tin-orbital molecular–dynamics (FP–LMTO–MD) search and GGA optimization methods to obtain lower-energy BₙCₙ (n = 1–13) isomers [44–46]. Previous studies on small GaₙNₙ, Geₙ, and Siₙ clusters [47–50] have confirmed the effectiveness and correctness of the FP–LMTO–MD method [51–54]. Firstly, we used FP–LMTO–MD method to systematically search the low energy structures of BₙCₙ (n = 1–13) clusters. A large number of initial geometric structures were used as seeds for relaxation until a local minimum of total energy was found. For very small BₙCₙ (n = 1–2) clusters, all possible connections between atoms were used as seeds. For larger BₙCₙ, the initial atomic configuration was established by random arrangement of atoms in three-dimensional space. The separation of B–B, B–C, and C–C atoms was limited to a certain range. The ranges of B–B, B–C, and C–C were 1.545–1.847, 1.457–1.743 and 1.275–1.524 Å, respectively. The separation of any pair of atoms was set randomly in the seed structure. In the present study, the radii of all MT sphere for B and C were taken as 1.00 a.u. and the LMTO basis sets included s, p, and d functions on all spheres. Convergence tolerance was set as maximum force less than 0.001 Ry Bohr⁻¹ and total energy change less than 10⁻⁴ Ry. A total of 50–300 initial structures were generated in accordance with the size of each cluster to obtain accurate ground-state structures. Then, the DMol³ program with GGA was used to further optimize the low-lying energy structure of each cluster size calculated by FP–LMTO–MD method. No obvious rearrangement occurred during the DMol³ optimization. We calculated the optical absorption spectra for the minimum-energy isomers of BₙCₙ (n = 4, 6, 8, 10, 12) clusters by using the TDDFT method implemented in the DMol³ code within adiabatic local density approximation (ALDA) [55]. This TDDFT method in DMol³ code have been successfully used to calculate the optical properties of ZnₙOₙ clusters [31], Bₙ clusters [34], Bₙ₀
3. Results and discussion

3.1. Geometrical structures

The structures, symmetries, and relative energies of the low-energy B\textsubscript{n}C\textsubscript{n} \((n = 2–13)\) isomers are presented in figures 1–5. We found that in some cases, the optimal final structures can be obtained from several different initial structures in the process of molecular dynamics for structural optimization. The spin multiplicities, binding energies, second-order difference of energies, HOMO–LUMO gaps, and vertical ionization potentials (VIPs) for the ground-state isomers are presented in table 1. The ESP charge distributions and bond lengths of the minimum-energy isomers are presented in table S1 is available online at stacks.iop.org/MRX/7/015041/mmedia.

3.1.1. B\textsubscript{2}C\textsubscript{1}–B\textsubscript{5}C\textsubscript{5} clusters

Our calculations show that the BC monomer converges to \(C_{\infty v}\) symmetry with \(4\sum\) ground electronic state, which is consistent with that reported by Wang et al \[23\]. Its bond length is 1.503 Å, which also is identical to the previously reported experimental result of 1.491 Å \[16\]. Some low-energy B\textsubscript{n}C\textsubscript{n} \((n = 2–5)\) isomers are presented in figure 1. All of these isomers exhibit planar geometry. As illustrated in figures 1(2a)–(2c), a rhombic-like structure is energetically favored for B\textsubscript{2}C\textsubscript{2}. The relative strength of the bond energies determines the relative stability of the three structures. Bond energy decreases with C–C, C–B, and B–B sequences. The minimum-energy structure (figure 1(2a)) contains one C–C bond and the highest number of C–B bonds. Furthermore, the energy of the linear B–C–C–B structure is 1.37 eV higher than that of the rhombic structure (figure 1(2a)). A multitude of local minima are present on the B\textsubscript{3}C\textsubscript{3} energy surface, and the minimum-energy structures of B\textsubscript{3}C\textsubscript{3} have polycyclic structures, as presented in figures 1(3a) and 3b. Isomers 3a and 3b are isoenergetic; this result is consistent with the results obtained by Shao using the CCSD(T)/6-311++G (3df, 2pd) method \[24\]. As presented in figure 1(4a), the ground-state isomer of B\textsubscript{4}C\textsubscript{4} is a circular C\textsubscript{2v} structure with a C–C bond. A similar structure provided in figure 1(4b) has a higher energy of 0.43 eV and is considered as the lowest-energy structure by Sharipov et al. \[9\]. The energy of the planar C\textsubscript{2v} structure with a C–C–C bond (figure 1(4c)) is 0.81 eV higher than that of the minimum-energy isomer. As shown in figures 1(5a)–(5c), the three structures of B\textsubscript{5}C\textsubscript{5} are all C\textsubscript{s} planar structures with a C–C bond and an internal B atom. The minimum-energy structure

fullerene \[36\] and Si\textsubscript{7} clusters \[37\]. Optical transitions were calculated by using the ALDA kernel exchange correlation terms in a singlet state with sufficient empty bands. The optical spectra of the clusters were obtained by subjecting eigenvalues to Gaussian broadening.
presents an eye-like structure, as shown in figure 1(5a) and is also considered by Wang et al [25] as the ground-state structure of B₅C₅.

### 3.1.2. B₆C₆–B₁₃C₁₃ clusters

To our knowledge, B₆C₆–B₁₃C₁₃ clusters have yet to be explored. We found numerous isomers in the cluster region through extensive searching. Several low-energy isomers for BₙCₙ (n = 6–13) clusters are represented in figures 2–5. The ESP charge distributions and bond lengths for the ground-state structures of BₙCₙ (n = 6–13) are presented in table S1. We found that the minimum-energy isomers of BₙCₙ (n = 6–10) clusters possess planar-ring structures. However, when the number of atoms in a cluster is gradually increased (starting from B₁₁C₁₁), atoms in the ring increase and form additional B–C bonds. Then, the planar structure gradually acquires a bowl-shaped structure that allows the energy of the cluster to remain at the lowest level. For example, the B₆C₆ cluster has a ground-state structure, as exhibited in figure 2(6a), and a B atom is contained in the ring. If the B atom is placed on the ring, the energy is at least 2.60 eV higher than isomer 6a. As illustrated in figures 2–5, B (or C) atoms inside the ring tend to bond with more than three surrounding atoms. Thus, the stability of the system can be further improved. The energy of isomers for a certain cluster size is mainly derived from the arrangement of the C and B atoms on the ring and the position of the atoms inside the ring given the differences in bond energies among C–C, C–B, and B–B. It should be pointed out here that with the increase of the number of atoms in the cluster, three-dimensional cluster structures can be found in the process of structure search, but these three-dimensional structures are metastable, their energies are much higher than that of the corresponding ground state structure. For example, the energies of first three-dimensional B₇C₇, B₈C₈, B₉C₉ and B₁₀C₁₀ structures we obtained are 3.14 eV, 1.50 eV, 2.85 eV and 1.38 eV higher than that of corresponding lowest-energy structure, respectively. The preferred (quasi) plane structure of BₙCₙ clusters can be further understood from the bonding between B and C atoms. In addition to the highly localized sp² hybridization, characterized by σ and σ bonds, there are also delocalized π bonds over the cluster plane (see figure S1). The formation of π bond helps to increase the stability of clusters.

Thus, for the structural features of BₙCₙ (n = 1–13) clusters, small BₙCₙ (n < 5) clusters tend to form planar cyclic structures. The number of atoms that prefers to reside inside rings increases as the number of cluster atoms increases. In addition, the structure of the cluster is gradually transformed from a ring to a plane or
a bowl-like (quasiplanar) structure. We may form two-dimensional (or quasi-two-dimensional) boron carbide materials with novel properties by using stable B–C clusters. This speculation requires a follow-up study.

3.2. Stabilities

The thermodynamic stability of clusters can be investigated by calculating several energy parameters. First, we examine the binding energy ($E_b$) of the ground-state structures of $B_nC_n$ ($n = 1–13$) clusters. $E_b$ is expressed as follows:

$$E_b(B_nC_n) = \frac{(nE[B] + nE[C] - E[B_nC_n])}{n},$$

where $E$ is the total energy of the corresponding cluster or atom. The $E_b$ values of the clusters are listed in table 1 and are illustrated in figure 6(a). $E_b$ is a parameter that represents cluster stability. High $E_b$ values are associated with high cluster relative stabilities. As shown in figure 6(a), the monotonous increase in the average $E_b$ of clusters indicates that the clusters become increasingly stable as the number of C and B atoms increases. The curve is steep, and the $E_b$ value increases rapidly from 2.69 eV to 5.93 eV when $n \leq 4$. The size dependence of $E_b$ tends to be low when $n > 4$. Figure 6(b) shows the variation in the second-order difference of energy ($\Delta^2E$) with cluster size $n$. In our work, $\Delta^2E$ is expressed as follows:

$$\Delta^2E = E(B_{n+1}C_n) - E(B_{n+1}C_{n+1}) - 2E(B_nC_n),$$

where $E$ represents the total energy of the corresponding system. $\Delta^2E$ analysis is highly instructive for the study of relative cluster stability. As depicted in figure 6(b), the $\Delta^2E$ value shows an ‘odd–even’ oscillation with the increase of cluster size $n$. The appearance of the wave peak when $n$ is even indicates that the cluster is stable. The maximum $\Delta^2E$ value is obtained when $n = 4$. This result indicates that the $B_4C_4$ cluster is more stable than other clusters. The stability of $B_4C_4$ cluster is mainly due to its large HOMO-LUMO energy gap and short C–C and C–B bond lengths. It has the largest HOMO-LUMO energy gap, in which the C–C and C–B bonds are also shorter than other clusters (see table S1). In addition, $B_4C_4$ cluster also has higher symmetry ($C_{2v}$).

Table 1 shows the HOMO–LUMO gaps of ground-state $B_nC_n$ clusters, and their size dependences are presented in figure 6(c). The gaps change from 0.30 eV to 3.43 eV and present a perfect ‘odd–even’ oscillation. The clusters with even $n$ have large HOMO–LUMO gaps. In general, the clusters have good stability and chemical inertia when they have large HOMO–LUMO gaps. Interestingly, the $B_4C_4$ isomer has the maximum HOMO–LUMO gap. The VIP is another parameter that is used to describe cluster stability. It is the energy
required to remove an electron from a neutral cluster under the assumption that the cluster structure remains unchanged after electron removal. The calculated VIP results for the minimum-energy structures of the $B_nC_n$ clusters are exhibited in Table 1, and Figure 6(d) shows the functional relationship between VIP values and cluster size $n$. A high VIP value indicates that the clusters have a deep HOMO energy level. Therefore, these structures will exhibit high chemical stability. Our calculations show that the VIP values of the $B_nC_n$ clusters range from 6.72 eV to 10.8 eV. $BC$, $B_2C_2$, and $B_4C_4$ clusters have large VIP values. Notably, the VIP of $Ga_n$ clusters with the same sizes ranges from 5.84 eV to 6.84 eV [44], whereas that of $Si_nC_n$ clusters ranges from 6.79 eV to 9.07 eV [45]. Therefore, the stability of $B_nC_n$ clusters should be similar to that of the corresponding $Si_nC_n$ clusters but should be higher than that of $Ga_n$ clusters. As shown in Figure 6(d), the VIP values of $B_4C_4$, $B_8C_8$, and $B_{12}C_{12}$ are larger than those of adjacent clusters. Overall, the VIP of $B_nC_n$ clusters gradually decreases as cluster size increases. In addition to the covalent bond and as shown from the ESP charge distributions in Table S1, the $B-C$ bonds in small $B_nC_n$ clusters show some ionic characteristics. The charges are transferred from boron to carbon.

3.3. Optical properties

According to the spin multiplicities of $B_nC_n$ clusters in Table 1, the nature of the relevant molecular orbitals, the optical absorption spectra with nonvanishing oscillator strength, and the electronic density of states (DOS) of stable $B_nC_n$ ($n = 4, 6, 8, 10, 12$) clusters are studied to identify the source of electronic transitions in $B_nC_n$ clusters. Absorption spectra are shown in Figure 7. Given that optical transitions are closely related to the relevant molecular orbitals and the electronic DOS on the molecular orbitals, the total and partial DOS (TDOS and PDOS) of the cluster structures are obtained and are shown in Figure 7. The rosy vertical lines in Figure 7 represent the levels of HOMO, LUMO, and some molecular orbitals related to transitions. The parameters of the representative and major intense transitions, including excitation energies and oscillator strengths, of the $B_nC_n$ clusters are listed in Table 2. Some molecular orbitals related to electron excitation are shown in Figure 8.

The calculated absorption spectra can be roughly divided into two regions: the visible region from 1.5 eV to 3.1 eV and the ultraviolet region from 3.1 eV to 6.5 eV. The absorption intensity is zero for all clusters at approximately less than 1.5 eV. The $B_4C_4$ cluster cannot absorb visible light. The optical absorption spectrum shows that all electronic excitation transitions are in the ultraviolet region mainly because of the

![Figure 4. Optimized structures of $B_{10}C_{10}$ and $B_{11}C_{11}$ clusters. Values enclosed in parentheses are relative energies (eV).](image-url)
large HOMO–LUMO gap of the cluster, which can be seen from TDOS of B$_4$C$_4$ (figure 7). The first excitation that appears at 3.71 eV corresponds to the H + 0 to L-0 orbital transition. Observable absorption begins to appear at 5.27 eV and has an oscillator intensity of 0.143 that mostly originates from the H-2 to L+2 orbital transition. The wide absorption appears within the transition energy range of 5 eV–6.5 eV, indicating that there are more optical transitions occur. From table 2, these absorption peaks arise primarily from the H–0, H–2, H–3, H–4, H–5, H–6 to L+1, L+2, L+4 orbitals transitions. The TDOS and rosy vertical orbitals lines of B$_4$C$_4$ (figure 7) show that the energy levels of the molecular orbitals near the HOMO and LUMO orbitals are relatively close in their respective energy regions, and corresponding TDOS is relatively large.

Table 1. The spin multiplicities, stabilities and electronic properties of the lowest-energy structures of B$_n$C$_n$ clusters. $E_b$ (eV): binding energy per atom, $\Delta_2E$ (eV): second-order difference of cluster energies, $E_{\text{gap}}$ (eV): HOMO–LUMO gap, and $E_i$ (eV): vertical ionization potential.

| B$_n$C$_n$ | Multiplicity | $E_b$ | $\Delta_2E$ | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | $E_{\text{gap}}$ | $E_i$ |
|-----------|--------------|------|-------------|----------------|----------------|----------------|-----|
| BC        | 4            | 2.69 | –6.75       | –5.37          | 1.38           | 10.80          |
| B$_2$C$_2$| 3            | 4.84 | –6.20       | –4.17          | 2.03           | 9.49           |
| B$_3$C$_3$| 2            | 5.51 | –5.96       | –4.96          | 1.00           | 8.92           |
| B$_4$C$_4$| 1            | 5.93 | –7.40       | –3.97          | 3.43           | 10.04          |
| B$_5$C$_5$| 2            | 6.00 | –6.53       | –5.65          | 0.88           | 9.06           |
| B$_6$C$_6$| 1            | 6.17 | –6.04       | –4.13          | 1.91           | 8.38           |
| B$_7$C$_7$| 2            | 6.20 | –6.07       | –5.57          | 1.24           | 8.95           |
| B$_8$C$_8$| 1            | 6.29 | –6.81       | –5.57          | 1.24           | 8.95           |
| B$_9$C$_9$| 2            | 6.36 | –5.46       | –5.00          | 0.46           | 7.48           |
| B$_{10}$C$_{10}$| 1 | 6.39 | –5.66 | –4.43 | 1.23 | 7.57 |
| B$_{11}$C$_{11}$| 2 | 6.40 | –5.29 | –4.98 | 0.32 | 7.23 |
| B$_{12}$C$_{12}$| 1 | 6.44 | –6.44 | –4.92 | 1.52 | 8.24 |
| B$_{13}$C$_{13}$| 2 | 6.43 | –5.33 | –5.03 | 0.30 | 6.72 |

Figure 5. Optimized structures of B$_4$C$_4$ and B$_{13}$C$_{13}$ clusters. Values enclosed in parentheses are relative energies (eV).
Figure 6. (a) Binding energies ($E_b$), (b): Second-order difference of cluster energies ($\Delta^2 E$), (c): HOMO–LUMO gaps ($E_g$), (d): Vertical ionization potential ($E_i$) for $B_nC_n$ ($n = 1–13$) clusters.

Figure 7. Absorption spectra and DOS of the lowest-energy $B_nC_n$ ($n = 4, 6, 8, 10, 12$) clusters. The molecular orbitals of these clusters are represented by rosy vertical lines.
which leads to more transition modes and forms wide absorption spectrum. Further molecular orbital analysis (see figure 8) shows that the strong transition in the ultraviolet region is mainly due to the contributions of the B–2p, C–2p and B–3d orbitals. This same nature is also observed in the other BₙCₙ clusters.

**Table 2.** Parameters of the representative and major intense transitions of BₙCₙ (n = 4, 6, 8, 10, 12) clusters.

| BₙCₙ  | Excitation energy (eV) | Oscillator strength (l) | Transition     |
|-------|------------------------|-------------------------|----------------|
| B₄C₄  | 3.71                   | 0.010                   | H-0 → L + 0    |
|       | 5.27                   | 0.143                   | H-2 → L + 2    |
|       | 6.02                   | 0.117                   | H-5 → L + 2    |
|       | 6.21                   | 0.302                   | H-3 → L + 1    |
|       | 7.25                   | 0.160                   | H-3 → L + 5    |
|       | 7.72                   | 0.190                   | H-6 → L + 4    |
|       | 7.84                   | 0.321                   | H-3 → L + 5    |
|       | 8.75                   | 0.157                   | H-3 → L + 7    |
|       | 10.07                  | 0.559                   | H-5 → L + 6    |
|       | 10.35                  | 0.654                   | H-5 → L + 6    |
| B₆C₆  | 2.89                   | 0.024                   | H-0 → L + 1    |
|       | 3.61                   | 0.032                   | H-2 → L + 0    |
|       | 4.31                   | 0.054                   | H-0 → L + 4    |
|       | 4.67                   | 0.157                   | H-1 → L + 4    |
|       | 5.56                   | 0.206                   | H-4 → L + 4    |
|       | 6.46                   | 0.113                   | H-2 → L + 7    |
|       | 6.54                   | 0.111                   | H-8 → L + 4    |
| B₈C₈  | 2.00                   | 0.058                   | H-0 → L + 0    |
|       | 2.72                   | 0.079                   | H-4 → L + 0    |
|       | 3.83                   | 0.036                   | H-1 → L + 2    |
|       | 4.06                   | 0.129                   | H-3 → L + 1    |
|       | 4.29                   | 0.101                   | H-9 → L + 0    |
|       | 4.79                   | 0.069                   | H-7 → L + 1    |
|       | 5.48                   | 0.103                   | H-3 → L + 6    |
|       | 5.95                   | 0.120                   | H-7 → L + 3    |
|       | 6.10                   | 0.135                   | H-1 → L + 7    |
|       | 6.14                   | 0.162                   | H-1 → L + 7    |
| B₁₀C₁₀| 1.56                   | 0.027                   | H-0 → L + 0    |
|       | 2.18                   | 0.011                   | H-2 → L + 0    |
|       | 2.46                   | 0.055                   | H-0 → L + 2    |
|       | 2.77                   | 0.020                   | H-1 → L + 1    |
|       | 2.80                   | 0.029                   | H-4 → L + 0    |
|       | 3.40                   | 0.057                   | H-3 → L + 1    |
|       | 3.81                   | 0.076                   | H-2 → L + 4    |
|       | 4.18                   | 0.090                   | H-0 → L + 8    |
|       | 4.41                   | 0.152                   | H-8 → L + 0    |
|       | 4.97                   | 0.109                   | H-6 → L + 3    |
|       | 5.11                   | 0.119                   | H-2 → L + 8    |
| B₁₂C₁₂| 1.77                   | 0.004                   | H-0 → L + 0    |
|       | 2.10                   | 0.055                   | H-1 → L + 0    |
|       | 2.39                   | 0.017                   | H-3 → L + 0    |
|       | 2.55                   | 0.045                   | H-0 → L + 1    |
|       | 2.83                   | 0.041                   | H-1 → L + 1    |
|       | 2.97                   | 0.020                   | H-2 → L + 2    |
|       | 3.21                   | 0.042                   | H-1 → L + 3    |
|       | 3.69                   | 0.032                   | H-3 → L + 3    |
|       | 3.88                   | 0.055                   | H-5 → L + 1    |
|       | 3.98                   | 0.056                   | H-7 → L + 2    |
|       | 4.04                   | 0.060                   | H-6 → L + 2    |
|       | 4.15                   | 0.091                   | H-7 → L + 2    |
|       | 4.22                   | 0.053                   | H-9 → L + 1    |
|       | 4.63                   | 0.062                   | H-6 → L + 4    |
|       | 4.64                   | 0.048                   | H-6 → L + 4    |
|       | 5.04                   | 0.080                   | H-4 → L + 8    |
|       | 5.20                   | 0.202                   | H-8 → L + 4    |
As shown in table 2 and figure 7, BₙCₙ (n = 6, 8, 10, 12) clusters retain strong absorption in the ultraviolet region. Interestingly, these clusters also exhibit absorption in visible region, and their absorption peaks intensify as cluster size increases. As can be seen from the TDOS, their HOMO-LUMO gaps are less than 3.1 eV, so the absorption peaks can be generated in the visible region. Besides, for B₆C₆, B₁₀C₁₀ and B₁₂C₁₂ clusters, the orbital energy levels of corresponding optical transition are densely distributed within the transition energy range of 1.5 eV – 3.1 eV, which also leads to more transition modes in the visible range. The spectral absorption occurs in the visible region, which is mainly determined by the HOMO-LUMO energy gap of BₙCₙ (n = 4, 6, 8, 10, 12) clusters. The HOMO-LUMO gap of clusters decreases from 3.43 eV to 1.23 eV. B₄C₄ cluster is characterized by H⁺ to L⁻ first excitation at 3.71 eV, while BₙCₙ (n = 8, 10, 12) clusters are characterized by 2.00 eV, 1.56 eV and 1.77 eV, respectively, which are optically active. It can be seen from table 2 that the BₙCₙ (n = 8, 10, 12) clusters have strong transitions in the range of 1.5 eV to 3.1 eV. Therefore, the red shift phenomenon is noted in the optical spectra. The optical absorption properties of these BₙCₙ clusters are different from those of recently reported Bₙ clusters [34]. The oscillator strength of almost all Bₙ clusters is suppressed in the whole visible region. As shown in table 2 and figure 7, B₆C₆ has one major transition; B₈C₈ has two major transitions; and B₁₀C₁₀ and B₁₂C₁₂ have five observable intensity transitions in the visible region, respectively. B₈C₄ has the strongest absorption peak of 0.079 at 2.72 eV. This peak corresponds to the transition from H₋ to L₋₀ orbital. This transition is mainly attributed the contribution of the 2p orbitals of B and C atoms and the 3d orbital of the B atom. The absorption intensity of this cluster should be observed experimentally. Clusters, such as B₈C₈, with strong absorption in the visible region can be deposited on the surfaces of certain substances or used to fabricate new two-dimensional cluster assembly materials for catalysis and other applications.

4. Conclusion

We systematically investigated the structures, stabilities, bonding nature, and optical properties of BₙCₙ (n = 1–13) clusters. Small BₙCₙ (n < 5) clusters tend to form planar-cyclic structures. The number of atoms that prefers to reside inside rings increases as cluster size n increases, and the cluster structure gradually transforms from a ring to a plane or a bowl-like (quasiplanar) structure. Eₙb varies monotonously with n, whereas B₄C₄ is highly stable. The HOMO–LUMO gaps exhibit a perfect ‘odd–even’ oscillation, and BₙCₙ clusters with even n have large HOMO–LUMO gaps. We acquired the optical absorption spectra for the minimum-energy structures of BₙCₙ (n = 4, 6, 8, 10, 12) through the TDDFT calculations. Moreover, we discussed the origin of the electronic excitation of these clusters. The light excitation of small B₄C₄ cluster occurs in the ultraviolet region. The clusters, beginning with B₄C₄, become optically active in the visible region but show strong absorption in the ultraviolet region. The B₄C₄ cluster has the strongest absorption intensity of 0.079 at 2.72 eV. Our detailed analysis of molecular orbitals revealed that electron transitions mainly originate from the contributions of the 2p orbitals of B and C atoms.
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